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Generation and Reactivity of Aromatic Thioether Radical Cations in Aqueous Solution As Studied by Pulse Radiolysis

Marcella Ioele and Steen Steenken*

Max-Planck-Institut für Strahlenchemie, D-45413 Mülheim, Germany

Enrico Baciocchi*

Dipartimento di Chimica, Università "La Sapienza", I-00185 Roma, Italy

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The radical cations of thioanisole (**1**), *p*-methylthioanisole (**2**), and the benzyl phenyl sulfides **3**−**5** have been produced by pulse radiolysis in aqueous solutions, using $SO_4^{\bullet -}$ or Tl^{2+} as oxidizing species. The radical cations $\mathbf{1}^{\bullet +}$−$\mathbf{5}^{\bullet +}$ exhibit very similar UV spectra, with strong absorptions between 300−350 and 500−600 nm. In contrast to *aliphatic* thioether radical cations, $\mathbf{1}^{\bullet +}$−$\mathbf{5}^{\bullet +}$ do not undergo dimerization (via formation of a three-electron bond with the parent thioethers). In the absence of bases, $\mathbf{1}^{\bullet +}$ is a long-lived species with a lifetime >30 ms, whereas $\mathbf{3}^{\bullet +}$, $\mathbf{4}^{\bullet +}$, and $\mathbf{5}^{\bullet +}$ decay rapidly by both C−S bond and C−H bond cleavage with $k_{C-H} = 1.3 \times 10^3$ s^{-1} and $k_{C-S} = 1.3 \times 10^3$ s^{-1} for $\mathbf{3}^{\bullet +}$and $k_{C-H} = 0.95 \times 10^3$ s^{-1} and $k_{C-S} = 2.65 \times 10^3$ s^{-1} for $\mathbf{4}^{\bullet +}$. In the presence of OH^- or HPO_4^{2-}, also $\mathbf{1}^{\bullet +}$ undergoes a deprotonation process, with a rate larger than those of the benzyl phenyl sulfide radical cations. For example, the rate constant for the OH^--induced deprotonation is 3.4×10^7 M^{-1} s^{-1} for $\mathbf{1}^{\bullet +}$and 9.5×10^6 M^{-1} s^{-1} for $\mathbf{3}^{\bullet +}$. Thioanisole radical cation $\mathbf{1}^{\bullet +}$ was also produced by reduction of thioanisole sulfoxide. Under these conditions, it was possible to study the reaction of $\mathbf{1}^{\bullet +}$ with a number of nucleophiles or electron donors. It was found that $\mathbf{1}^{\bullet +}$ reacts with I^-, N_3^-, PhS^-, PhSH, Br^-, and SCN^- by an electron transfer mechanism, producing the oxidized form of the nucleophile. This reaction is diffusion controlled with the first four nucleophiles, which are more easily oxidized than **1** ($E° < 1.45$ V); slower reactions were observed with SCN^- ($E° = 1.62$ V) and with Br^- ($E° = 1.96$ V). NO_3^- ($E° = 2.3$V) is unreactive ($k < 10^6$ M^{-1} s^{-1}).

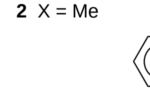
Introduction

Free radicals and radical ions derived from sulfur-containing compounds have been the subject of continuous study, as they are involved in a great variety of chemical processes, extending from those of industrial importance to the biological ones. In this research area, considerable attention has been devoted to the chemistry of sulfur-centered radical *cations,* due to their importance as intermediates in many enzymatic oxidations of organic sulfides.[1−3] So far, however, most of the work dealing with the fundamental properties (electronic structure and reactivity) of these species has concerned di*alkyl* sulfide radical cations, which have mainly been investigated by using the EPR and the pulse radiolysis techniques.[4−7]

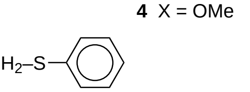
A special feature of the (monomeric) dialkyl sulfide radical cations is their reaction with the neutral parent to form relatively stable "dimer" radical cations where the two sulfur atoms are held together by a two-center−three-electron bond.[5] The equilibrium between the dimer and the monomer therefore has to be carefully considered in quantitative studies of the reactivity of dialkyl sulfide radical cations (which mainly involves deprotonation of an α-C−H bond that is generally attributed to the monomeric form).

Radical cations from *aromatic* sulfides have been much less investigated. Quantitative information on these systems would be of interest since in this case the reactivity is expected to be influenced by the degree of spin delocalization in the aromatic ring, for which the conformation of the radical cation is important.[8] It has also been noted that spin delocalization should reduce the propensity of the radical cation to form dimers, and this has recently been shown to be the case for diphenyl sulfide radical cations.[9] Clearly, this information is very important since if only monomeric radical cations are formed, the interpretation of reactivity data is much less complicated.

In this paper we report the results of a pulse radiolysis study of the radical cations formed in aqueous solution from thioanisole (**1**), 4-methylthioanisole (**2**), and the benzyl phenyl sulfides **3**−**5**. The solubility of **5** turned out to be too low to obtain sufficiently precise kinetic data on the reactivity of its radical cation or a complete characterization of its decay products. Thus, in addition to **5**, the benzyl phenyl sulfides **3** and **4** were studied, where the sulfonate functionality provides for sufficient water solubility, whereas the oxidation potential of the sulfide as well as the electronic structure of the radical cation are not expected to be much different from those of **5**.



1 X = H
2 X = Me



3 X = H
4 X = OMe

5

Experimental Section

Chemicals. Potassium peroxydisulfate, thallium(I) sulfate, *tert*-butyl alcohol, and sodium phosphate were all analytical grade from Merck. Thioanisole (Aldrich) was distilled prior to use to a purity of 99.5%; benzyl phenyl sulfide, 4-methyl-

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thioanisole, and thiophenol (Aldrich) were used as supplied (purity >99%). The compounds **3** and **4** were obtained with purity >99% (HPLC) by the reaction of 4-mercaptobenzenesulfonic acid with benzyl or 4-methoxybenzyl chloride, respectively, in the presence of anhydrous potassium carbonate in refluxing acetone.[10] 4-Mercaptobenzenesulfonic acid was prepared as follows: 4-nitrobenzyl chloride was sulfonated to sodium 4-nitrobenzenesulfonate,[11] subsequently reduced to 4-aminobenzenesulfonic acid and converted into 4-mercaptobenzenesulfonic acid according to a literature procedure.[12]

Sulfoxides of **1**−**5** (purity >99.5%) were obtained by oxidation of the corresponding sulfides with $NaIO_4$ in ethanol−water[13] and were purified by silica gel chromatography (eluent petroleum ether/ethyl ether = 4/1).

Pulse Radiolysis. Pulse radiolysis was carried out using a 3 MeV van de Graaff electron accelerator, which delivered 400 ns electron pulses with doses between 3 and 30 Gy, by which $OH^\bullet$, H^+, e_{aq}^- are generated (eq a), with concentrations of 2−20 μM. The pulse radiolysis setup and the methods of data handling have been described elsewhere.[14] For the optical experiments, dosimetry was performed with N_2O-saturated 10^{-2} mol dm^{-3} aqueous KSCN solutions, for which $G[(SCN_2)^{\bullet-}] = 6.0 \times 10^{-7}$ mol J^{-1} and $\epsilon[(SCN_2)^{\bullet-}] = 7600$ M^{-1} cm^{-1} at 480 nm.[15] Experiments were all conducted at room temperature (20 ± 1 °C), using water purified with a Millipore Milli-Q system. The pH was adjusted with NaOH or $HClO_4$, and, when close to neutrality, the solutions were buffered with 0.1−1 mM phosphate.

As oxidizing species to convert sulfides into the corresponding radical cations we used $SO_4^{\bullet-}$ and Tl^{2+}. The use of $^\bullet OH$ for the oxidation of the aromatic thioethers was avoided, since $^\bullet OH$ is known[16] to react by addition rather than by electron transfer. $SO_4^{\bullet-}$ was generated by pulse radiolysis of Ar-saturated solutions containing 2 mM $S_2O_8^{2-}$ and 0.1−1 M *t*-BuOH at pH values between 4 and 12. Under these conditions, the hydrated electrons (e_{aq}^-) react with $S_2O_8^{2-}$ to give $SO_4^{\bullet-}$ (eq 1), whereas the hydroxyl radicals produced by the radiolytic decomposition of water are scavenged by the alcohol (eq 2) with a rate constant of 5×10^8 M^{-1} s^{-1}. The *t*-BuOH-derived radical is of low reactivity and also has a low extinction coefficient at $\lambda > 200$ nm and therefore does not interfere with the measurement.

$$H_2O \rightsquigarrow H^+ + OH^\bullet + e_{aq}^- \qquad (a)$$

$$e_{aq}^- + S_2O_8^{2-} \longrightarrow SO_4^{2-} + SO_4^{\bullet -} \qquad (1)$$

$$^\bullet OH + (CH_3)_3COH \longrightarrow H_2O + {}^\bullet CH_2C(CH_3)_2OH \qquad (2)$$

In order to produce Tl^{2+}, N_2O-saturated solutions containing 2 mM Tl^+ at pH 3.2−3.7 were irradiated. The function of N_2O is to scavenge the hydrated electron and lead to a further $^\bullet OH$ radical (eq 3). Tl^{2+} is produced by oxidation of Tl^+ by $^\bullet OH$ (eq 4).[17] The pH was maintained below 3.7 in order to avoid the formation of $Tl(OH)^+$, which is a less powerful oxidant.[18]

$$e_{aq}^- + N_2O + H_2O \rightarrow N_2 + {}^\bullet OH + OH^- \qquad (3)$$

$$^\bullet OH + Tl^+ + H^+ \rightarrow H_2O + Tl^{2+} \qquad (4)$$

In some experiments the benzyl sulfide radical cations were also generated starting from the corresponding sulfoxides[9] (eq 5). In this case, Ar-saturated aqueous solutions containing 0.2−0.5 mM of the sulfoxide and 0.2 M *t*-BuOH (to scavenge $^\bullet OH$) were irradiated to generate e_{aq}^-, which is the reactive species:

$$e_{aq}^- + C_6H_5S(O)CH_3 \rightarrow C_6H_5S(O^{\bullet -})CH_3 \xrightarrow[-2OH^-]{H_2O} (C_6H_5SCH_3)^{\bullet +} \qquad (5)$$

The carbon-centered radicals **(1-H)**$^\bullet$, **(3-H)**$^\bullet$, and **(4-H)**$^\bullet$ were generated by H atom abstraction from **1**, **3**, and **4**, respectively, by $O^{\bullet-}$. The latter was obtained by pulse radiolysis of N_2O-purged aqueous solutions containing 0.5 M KOH, by deprotonation of $^\bullet OH$ ($pK_a = 11.8$). Accordingly, at such a high $[OH^-]$, the equilibrium $OH\cdot + OH^- \rightleftharpoons H_2O + O^{\bullet-}$ is shifted completely to the right; thus, $G(O^{\bullet-}) = G(OH^\bullet)$.[16] For the determination of the extinction coefficients of **(1-H)**$^\bullet$, **(3-H)**$^\bullet$, and **(4-H)**$^\bullet$ a G value of 6.6 was taken, which is the sum of $G(OH^\bullet) = 6$ and $G(H^\bullet) = 0.6$ since $H^\bullet$ reacts with OH^- producing e_{aq}^- that is then scavenged by N_2O to form another $OH^\bullet$ (eq 3).

Results

Formation of the Radical Cations. On reaction of (**1**−**5**) with $SO_4^{\bullet-}$ or Tl^{2+}, the decay of $SO_4^{\bullet-}$ (determined at 450 nm) or of Tl^{2+} (determined at 360 nm) was found to be synchronous with the buildup of two strong absorptions at 300−350 and at 500−600 nm (see Figure 1A in the case of **1** and Figure 1B in the case of **3**, **4**, and **5**). These bands are assigned to the radical cations of the sulfides in the monomeric form (see below), which are produced by electron transfer oxidation by Tl^{2+} or $SO_4^{\bullet-}$ (eqs 6 and 7). In agreement with this assignment, the absorption spectra and the lifetimes of these transients are not affected by the presence of oxygen. The spectral data for the radical cations are reported in Table 1 together with those of the products of their decay, which will be discussed later. It should be noted that the values of the extinction coefficients of the radical cations when obtained by oxidation of the parent sulfides with $SO_4^{\bullet-}$ are lower by about 10% compared to those measured by oxidation of the same substrates with Tl^{2+}. This suggests that eq 6 is the main but not the only reaction occurring between the $SO_4^{\bullet-}$ radical and the substrates (see eq 9 below).

$$(\mathbf{1}-\mathbf{5}) + SO_4^{\bullet -} \rightarrow (\mathbf{1}^{\bullet +}-\mathbf{5}^{\bullet +}) + SO_4^{2-} \qquad (6)$$

$$(\mathbf{1}-\mathbf{5}) + Tl^{2+} \rightarrow (\mathbf{1}^{\bullet +}-\mathbf{5}^{\bullet +}) + Tl^{+} \qquad (7)$$

The bimolecular rate constants for reaction of **1**−**5** with Tl^{2+} and $SO_4^{\bullet-}$ were determined by measuring k_{obs}, the rate of optical density (ΔOD) increase of the radical cation at 530 nm ($\mathbf{1}^{\bullet+}$, $\mathbf{5}^{\bullet+}$) or at 550 nm ($\mathbf{2}^{\bullet+}$, $\mathbf{3}^{\bullet+}$, $\mathbf{4}^{\bullet+}$) as a function of the concentration of added thioether. In all cases the k_{obs} increased linearly with [thioether]. From the slopes of the linear plots the bimolecular rate constants shown in Table 2 were obtained.

In the case of thioanisole, the monomeric nature of the radical cation was established by generating the radical cation of thioanisole via a different pathway, i.e., via reduction of thioanisole sulfoxide by the hydrated electron (eq 5). Under these conditions, the formation of symmetric dimers is not possible since no neutral sulfide is present. A spectrum was obtained (Figure 1; $\lambda_{max} = 310, 530$ nm) identical to that found when the radical cation was formed by oxidation of thioanisole with $SO_4^{\bullet-}$ or with Tl^{2+}. The same result was obtained when $\mathbf{2}^{\bullet+}$ was produced by reduction of 4-methylthioanisole sulfoxide ($\lambda_{max} = 320, 550$ nm; see Table 1). Thus, and also on the basis of the previous work,[9] it is concluded that radical cations of *aromatic* sulfides have only a very weak tendency to react with the neutral sulfide to form a three-electron-bonded dimer, in contrast to the situation found for *aliphatic* sulfides.[6,7,19]

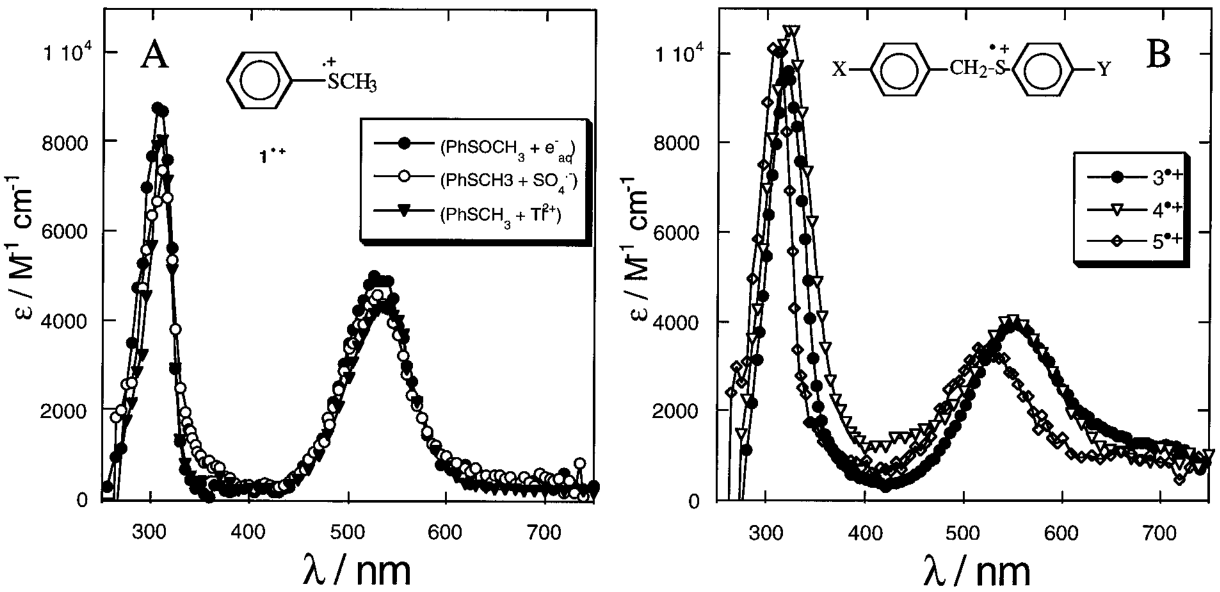


Figure 1. (A) Absorption spectra of $1^{\bullet+}$. (Full circles): data obtained on radiolysis of an Ar-purged aqueous solution of $PhSOCH_3$ (0.5 mM), Na_2HPO_4 (1 mM), *t*-BuOH (0.2 M), pH 8.5, 2 μs after the pulse. (Open circles): data from radiolysis of an Ar-purged aqueous solution (pH 6.0) of $PhSCH_3$ (0.2 mM), $K_2S_2O_8$ (2 mM), *t*-BuOH (0.1 M), 15 μs after the pulse. (Triangles): data from radiolysis of a N_2O-purged aqueous solution (pH 3.2) of $PhSCH_3$ (0.2 mM), Tl_2SO_4 (1 mM), 60 μs after the pulse. For the reaction with $SO_4^{\bullet-}$ and with e_{aq}^- the ϵ values are based on $G = 3.0 \times 10^{-7}$ mol J^{-1}. For the reaction with Tl^{2+} ϵ values are based on $G = 6.0 \times 10^{-7}$ mol J^{-1}. (B) Absorption spectra of $3^{\bullet+}$ (circles), $4^{\bullet+}$ (triangles), and $5^{\bullet+}$ (diamonds). Data obtained on radiolysis of Ar-purged aqueous solutions (pH 6.0) of **3**−**5** (0.1 mM), $K_2S_2O_8$ (2 mM), Na_2HPO_4 (1 mM), *t*-BuOH (0.1−1M), 10 μs after the pulse. Due to the very low solubility of **5** in water (saturated solution = 0.04 mM), a spectrum with a lower apparent ϵ was obtained for $5^{\bullet+}$. In the figure, in order to compare the absorption spectra of $5^{\bullet+}$ with those of $3^{\bullet+}$ and $4^{\bullet+}$, that of $5^{\bullet+}$was enlarged by the factor 1.5. ϵ values are based on $G(\text{radical}) = G(e_{aq}^-) = G(SO_4^{\bullet-}) = 3.0 \times 10^{-7}$ mol J^{-1}.

TABLE 1: Spectral Data for the Radical Cations of 1−5 and for the Radicals Produced in Their Decay

transient		λ_{max}/nm	ϵ_{max}/M^{-1} cm^{-1}	method of generation[a]
$\mathbf{1}^{\bullet+}$	$(PhSCH_3)^{\bullet+}$	310, 530	9200, 5400	1, 2, 3[b]
$\mathbf{2}^{\bullet+}$	$(4\text{-}CH_3PhSCH_3)^{\bullet+}$	320, 550	11000, 6700	1
$\mathbf{3}^{\bullet+}$	$(PhCH_2SPhCH_2SO_3^-)^{\bullet+}$	320, 550	10000, 4000	2, 3[b]
$\mathbf{4}^{\bullet+}$	$(4\text{-}CH_3OPhCH_2SPhCH_2SO_3^-)^{\bullet+}$	320, 550	11000, 6700	3
$\mathbf{5}^{\bullet+}$	$(PhSCH_2Ph)^{\bullet+}$	310, 530	6300,[c] 2100[c]	1
6	$^{\bullet}SPhCH_2SO_3^-$	305, 470, 500	12700, 2300, 2400	2
7	$PhS^{\bullet}$	295, 460	9000, 1800	2, 4
(1-H)$^{\bullet}$	$PhSCH_2^{\bullet}$	330	3800	5
(3-H)$^{\bullet}$	$PhCH^{\bullet}SPhCH_2SO_3^-$	360, 480	8000, 1000	5
(4-H)$^{\bullet}$	$4\text{-}CH_3OPhCH^{\bullet}SPhCH_2SO_3^-$	310, 360, 490	7000, 8800, 1300	5

[a] Radical cations and radicals were generated by the following methods: (1) Reduction of the sulfoxide by e_{aq}^- (0.4 mM sulfoxide, 0.2 M *t*-BuOH, Ar). $G(\text{radical}) = G(e_{aq}^-) = 3.0 \times 10^{-7}$ mol J^{-1}. (2) Oxidation by Tl^{+2} (pH 3.2−3.5) (0.1 mM substrate, 1 mM Tl_2SO_4, N_2O). $G(\text{radical}) = G(OH) = 6.0 \times 10^{-7}$ mol J^{-1}. (3) Oxidation by $SO_4^{\bullet-}$ (pH 4−8) (0.1 mM substrate, 2 mM $K_2S_2O_8$, 0.1 M *t*-BuOH, Ar). $G(\text{radical}) = G(SO_4^{\bullet-}) = 3.0 \times 10^{-7}$ mol J^{-1}. (4) Dehydrogenation of thiophenol by $^{\bullet}CH_2C(CH_3)_2OH$ (or by $(CH_3)_2C^{\bullet}OH$) (0.1 mM PhSH, 5% *t*-BuOH/*i*-PrOH, pH 4.0, N_2O). $G(\text{radical}) = G(OH) = 6.0 \times 10^{-7}$ mol J^{-1}. (5) Dehydrogenation of the parent compound by $O^{\bullet-}$ (0.1 mM substrate, 0.5 M KOH, N_2O). $G(\text{radical}) = G(OH^{\bullet}) + G(H) = 6.6 \times 10^{-7}$ mol J^{-1}. [b] In this case a lower value (5−10%) of ϵ was obtained; see text. [c] The lower ϵ value of $\mathbf{5}^{\bullet+}$ compared to those of the other radical cations is probably an artifact due to the very low solubility of **5** in water, which results in the primary radicals $SO_4^{\bullet-}$and Tl^{+2} not being quantitatively scavenged to yield $\mathbf{5}^{\bullet+}$.

TABLE 2: Rate Constants for the Oxidation of 1−5 by $SO_4^{\bullet-}$ and Tl^{2+} to Their Corresponding Radical Cations in Aqueous Solutions

substrate	oxidant	k/M^{-1} s^{-1} [a]	pH
$PhSCH_3$	$SO_4^{\bullet-}$	3.9×10^9	7.5
$PhSCH_3$	Tl^{2+}	$>1.5 \times 10^9$	3.2
$4\text{-}CH_3PhSCH_3$	$SO_4^{\bullet-}$	3.3×10^9	7.5
$PhCH_2SPhCH_2SO_3^-$	Tl^{2+}	2.1×10^9	3.5
$4\text{-}CH_3OPhCH_2SPhCH_2SO_3^-$	$SO_4^{\bullet-}$	3.9×10^9	7.5
$4\text{-}CH_3OPhCH_2SPhCH_2SO_3^-$	Tl^{2+}	2.4×10^9	3.5
$PhCH_2SPh$	$SO_4^{\bullet-}$	3.3×10^9 [b]	7.5

[a] Error limits ±10%. [b] Due to the low solubility of **5** in water, this rate constant is affected by a larger error (±20%).

Decay of the Radical Cations in the Absence of Bases and Nucleophiles. The decay of the sulfide radical cations was followed by measuring the rate of optical density decrease of the radical cations at 530 nm ($\mathbf{1}^{\bullet+}$, $\mathbf{5}^{\bullet+}$) or at 550 nm ($\mathbf{2}^{\bullet+}$, $\mathbf{3}^{\bullet+}$, $\mathbf{4}^{\bullet+}$). In the absence of a base, the aromatic radical cations decay predominantly by first order.

The measured rates for the decay were found to be dose dependent, which indicates the presence of second-order contributions due to radical−radical reactions. To correct for this effect, rates were measured at different (small) doses and extrapolated to dose = 0. The first-order rate constants thus obtained are shown in Table 3. The decay of $\mathbf{1}^{\bullet+}$ is so slow (k_{decay} less than 30 s^{-1}) that it was not possible to obtain information on the nature of the radical *product* formed. $\mathbf{3}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$ decayed at a much faster rate (k_{decay} *ca.* 10^3 s^{-1}) leading to the formation of two transients (Figure 2A,B). The transients with λ_{max} = 360 nm can be quenched by oxygen (see insets c and d), and on this basis they are identified as the carbon-centered radicals **(3-H)**$^{\bullet}$ and **(4-H)**$^{\bullet}$. This assignment is confirmed by comparison with the authentic spectra of the radicals **(3-H)**$^{\bullet}$ and **(4-H)**$^{\bullet}$, shown in Figure 3, respectively,

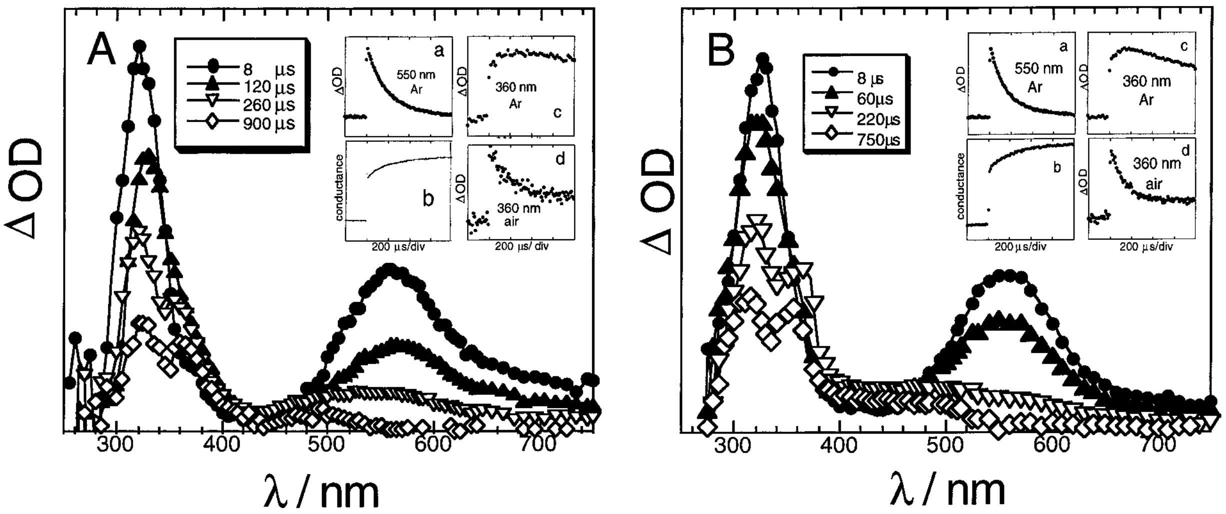


Figure 2. (A) Absorption spectra recorded on pulse radiolysis (dose = 5 Gy) of Ar-purged aqueous solution (pH 4.0) of **3** (0.1 mM), $K_2S_2O_8$ (2 mM), and *t*-BuOH (0.1 M) at the times after the pulse as indicated by the symbols. Inset a shows the decay of the radical cation $\mathbf{3}^{\bullet+}$ at 550 nm, inset b shows the rise of conductance resulting from the decay of the radical cation $\mathbf{3}^{\bullet+}$ at pH 4.5 (dose = 4 Gy), and inset c shows the formation and decay (by radical−radical reaction) of the carbon-centered radical **(3-H)**$^\cdot$ at 360 nm, in the absence of O_2. From inset **d** it is evident that radical **(3-H)**$^\cdot$ is scavenged by O_2. The decay seen has the same rate as that of the radical cation $\mathbf{3}^{\bullet+}$, and it is due to its weak absorption at 360 nm. (B) Absorption spectra recorded on pulse radiolysis (dose = 5 Gy) of an Ar-purged aqueous solution (pH 4.0) of **4** (0.1 mM), $K_2S_2O_8$ (2 mM), and *t*-BuOH (0.1 M) at the times after the pulse as indicated by the symbols. The insets are analogous to those in (A), with the exception that in inset b the dose was 0.2 Gy.

TABLE 3: Rate Constants for the Decay in Water (k_{decay}) and for the Base-Induced Deprotonation (k_{dep}) of the Radical Cations $1^{\bullet+}$−$5^{\bullet+}$

radical cation	k_{decay}/s^{-1} [a]	base	k_{dep}/M^{-1} s^{-1} [b]
$\mathbf{1}^{\bullet+}$	<30	OH^-	3.4×10^7 [c]
		HPO_4^{-2} [d]	2.6×10^6
$\mathbf{3}^{\bullet+}$	2.6×10^3	OH^-	2.5×10^7 [c]
		HPO_4^{-2} [d]	9.5×10^5 [c]
$\mathbf{4}^{\bullet+}$	3.5×10^3	OH^-	9.5×10^6 [c]
		HPO_4^{-2} [d]	2.2×10^5
$\mathbf{5}^{\bullet+}$	2.5×10^3	OH^-	2.0×10^7 [c]
		HPO_4^{-2} [d]	1.8×10^6

[a] The k_{decay} values have been obtained by extrapolation to zero dose; see text. The values do not depend on the oxidant ($SO_4^{\bullet-}$ or Tl^{2+}) and do not change in the pH range 3.5−8. [b] Determined from the slope of the plot k_{decay} (550 nm) vs [base]. Error limits ±10%; with $\mathbf{5}^{\bullet+}$ it is probably twice as large. The radical cations were produced by oxidation with $SO_4^{\bullet-}$. [c] Within the experimental error these rates coincide with those obtained by measuring the buildup of the transient absorbing at 350 nm (the carbon-centered radical). [d] pH 9.0.

independently generated by hydrogen atom abstraction from **3** or **4** by $O^{\bullet-}$.

The other transient absorbs at 310 and 450−510 nm and is not quenched by oxygen. This species is identified as the sulfur-centered radical $^\bullet S-C_6H_4CH_2SO_3^-$ (**6**), on the basis of the comparison with the authentic spectrum of **6** (shown in Figure 4A, independently produced by reaction of *p*-HS-$C_6H_4CH_2SO_3^-$ with Tl^{2+} (eq 8).

$$^-O_3SCH_2C_6H_4SH + Tl^{2+} \rightarrow \underset{\mathbf{(6)}}{^-O_3SCH_2C_6H_4S^\bullet} + Tl^+ + H^+ \qquad (8)$$

The radical cation $\mathbf{5}^{\bullet+}$ decayed at the same rate as $\mathbf{3}^{\bullet+}$; thus, the $CH_2SO_3^-$ group has no noticeable influence on the lifetime of the radical cation. As $\mathbf{5}^{\bullet+}$ decays, two transients are formed, one with λ_{max} = 360 nm and the other with λ_{max} = 295 and 465 nm, which are assigned to the carbon-centered radical **(5-H)**$^\bullet$ and the thiophenoxyl radical $^\bullet SC_6H_5$ (**7**), respectively.[20] The authentic spectrum of this radical (see Figure 4B) was obtained by oxidation of thiophenol with Tl^{2+} at pH 4 or by reaction with the radical $^\bullet CH_2C(CH_3)_2OH$ or $(CH_3)_2C^\bullet OH$, produced by H-abstraction from *t*-BuOH or *i*-PrOH, respectively, by $^\bullet OH$. The attempt to produce the radical **(5-H)**$^\bullet$ by H-abstraction from **5** with $O^{\bullet-}$ was unsuccessful, which is probably due to the extremely low solubility of **5** in water (the rate constant for H-abstraction by $O^{\bullet-}$ appears to be $<10^8$ M^{-1} s^{-1}). Therefore the assignment of the band at 350 nm to **(5-H)**$^\bullet$ was made by analogy with the absorption spectrum of **(3-H)**$^\bullet$.

The observations reported above indicate that, in the absence of bases and nucleophiles, the decay of the benzyl phenyl sulfide radical cations $\mathbf{3}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$ occurs by deprotonation at the benzylic position (Scheme 1, path a) and by cleavage of the C−S bond (path b). In line with these findings is the observation that the steady state oxidation of **3** and **4** by $SO_4^{\cdot-}$ leads to the formation of 4-methoxybenzyl alcohol and 4-methoxybenzaldehyde in an alcohol:aldehyde ratio of 0.9 and 2,5, respectively.[21] The aldehydes arise via deprotonation of the radical cation to yield **(3-H)**$^\bullet$/**(4-H)**$^\bullet$ followed by oxidation with $S_2O_8^{2-}$, addition of water, and hydrolysis of the resulting α-hydroxysulfide. The benzyl alcohols derive from the benzyl cation, formed by heterolytic C−S bond cleavage (reaction b in Scheme 1).

It was found that during the decay of the radical cations the conductance of the solutions changes. In acidic solution, the conductance *in*creases whereas in alkaline solution it *de*creases (with the same rate). The increase in conductance is thus due to the production of H^+ (Scheme 1). The *rate* of H^+ production was the same as that of the decay of the radical cation. However, the *amplitude* of this *decay*-related conductance increase was smaller than that of the increase in conductance originating from the *formation* of the radical cation and due to the "fast reactions" leading to e_{aq}^- and from there to $SO_4^{\bullet-}$ and the radical cation (eqs a, 1, and 6). This means that a part of $SO_4^{\bullet-}$ reacts with the sulfide in a process that is accompanied by production of H^+ and that occurs concomitantly with the formation of the radical cation. We suggest that this process consists of the $SO_4^{\bullet-}$ radical abstracting a H atom from the substrate's side chain (eq 9), in addition to the electron abstraction from the aromatic part of the molecule (eq 6).

$$SO_4^{\bullet-} + \mathbf{3/4} \rightarrow HSO_4^- \; (H^+ + SO_4^{2-}) + \mathbf{(3\text{-}H)}^\bullet/\mathbf{(4\text{-}H)}^\bullet \qquad (9)$$

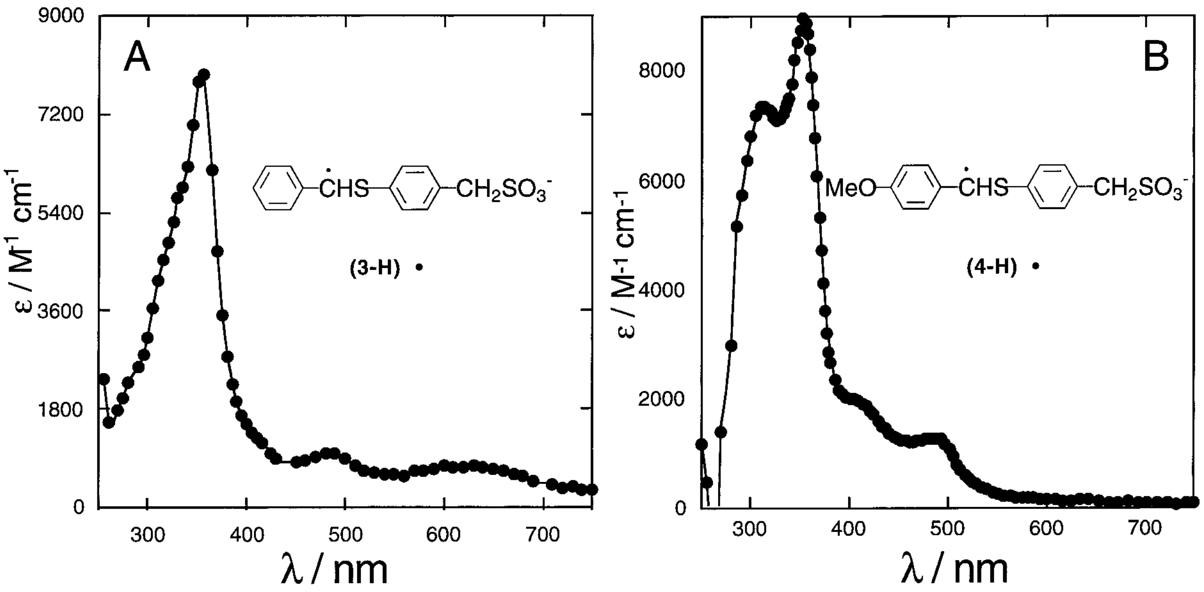


Figure 3. Absorption spectra recorded at 8 μs after the pulse on irradiation of N_2O-saturated aqueous solutions containing 0.5 M KOH and 0.1 mM **3** (A) or **4** (B).

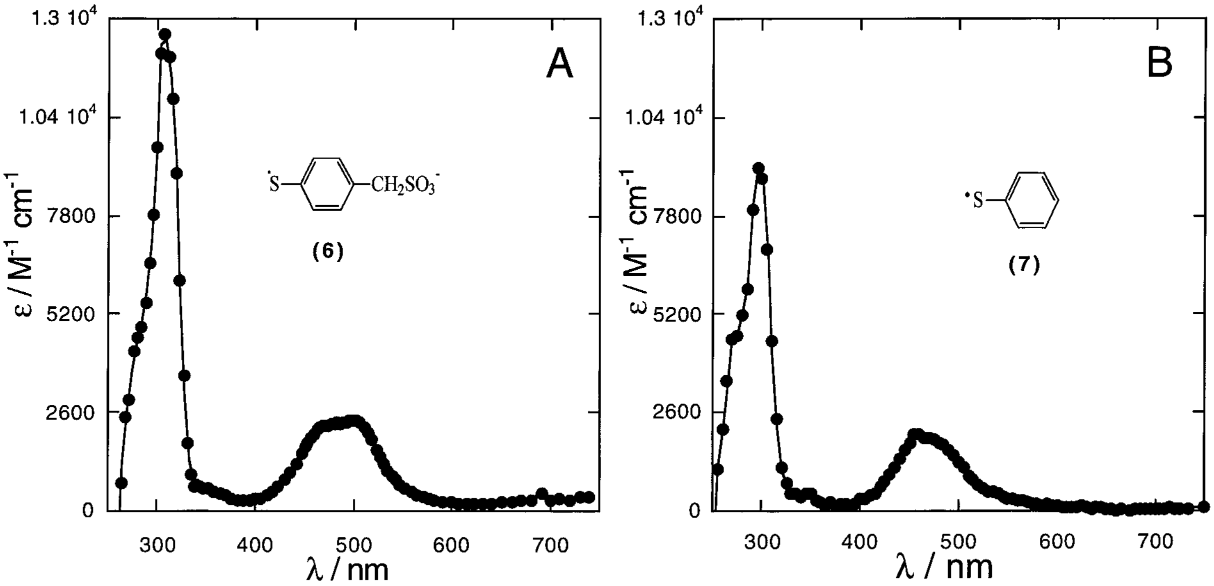
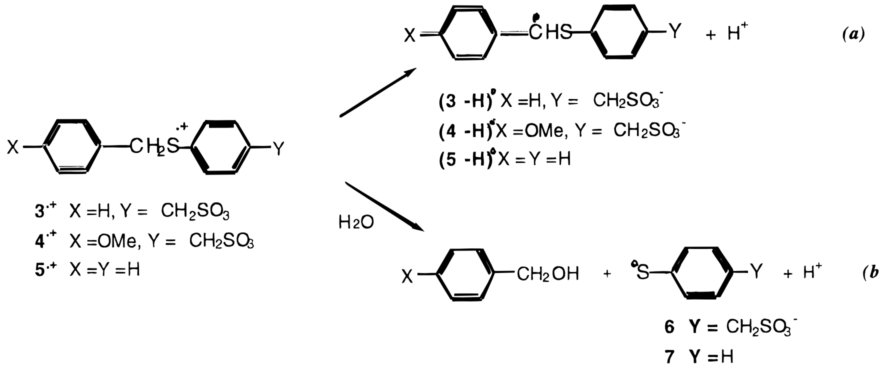


Figure 4. Absorption spectra recorded at 15 μs on pulse radiolysis of a N_2O-saturated solution of 1 mM Tl_2SO_4, pH 3.5, and containing 0.1 mM 4-mercaptobenzenesulfonic acid (A) or 0.1 mM thiophenol (B).

SCHEME 1



From the ratio between the conductance increase in the formation reaction and that due to the decay of the radical cation (slow reaction) $\Delta\Lambda_{fast}/\Delta\Lambda_{slow}$ extrapolated to dose = 0, and taking the following values for the single-ion equivalent conductivities in water at 20 °C:[22,23] $\lambda_0 H^+ = 314$, $^1/_2\lambda_0\ SO_4^{-2} = 72$, $^1/_2\lambda_0\ S_2O_8^{-2} = 77$, $\lambda_0\ \mathbf{3}^{•+}(\mathbf{4}^{•+}) \simeq \lambda_0 C_6H_5CO_2^- = 29$ ($cm^2/(\Omega^{-1}$ mol^{-1})),[24] it is calculated that the contribution of eq 9 to the overall reaction of $SO_4^{•-}$ is ≤10% for **3** and *ca.* 13% for **4**.

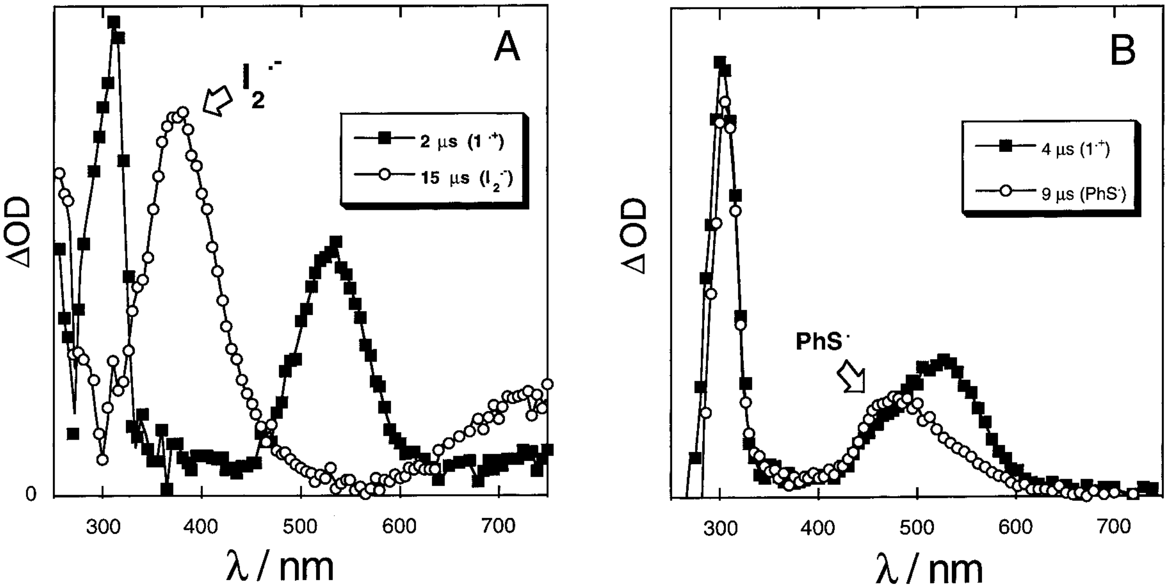


Figure 5. (A) Absorption spectra recorded on pulse radiolysis of an Ar-purged aqueous solution (pH 7.5) of 0.4 mM $PhSOCH_3$ and 0.2 M *t*-BuOH and containing 0.02 mM KI. (B) Absorption spectra on pulse radiolysis of an Ar-purged aqueous solution (pH 10) of 0.4 mM $PhSOCH_3$ and 0.2 M *t*-BuOH and containing 0.03 mM PhSH.

The complication introduced by eq 9 as well as some overlapping of the absorption spectra of thiophenoxyl and carbon-centered radicals do not allow a precise dissection of the decay rate of the radical cation into the contributions by C−H and C−S bond cleavage, respectively. However, information in this respect can be derived from the already mentioned observation that the steady state oxidation of **3** and **4** by $SO_4^{\bullet-}$ leads to the formation of benzyl alcohol (4-methoxybenzyl alcohol) and benzaldehyde (4-methoxybenzaldehyde) in an alcohol:aldehyde ratio of 0.9 and 2.5, respectively. On this basis, after correction for eq 9, it is possible to estimate the rate of the C−H and C−S bond cleavage at pH 4.0. The values obtained (extrapolated to zero dose) are $k_{C-H} = 1.3 \times 10^3$ s^{-1} and $k_{C-S} = 1.3 \times 10^3$ s^{-1} for $\mathbf{3}^{\bullet+}$ and $k_{C-H} = 0.95 \times 10^3$ s^{-1} and $k_{C-S} = 2.65 \times 10^3$ s^{-1} for $\mathbf{4}^{\bullet+}$.

Decay of the Radical Cations in the Presence of Bases. In the presence of a base such as OH^- or HPO_4^{-2}, an accelerated decay of thioanisole radical cation, $\mathbf{1}^{\bullet+}$, was observed. This base-induced decay leads to a transient with an absorption at 320−360 nm, quenchable with oxygen, which is identified as the carbon-centered radical $\mathbf{(1\text{-}H)}^\bullet$, by comparison with the authentic spectrum of this radical, obtained by H-abstraction from the methyl group of thioanisole with $O^{\bullet-}$ at pH 13.5. Thus, the decay of $\mathbf{1}^{\bullet+}$ is ascribed to base-induced deprotonation from the methyl group (eq 10):

$$(C_6H_5SCH_3)^{\bullet+} \xrightarrow[-H_2O,\ -H_2PO_4^-]{OH^-,\ HPO_4^{-2}} C_6H_5SCH_2^{\bullet} \quad \mathbf{(1\text{-}H)}^\bullet \qquad (10)$$

Also the rates of decay of the radical cations $\mathbf{3}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$ significantly increase in the presence of OH^- and HPO_4^{2-} such that in basic medium deprotonation is the dominant reaction of the radical cation. From the absorption spectra measured under these conditions, it became clear that the deprotonation process is accelerated by the presence of the base while the rate of C−S bond cleavage reaction remains unaffected, so that the latter becomes negligible at a sufficiently high base concentration. The second-order rate constants for the reactions of $\mathbf{1}^{\bullet+}$, $\mathbf{3}^{\bullet+}$, $\mathbf{4}^{\bullet+}$, and $\mathbf{5}^{\bullet+}$ with OH^- and with HPO_4^{-2} were determined from the linear plots of the observed decay rates vs the base concentrations. The values, collected in Table 3, were found to be independent of the dose used and of the substrate concentration (from 0.05 to 0.3 mM).

Decay of Thioanisole Radical Cation in the Presence of Nucleophiles. The decay of $\mathbf{1}^{\bullet+}$ was also studied in the presence of compounds that are weak bases but strong nucleophiles or electron donors (I^-, $C_6H_5S^-$, C_6H_5SH, N_3^-, Br^-, SCN^-, and NO_3^-). For this investigation $\mathbf{1}^{\bullet+}$ was generated under the reductive conditions of eq 5, to circumvent the oxidation of the nucleophile by $SO_4^{\bullet-}$ or Tl^{2+}.

The rate of decay of $\mathbf{1}^{\bullet+}$ at 530 nm was found to increase strongly in the presence of I^-, N_3^-, PhS^-, and PhSH. A much smaller increase was observed in the presence of Br^- and SCN^-, whereas there was no effect on the lifetime of $\mathbf{1}^{\bullet+}$ in the presence of NO_3^-. In the case of the quenching with I^-, the decay of $\mathbf{1}^{\bullet+}$ was synchronous with the buildup of a transient with λ_{max} = 380 nm, which is identified as $I_2^{\cdot-}$ (see Figure 5A). Analogously, $(SCN)_2^{\bullet-}$ (λ_{max} = 480 nm) and $Br_2^{\bullet-}$ (λ_{max} = 370 nm) were produced by quenching of $\mathbf{1}^{\bullet+}$ with SCN^- and Br^-, respectively. These findings clearly show that the reaction between $\mathbf{1}^{\bullet+}$ and the above halide or pseudohalide anions (X^-) involves an electron transfer process leading to the formation of the neutral thioanisole (**1**) and the radical $X^\bullet$ (eq 11) followed by reaction of $X^\bullet$ with X^- to form $X_2^{\bullet-}$. This reaction (eq 12) occurs in water with a diffusion-controlled rate ($k = 1.2 \times 10^{10}$ M^{-1} s^{-1})[25,26] for $X^- = I^-$, Br^-, SCN^-.

$$(PhSCH_3)^{\bullet+} + X^- \rightarrow PhSCH_3 + X^\bullet \qquad (11)$$

$$X^\bullet + X^- \rightarrow X_2^{\bullet-} \qquad (12)$$

No absorbing products were observed on quenching of $\mathbf{1}^{\bullet+}$ with N_3^-, but this is very probably due to the fact that $N_3^{\cdot}$ does not readily form the $N_6^{\bullet-}$ dimer in aqueous solutions and the monomer radical absorbs only weakly above λ = 250 nm.[27] We therefore assume that also N_3^- reacts with $\mathbf{1}^{\bullet+}$ by an electron transfer mechanism.

The same mechanism holds for the reactions of $\mathbf{1}^{\bullet+}$ with PhS^- and PhSH, which were carried out by adding thiophenol (pK_a = 6.6) to the aqueous solution of thioanisole sulfoxide at pH 10 and 4.5, respectively. These reactions lead to thioanisole and the thiophenoxyl radical $C_6H_5S^\bullet$, according to eq 13. As

TABLE 4: Experimental Rate Constants (k_{red}) for the Reactions of Thioanisole Radical Cation ($E° = 1.45$ V)[32] with a Number of Nucleophiles (Nu) and Calculated Rate Constants (k_d) for the Diffusion-Controlled Reactions of Thioanisole Radical Cation with the Same Nucleophiles in Water at 20 °C

Nu	$E°$ [a]	k_{red}/M^{-1} s^{-1} [b]	k_d/M^{-1} s^{-1} [c]	D/cm^2 s^{-1} [d]	R/Å [e]	pH [f]
I^-	1.27[39]	1.9×10^{10}	1.9×10^{10}	1.79×10^{-5}	8.7	7.5
N_3^-	1.33[39]	1.7×10^{10}	1.7×10^{10}	1.61×10^{-5}	8.3	7.5
PhS$^-$	0.69[20]	8.5×10^{9}	1.1×10^{10}	0.67×10^{-5}	8.7	10.0
PhSH	1.08[20]	3.5×10^{9}	6.0×10^{9}			4.5
SCN$^-$	1.62[39]	2.4×10^{8}	1.65×10^{10}	1.54×10^{-5}	8.5	7.5
Br$^-$	1.96[26]	8.0×10^{5}	1.85×10^{10}	1.83×10^{-5}	8.5	7.5
NO_3^-	2.3[39]		1.7×10^{10}	1.65×10^{-5}	8.5	7.5

[a] Standard reduction potential (vs NHE) of the nucleophile in its oxidized form. [b] Determined from the linear plot k_{obs} vs [Nu]. [c] Calculated from the Debye–Smoluchowsky equation, $k_d = \alpha_R N R(D_A + D_B)/1000$ (15),[36] when Nu is an anion and from the Stokes–Einstein equation, $k_d = (2RT/3000\eta)(2 + r_A/r_B + r_B/r_A)$ (16)[38] for Nu = PhSH. In eq 15, N is the Avogadro number, D_A and D_B are the diffusion coefficients of the two ions (reported in the fifth column of the table), α_R is taken as 4π, and R (sixth column of the Table) is calculated as described in footnote *d*. In eq 16, η is the viscosity of the medium (0.0102 poise for water at 20 °C), r_A and r_B are the reactants' radii, which are assumed to have the same value. [d] Diffusion coefficients for ions were calculated from their limiting single-ion equivalent conductivities, λ_0, using the formula $D = 2.6 \times 10^{-7}\lambda_0$ at 20 °C. Λ_0 values at 20 °C were obtained from the λ_0 at 25 °C, by multiplying by 0.9.[22] The λ_0 of PhS$^-$ was approximated as the λ_0 of *p*-anisate (26 cm^2/(Ω^{-1} mol^{-1})), whereas the λ_0 of PhSCH$_3^{\bullet+}$ was approximated as the λ_0 of the tetramethylammonium ion (40 cm^2/(Ω^{-1} mol^{-1})).[36] [e] $R = r_c/[\exp(r_c/r_0)^{-1}]$, where r_0 is the encounter distance and r_c accounts for Coulombic interactions between the two ions. For singly charged ions of opposite charge, the value of r_c in water at 20 °C is −7.5 Å. The value r_0 is approximated as the sum of the ionic radii of the reacting ions. The contact distance for the radical cation was taken as 1.8 Å.[36] [f] pH at which the reaction was carried out.

an example, in Figure 5B is shown the absorption spectrum following reaction of $\mathbf{1}^{\bullet+}$ with PhS$^-$, where it is evident that $\mathbf{1}^{\bullet+}$ is replaced after 9 μs by PhS$^\bullet$.

$$\mathbf{1}^{\bullet+} + C_6H_5S^-/C_6H_5SH \rightarrow \mathbf{1} + C_6H_5S^\bullet/C_6H_5S^\bullet + H^+ \quad (13)$$

The decay of $\mathbf{1}^{\bullet+}$ induced by the various nucleophiles followed first-order kinetics, and the second-order rate constants were determined by plotting the observed first-order rates versus the nucleophile concentrations. From the slopes of the linear plots the rate constants shown in Table 4 were obtained.

Discussion

The rate constants for formation of the radical cations by reaction with SO$_4^{\bullet-}$ (Table 2) are almost the same for all substrates (k around 3×10^9 M^{-1} s^{-1}). On the basis of this value, the reactions are classified as diffusion controlled, as expected for processes that are highly exoergonic. Another observation is that, different from the aliphatic counterparts,[6,7,19] aromatic sulfide radical cations appear to have only a very weak tendency to react with the neutral parent to form a three-electron-bonded dimer. A reasonable explanation is that, in the radical cation, part of the positive charge and/or spin density is delocalized into the aromatic ring, thus decreasing the strength of a sulfur–sulfur three-electron bond. A similar delocalization of the sulfur 3p-type nonbonding electron pair in the neutral substrate should act in the same direction; however, such a delocalization, certainly possible for **1** and **2**, might become difficult in **3**–**5** due to the bulkiness of the benzyl group, which destabilizes the conformation where the sulfur p-type orbital is aligned with the aromatic π system.[8] This conformational effect should also be present in the radical cation, where, however, it could be outweighed by the greater energetic gain due to the delocalization of the positive charge/spin density.

The UV/vis spectra of $\mathbf{1}^{\bullet+}$–$\mathbf{5}^{\bullet+}$ are very similar, with a λ_{max} around 550 nm. This suggests a similar electronic structure for these radical cations and, specifically, that in all cases one is dealing with *sulfur*-centered radical cations. This conclusion is expected for $\mathbf{1}^{\bullet+}$, $\mathbf{2}^{\bullet+}$, $\mathbf{3}^{\bullet+}$, and $\mathbf{5}^{\bullet+}$, but it is not the one predicted for $\mathbf{4}^{\bullet+}$ on the basis of PES experiments,[28] which indicate that the SOMO resides on the methoxy-substituted aromatic ring and not on the sulfur atom. If this were the case, however, the radical cation should absorb in the 450–470 nm region of the spectrum,[29] which is not observed. This discrepancy between the predictions based on PES experiments and the behaviors of radical cations in water is, however, only an apparent one. PES experiments refer to properties in the gas phase. In solution, localization of the charge on the sulfur atom in $\mathbf{4}^{\bullet+}$ may be favored by solvation at this site.[30]

From the data displayed in Table 3 it is clear that in the absence of base the decay rate of $\mathbf{1}^{\bullet+}$ is dramatically smaller than those of the benzyl phenyl sulfide radical cations $\mathbf{3}^{\bullet+}$, $\mathbf{4}^{\bullet+}$, and $\mathbf{5}^{\bullet+}$, whose decay rates are very close to one another. Since with $\mathbf{3}^{\bullet+}$–$\mathbf{5}^{\bullet+}$ deprotonation is a substantial part of the decay, the above finding indicates that the latter radical cations are deprotonated at a rate that is at least 3–4 orders of magnitude larger than that of $\mathbf{1}^{\bullet+}$. A reason for this huge difference in rates is possibly the relatively low acidity of the C–H bonds of the methyl group in $\mathbf{1}^{\bullet+}$ (estimated pK_a *ca.* 0.9),[31–34] which is too low to allow the observation, on the ≈1 ms time scale of the pulse radiolysis experiment, of a deprotonation process induced by so weak a base as H$_2$O (pK_a = −1.7) . In contrast, with $\mathbf{3}^{\bullet+}$–$\mathbf{5}^{\bullet+}$, the benzylic C–H bonds are much more acidic (a pK_a value of about −10.8 is estimated for $\mathbf{5}^{\bullet+}$),[35] due to the presence of the phenyl group. Thus, with $\mathbf{3}^{\bullet+}$–$\mathbf{5}^{\bullet+}$, H$_2$O is apparently a base strong enough to enable deprotonation.

When in the aqueous solution a base like OH$^-$ (pK_a(H$_2$O) = 15.4) or HPO$_4^{2-}$ (pK_a(H$_2$PO$_4^-$)= 7.2) is added, also $\mathbf{1}^{\bullet+}$ is rapidly deprotonated with a (second-order) rate very similar (in fact, it is slightly larger!) to those of $\mathbf{3}^{\bullet+}$, $\mathbf{4}^{\bullet+}$, and $\mathbf{5}^{\bullet+}$. This situation is very surprising in view of the great differences in pK_a of the radical cations as mentioned above. A tentative explanation is that deprotonation of $\mathbf{1}^{\bullet+}$ (the weakest acid) exhibits a much higher sensitivity to the strength of the base than the deprotonation of the more acidic radical cations.

It is also noteworthy that the presence of the strong electron donor MeO on the benzylic phenyl ring does not exert a significant influence on the decay of the radical cation. For example, $\mathbf{3}^{\bullet+}$ and $\mathbf{4}^{\bullet+}$ exhibit very similar decay rates both in the absence and in the presence of base. More significantly, the rates of C–S bond cleavage are also very similar. This is in contrast to expectation since, as the radical cations of **3** and **4** are both sulfur centered, as suggested above, one expects a larger rate of C–S bond cleavage for $\mathbf{4}^{\bullet+}$ than for $\mathbf{3}^{\bullet+}$ since a much more stable carbocation is formed in the former case. It seems, therefore, that in the transition state of the C–S bond cleavage very little charge is transferred from sulfur to carbon. An alternative is that, as the positive charge develops on the

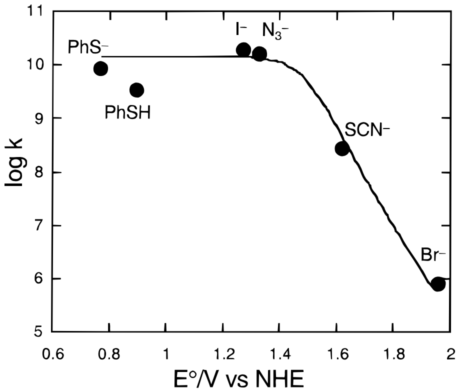


Figure 6. Values of log k for the electron transfer reduction of thioanisole radical cation by nucleophiles in water at 20 ± 1 °C, *vs* $E°(Nu^{\bullet}/Nu^{-})$.

carbon atom, it is immediately neutralized by a water molecule, e.g., by that solvating the sulfur, so that a carbocation is never formed along the reaction coordinate.

Finally, we would like to comment on the data concerning the electron transfer reactions of $\mathbf{1}^{\bullet+}$ with a number of strong nucleophiles or electron donors as reported in Table 4 and Figure 6. The reaction rate increases with the reducing power of the nucleophile Nu^- up to a limiting value characterized by the $E°$ value of the $Nu^{\bullet}/Nu^-$ couple becoming lower than that of the $\mathbf{1}^{\bullet+}/\mathbf{1}$ couple (1.45 V), i.e., by the process becoming exoergonic (see Figure 6). The limiting rate constants have magnitudes in the vicinity of 10^{10} M^{-1} s^{-1}, the diffusion-controlled value in water. This was checked by calculating the diffusional rate constants in water (k_d) using the Debye−Smoluchowsky equation[36−38] and the Stokes−Einstein equation[38] for the reactions of thioanisole radical cation with anions and with neutral nucleophiles, respectively.

The results of these calculations, which are reported in Table 4, show that for I^-, N_3^-, PhS^-, and PhSH the experimentally observed rate constants are very close to those calculated for a diffusional process. However, with SCN^- and Br^-, the rate constants measured are significantly smaller than the diffusional limit. The data can be fitted by the conventional model[36] (eq 14), which involves a diffusional encounter of the radical cation and the nucleophile Nu, with the diffusion step being rate limiting for the donors that are more easily oxidizable than thioanisole ($E° > 1.45$ V) and the electron transfer step becoming (at least in part) rate limiting for Br^- and SCN^- whose $E°$ is somewhat higher than 1.45 V. In line with this scheme, no reaction was observed with NO_3^- ($E° = 2.3$ V), for which the electron transfer step is highly endoergonic. It has, however, been reported that sulfur radical cations react with NO_3^- to give sulfoxides.[40] Clearly, in the light of the present results this process must be relatively slow. For the reaction of $\mathbf{1}^{\bullet+}$ with NO_3^-, the rate constant is estimated to be $<10^6$ M^{-1} s^{-1}.

$$(PhSCH_3)^{\bullet+} + Nu \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} (PhSCH_3)^{\bullet+}\cdots Nu \xrightarrow{k_{et}} Nu^{\bullet+} + PhSCH_3 \quad (14)$$

Concerning the nature of the electron transfer step, we are faced with the usual problem: inner-sphere or outer-sphere electron transfer? At present, no definitive answer is possible. However, the formation of loose complexes between sulfide radical cations and halide ions, particularly iodide and bromide,[6] has been reported and more recently, the formation of a short lived intermediate $(Ph_2SBr)^{\bullet}$ between $Ph_2S^{\bullet+}$ and Br^-. These are arguments in favor of an inner-sphere mechanism.

Summary and Conclusions

In the present work radical cations from the aromatic thioethers **1**−**5** were produced by pulse radiolysis in aqueous solutions, using $SO_4^{\bullet-}$ or Tl^{2+} as the oxidizing species. The radical cations $\mathbf{1}^{\bullet+}$−$\mathbf{5}^{\bullet+}$ are present as monomers; i.e., they do not form three-electron-bonded dimers as in the case of the aliphatic sulfides. The radical cations $\mathbf{3}^{\bullet+}$, $\mathbf{4}^{\bullet+}$, and $\mathbf{5}^{\bullet+}$ decay by two pathways: cleavage of the C−S bond, producing a thiophenoxyl radical, and deprotonation from the benzylic position, producing a carbon-centered (benzyl type) radical. The second process is accelerated in the presence of a base, such as OH^- or HPO_4^{2-}. In the case of thioanisole, the base-catalyzed deprotonation is the only pathway of decay of the radical cation. Thioanisole radical cation can be alternatively produced by reduction of thioanisole sulfoxide. Under these conditions, it is possible to study the reaction of the radical cation with reductants. It was found that thioanisole radical cation is reduced to neutral thioanisole with diffusion-controlled rates by I^-, N_3^-, PhS^-, and PhSH ($E° < 1.45$ V), whereas the electron transfer is rate limiting for Br^- and SCN^-. No reaction was observed with NO_3^-.

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