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Photosensitized Oxidation of Sulfides: Discriminating between the Singlet-Oxygen Mechanism and Electron Transfer Involving Superoxide Anion or Molecular Oxygen

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Abstract: The oxidation of diethyl and diphenyl sulfide photosensitized by dicyanoanthracene (DCA), *N*-methylquinolinium tetrafluoroborate (NMQ$^+$), and triphenylpyrylium tetrafluoroborate (TPP$^+$) has been explored by steady-state and laser flash photolysis studies in acetonitrile, methanol, and 1,2-dichloroethane. In the Et$_2$S/DCA system sulfide-enhanced intersystem crossing leads to generation of ^{1}O$_2$, which eventually gives the sulfoxide via a persulfoxide; this mechanism plays no role with Ph$_2$S, though enhanced formation of ^{3}DCA has been demonstrated. In all other cases an electron-transfer (ET) mechanism is involved. Electron-transfer sulfoxidation occurs with efficiency essentially independent of the sulfide structure, is subject to quenching by benzoquinone, and does not lead to Ph$_2$SO cooxidation. Formation of the radical cations R$_2$S$^{\bullet+}$ has been assessed by flash photolysis (medium-dependent yield, dichloroethane $\gg$ CH$_3$CN $>$ CH$_3$OH) and confirmed by quenching with 1,4-dimethoxybenzene. Electron-transfer oxidations occur both when the superoxide anion is generated by the reduced sensitizer (DCA$^{\bullet-}$, NMQ$^\bullet$) and when this is not the case (TPP$^\bullet$). Although it is possible that different mechanisms operate with different ET sensitizers, a plausible unitary mechanism can be proposed. This considers that reaction between R$_2$S$^{\bullet+}$ and O$_2^{\bullet-}$ mainly involves back electron transfer, whereas sulfoxidation results primarily from the reaction of the sulfide radical cation with molecular oxygen. Calculations indeed show that the initially formed fleeting complex RS$_2{}^+\cdots$O–O$^\bullet$ adds to a sulfide molecule and gives strongly stabilized R$_2$S–O$^\bullet$–$^+$O–SR$_2$ via an accessible transition state. This intermediate gives the sulfoxide, probably via a radical cation chain path. This mechanism explains the larger scope of ET sulfoxidation with respect to the singlet-oxygen process.

Keywords: electron transfer · oxidation · photochemistry · reaction mechanisms · sulfides

Introduction

Methods for the mild and selective oxidation of sulfides to sulfoxides that minimize production of sulfones and side reactions are interesting from both synthetic and mechanistic points of view.[1] Photosensitized reactions play an important role in this field and occur according to two main mechanisms. Singlet oxygen produced on energy transfer from the sensitizer reacts efficiently with dialkyl sulfides to yield the sulfoxide via an intermediate persulfoxide [Eqs. (1)–(3)].[2] A peculiarity of sulfide oxidation via ^{1}O$_2$ is the strong medium effect on the efficiency of the reaction, which is high in protic media, in which the intermediate persulfoxide is hydrogen-bonded.[2] Sulfide oxidation by the singlet-oxygen mechanism is sluggish in aprotic media and in the case of aryl alkyl and diaryl sulfides.[2]

$$\mathrm{Sens}^* + \mathrm{O_2} \rightarrow \mathrm{Sens} + {}^1\mathrm{O_2} \qquad (1)$$

$$^1\mathrm{O_2} + \mathrm{R_2S} \rightarrow \mathrm{R_2S^+{-}O{-}O^-} \qquad (2)$$

$$\mathrm{R_2S^+{-}O{-}O^-} + \mathrm{R_2S} \rightarrow 2\,\mathrm{R_2SO} \qquad (3)$$

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The second mechanism involves photosensitized electron-transfer (ET) oxidation[3] and operates with electron poor (hetero)aromatics[3a–h] or aryl ketones[3f,h,4] as sensitizers [Eqs. (4)–(6)].

$$^1\mathrm{Sens}^* + \mathrm{R_2S} \rightarrow \mathrm{Sens}^{\cdot-} + \mathrm{R_2S}^{\cdot+} \qquad (4)$$

$$\mathrm{Sens}^{\cdot-} + \mathrm{O_2} \rightarrow \mathrm{O_2}^{\cdot-} + \mathrm{Sens} \qquad (5)$$

$$\mathrm{O_2}^{\cdot-} + \mathrm{R_2S}^{\cdot+} \rightarrow \mathrm{R_2SO} \qquad (6)$$

The sulfide radical cation forms on electron transfer to the excited sensitizer, which is then regenerated by reaction with oxygen yielding the superoxide anion. Recombination of the sulfide radical cation and the superoxide anion yields the final sulfoxide. Both Baciocchi et al.[3d] and Lacombe et al.[3f] recently showed that the oxidation of dibutyl sulfide in acetonitrile with 9,10-dicyanoanthracene (DCA), *N*-methylquinolinium tetrafluoroborate (NMQ^+), and benzophenone can occur both via the ET path [Eqs. (4)–(6)] and via the $^1O_2$ mechanism [Eqs. (1)–(3), Sens = DCA or benzophenone]. Only the ET path is followed in the case of sulfoxidation of thioanisole sensitized by DCA and NMQ^+. Discriminating between the two mechanisms is not trivial, because these sensitizers also generate singlet oxygen; indeed, formation of $^1O_2$ with a limiting quantum yield of two has been demonstrated for some "typical" ET sensitizers.[3d,5] Furthermore, Baciocchi et al. proposed a different ET mechanism in which recombination of sulfide radical cation and superoxide anion gives a cyclic adduct, namely, a thiadioxirane, rather than the persulfoxide involved in the $^1O_2$ reactions.[3d] Since the efficiency of the singlet-oxygen mechanism strongly depends on the nature of the medium,[2,6] it appeared likely that extending the exploration of photosensitized sulfide oxidation to other solvents could offer new mechanistic insight. We decided to extend the sulfoxidation from CH_3CN to dichloroethane (DCE), a less polar solvent, and to methanol, a protic solvent. Two prototype sulfides were studied, diethyl sulfide and diphenyl sulfide; the former is known to react smoothly with $^1O_2$, and the latter is virtually unreactive (rate constant $k = 3.9\times10^4\,\mathrm{M^{-1}s^{-1}}$ and $2.7\times10^7\,\mathrm{M^{-1}s^{-1}}$ for Ph_2S and Et_2S, respectively).[7] Moreover Ph_2S lacks α-hydrogen atoms which could be involved in the reaction. Reasoning that a sensitizer with different characteristics could in turn afford useful information, we added triphenylpyrylium tetrafluoroborate (TPP^+) to the above-mentioned sensitizers, DCA and NMQ^+. In contrast to DCA and NMQ^+, singlet excited TPP^+ is known to be a poor oxygen sensitizer because of its small singlet–triplet energy gap ($11\,\mathrm{kcal\,mol^{-1}}$)[8] compared to the activation energy of singlet oxygen ($22\,\mathrm{kcal\,mol^{-1}}$). Furthermore, TPP^+ in the ground state is a worse oxidizer than NMQ^+ and DCA,[9] but both singlet and triplet excited TPP^+ are known as very strong oxidizing agents.[8] In the ET mechanism, ET from the radical $TPP^\cdot$ to oxygen according to Equation (5) is an endothermic process, so no formation of superoxide anion is expected.[8] To obtain further mechanistic indications from the effect of additives, we used diphenyl sulfoxide and *p*-benzoquinone (BQ), known as quenchers of potential intermediates, that is, persulfoxide and superoxide anion, respectively.[3d] We also employed 1,4-dimethoxybenzene (DMB) in low concentrations, which is expected to quench the sulfide radical cations.

Results

Photosensitized oxidation: Electron transfer from both sulfides to the singlet excited sensitizers is exoergonic. In the case of Et_2S (Ph_2S) in CH_3CN, the Gibbs free energy change for electron transfer ΔG_{ET} calculated according to Weller's equation[10] is -8.7 (-13.7) $\mathrm{kcal\,mol^{-1}}$, -23.4 (-28.4) $\mathrm{kcal\,mol^{-1}}$, and -19.9 (-24.9) $\mathrm{kcal\,mol^{-1}}$ for ^{1}DCA, $^1NMQ^+$, and $^1TPP^+$, respectively.[9] Experimentally, it was found that the fluorescence of all of the sensitizers was quenched at close to diffusion-controlled rate by both sulfides in the considered solvents. (e.g., K_{SV} is 110, 248, and $150\,\mathrm{M^{-1}}$ for DCA with Ph_2S in DCE, CH_3CN, and CH_3OH; 77, 102, and $77\,\mathrm{M^{-1}}$ for TPP^+ with Ph_2S in the same solvents; and $77\,\mathrm{M^{-1}}$ for TPP^+ with Et_2S in DCE). No significant change in the emission spectrum was observed in any case, and thus there is no spectral evidence of exciplex formation. Irradiation of oxygen-free solutions of the sensitizers in the presence of the sulfides caused at most a sluggish reaction, except for the case of TPP^+, which was rapidly bleached under these conditions. The sulfides were consumed by irradiation in oxygen-equilibrated solutions with conservation of the photosensitizer and were converted to the corresponding sulfoxides, by far the main photoproducts up to high conversion. However, in the case of TPP^+, addition of a further portion of the sensitizer was required in MeOH and MeCN for high sulfide conversion, while no sensitizer consumption took place in DCE. The oxidation efficiency was compared for $0.01\,\mathrm{M}$ solutions of the sulfides. The amount of sulfoxide formed (μmol per min) under various conditions is reported in Tables 1 and 2. To avoid interference by secondary reac-

Table 1. Amount [$\mu\mathrm{mol\,min^{-1}}$] of sulfoxide formed on photosensitization of diethyl sulfide.

	DCA				TPT^+				NMQ^+			
		$BQ^{[a]}$	$DMB^{[b]}$	$Ph_2SO^{[c]}$		$BQ^{[a]}$	$DMB^{[b]}$	$Ph_2SO^{[c]}$		$BQ^{[a]}$	$DMB^{[b]}$	$Ph_2SO^{[c]}$
CH_3CN	2.5	5.1	1.8	2.4 (0.05)[e]	0.89	–[d]	–[d]	1.0[f]	3.3	–[d]	1	3.5[f]
DCE	1.7	1.6	1.9	2.5 (0.06)[e]	0.73	0.58	0.41	1.0[f]	4.5	1.5	2.5	3.9[f]
CH_3OH	5.1	4.5	3.4	4.5 (0.12)[e]	0.77	–[d]	0.4	1.0[f]	0.56	–[d]	0.39	0.52[f]

[a] $5\times10^{-2}\,\mathrm{M}$ BQ. [b] $1.25\times10^{-3}\,\mathrm{M}$ DMB. [c] $2.5\times10^{-3}\,\mathrm{M}$ Ph_2SO. [d] $<0.008\,\mu\mathrm{mol\,min^{-1}}$ sulfoxide formed. [e] Ph_2SO_2 formed [$\mu\mathrm{mol\,min^{-1}}$]. [f] No appreciable amount of Ph_2SO_2 formed.

Table 2. Amount [µmol min^{-1}] of sulfoxide formed on photosensitization of diphenyl sulfide.[a]

	DCA			TPT$^+$			NMQ$^+$		
		BQ	DMB		BQ	DMB		BQ	DMB
CH_3CN	1.5	–[b]	–[b]	0.7	–[b]	–[b]	1.6	–[b]	0.25
DCE	0.02	0.008	–[b]	0.5	–[b]	–[b]	1.4	–[b]	0.36
CH_3OH	0.04	–[b]	–[b]	0.8	–[b]	–[b]	0.065	–[b]	–[b]

[a] Additives as in Table 1. [b] <0.008 µmol min^{-1} sulfoxide formed.

tions, the data reported refer to a conversion of 5 % or less. DMB was used at low concentration (1.25×10^{-3} M) so that competition with the sulfide in the quenching of the excited sensitizer could be neglected. The concentrations of BQ and Ph_2SO were 2.5×10^{-3} and 5×10^{-2} M, respectively.

As can be seen from Tables 1 and 2, Et_2S underwent DCA-sensitized sulfoxidation with increasing efficiency in the order DCE < CH_3CN < CH_3OH, and under these conditions Ph_2SO was susceptible to cooxidation yielding the sulfone Ph_2SO_2. The results were different with the other two sensitizers; in the case of TPP$^+$ the oxidation efficiency was low in the three solvents examined and no cooxidation of Ph_2SO occurred. In the presence of NMQ$^+$ the oxidation efficiency was similar to that obtained with DCA in DCE and CH_3CN, while it was lower in CH_3OH; again no cooxidation of Ph_2SO was observed. A small amount of acetaldehyde was formed in CH_3OH. In the case of NMQ$^+$ and TPP$^+$ sulfide oxidation was inhibited by both BQ and DMB.

Photosensitized sulfoxidation of Ph_2S occurred at rates generally lower than those of Et_2S. DCA-sensitized sulfoxidation occurred only in CH_3CN. In the presence of the two cationic sensitizers the sulfoxide was formed in the three solvents, though for NMQ$^+$ the yield was lower in CH_3OH. The sulfoxidation was inhibited by both DMB and BQ regardless of the type of sensitizer or solvent, contrary to what was observed with Et_2S.

Study of the intermediates: Laser flash photolysis (LFP) in the presence of NMQ$^+$ is first illustrated. Excitation of NMQ$^+$ in the presence of Et_2S in argon-saturated dichloroethane resulted in a transient absorption spectrum consisting of a broad band with maximum at 525 nm, attributable to overlap of the absorptions of the radical NMQ$^{\cdot}$ (λ_{max} = 550 nm)[11] and the sulfide radical cation dimer $(Et_2S)_2^{\cdot+}$ ($\lambda_{max}\approx485$ nm).[12] In the presence of oxygen, the absorption was less intense in the long-wavelength region, consistent with quenching of NMQ$^{\cdot}$. The decay was fitted satisfactorily with a second-order rate law (see Table 4; representative decays are reported as insets in the figures) both in argon- and in oxygen-saturated solutions. In CH_3CN and CH_3OH, transient absorptions of similar shape but much lower intensity were recorded (see Figure 1 and Table 3)

In the case of Ph_2S and NMQ$^+$ in argon-saturated CH_3CN the transient absorption consisted of two distinct bands with maxima at 550 and 740 nm. The former is attributable to the NMQ$^{\cdot}$ radical and the latter to the diphenyl sulfide radical cation $Ph_2S^{\cdot+}$ (see Figure 2 a).[13] In the pres-

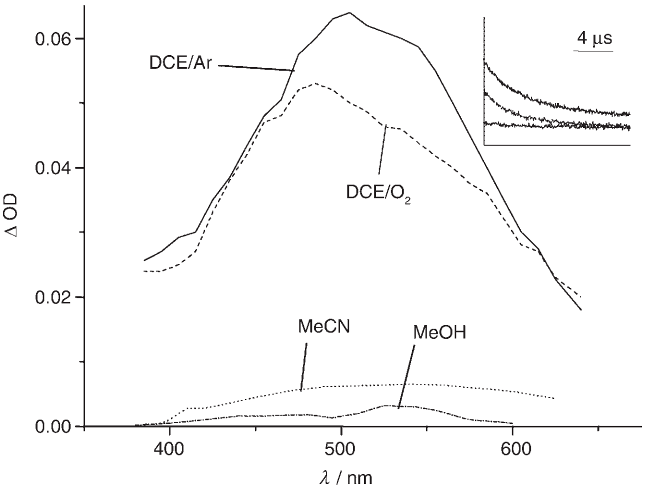


Figure 1. Transients observed 1 µs after flashing a NMQ$^+$ solution in the presence of 0.02 M Et_2S in DCE/Ar, DCE/O_2, MeCN, and MeOH. Inset: decay of the absorbance at 520 nm in Ar-equilibrated DCE, MeCN, MeOH (top to bottom; spectrum in MeCN multiplied ×5).

Table 3. Transient formation quantum yield Φ obtained on LFP in argon-saturated solution and sulfoxidation quantum yield Φ_{SO} obtained for diethyl and diphenyl sulfides.

Sensitizer	Sulfide, solvent	Transient (Φ)	Φ_{SO}
NMQ$^+$	Et_2S, CH_3CN	$(Et_2S)_2^{\cdot+}$ (0.10)	0.14
	Et_2S, DCE	$(Et_2S)_2^{\cdot+}$ (0.82)	0.19
	Et_2S, CH_3OH	$(Et_2S)_2^{\cdot+}$ (0.04)	0.02
DCA	Et_2S, CH_3CN	$(Et_2S)_2^{\cdot+}$ (0.025)	0.10
TPP$^+$	Et_2S, CH_3CN	$(Et_2S)_2^{\cdot+}$ (0.025)	0.038
	Et_2S, DCE	$(Et_2S)_2^{\cdot+}$ (0.11)	0.031
	Et_2S, CH_3OH	$(Et_2S)_2^{\cdot+}$ (0.02)	0.033
NMQ$^+$	Ph_2S, CH_3CN	$Ph_2S^{\cdot+}$ (0.23), NMQ$^{\cdot}$ (0.30)	0.07
	Ph_2S, DCE	$Ph_2S^{\cdot+}$ (1.0), NMQ$^{\cdot}$ (1.0)	0.06
	Ph_2S, CH_3OH	–	0.003
DCA	Ph_2S, CH_3CN	–	0.064
	Ph_2S, DCE	^{3}DCA (0.77, 800 nm)	0.001
	Ph_2S, CH_3OH	–	0.002
TPP$^+$	Ph_2S, CH_3CN	$Ph_2S^{\cdot+}$ (0.04), TPP$^{\cdot}$ (0.04)	0.03
	Ph_2S, DCE	$Ph_2S^{\cdot+}$ (0.27), TPP$^{\cdot}$ (0.27)	0.03
	Ph_2S, CH_3OH	–	0.03

Table 4. Rate constant for the decay of the transients observed on flash photolysis of diethyl and diphenyl sulfides.[a]

Sensitizer	Sulfide, solvent	$10^9 k_2$ [M^{-1}s^{-1}]	
		Sulfide radical cation	Reduced sensitizer, other transients
DCA	Ph_2S, CH_3CN	30 (Ar), 60 (O_2)	31 (Ar)[a]
	Ph_2S, DCE	–	12 (^{3}DCA, Ar)[a]
NMQ$^+$	Et_2S, DCE	23 (Ar), 26 (O_2)	
	Ph_2S, CH_3CN	8.0 (Ar), 24 (O_2)	28 (Ar)[a]
	Ph_2S, DCE	3.1 (Ar), 8.8 (O_2)	2.2 (Ar), 30 (O_2)
TPP$^+$	Et_2S, DCE	17 (Ar), 17 (O_2)	
	Ph_2S, CH_3CN	22 (Ar), 8.3 (O_2)	
	Ph_2S, DCE	3.8 (Ar), 4.1 (O_2)	3.9 (Ar), 4.1 (O_2)

[a] The signal is quenched by oxygen.

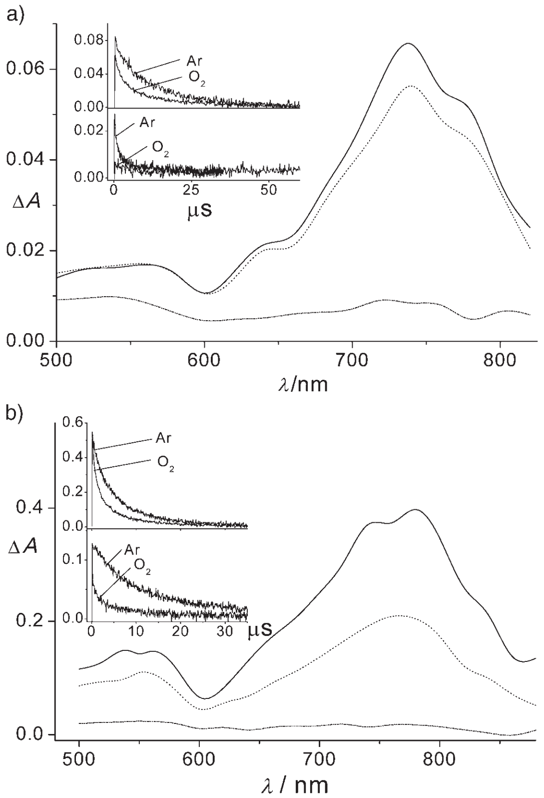


Figure 2. Transients observed on flashing a NMQ^+ solution in the presence of 0.02 M Ph_2S. Solvent: a) DCE (1 (——), 3 (•••••), 30 μs (–•–•)), b) MeCN (0.6 (——), 4 (•••••), 30 μs (–•–•)). Inset: decay of the absorbance at 750 and 550 nm in argon- and oxygen-equilibrated solutions.

ence of oxygen the transient absorption band centered at 550 nm disappeared because of $NMQ^{\bullet}$ radical quenching (see inset). The decay at 550 and 740 nm, both in the presence of Ar and O_2, was perfectly fitted with a second-order rate law. Similar transient absorption spectra were recorded in DCE, but the intensity was much higher (Figure 2b). In the presence of oxygen the decay at 550 and 740 nm perfectly fitted a second-order rate law, while in the argon-saturated medium neither a second-order rate law nor exponential analysis gave a perfect fitting of the decays at 740 and 550 nm. No transient absorption signals were measured in methanol.

With DCA as sensitizer the behavior changed with the solvent, as can be seen for Ph_2S in Figure 3. In argon-saturated CH_3CN the transient absorption extended over the range 600–850 nm, where the $DCA^{\bullet-}$ radical anion (λ_{max} = 704 nm),[14] triplet ^3DCA (λ_{max} = 735 nm, 810 nm),[15] and the diphenyl sulfide radical cation (λ_{max} = 740 nm) all absorb (Figure 3a). In oxygen-saturated CH_3CN the spectrum changed shape and was less intense (Figure 3b). This was mainly attributable to $Ph_2S^{\bullet+}$, in accordance with the known quenching by oxygen of both triplet ^3DCA and $DCA^{\bullet-}$. The decay at 740 nm followed a second-order rate law. In argon-saturated DCE, the transient absorption spectrum extended from 600 nm up to the red edge of the visible region (Figure 3c). This absorbance disappeared completely in the presence of oxygen. The maxima at 730 and 810 nm correspond well to the values reported for the triplet–triplet absorption of DCA.[15] In methanol, only a very weak signal was detected around 730 nm under argon and none under oxygen. Essentially the same situation was observed for Et_2S. A transient around 500 nm was barely detected in argon-saturated CH_3CN, but not in CH_3OH or DCE.

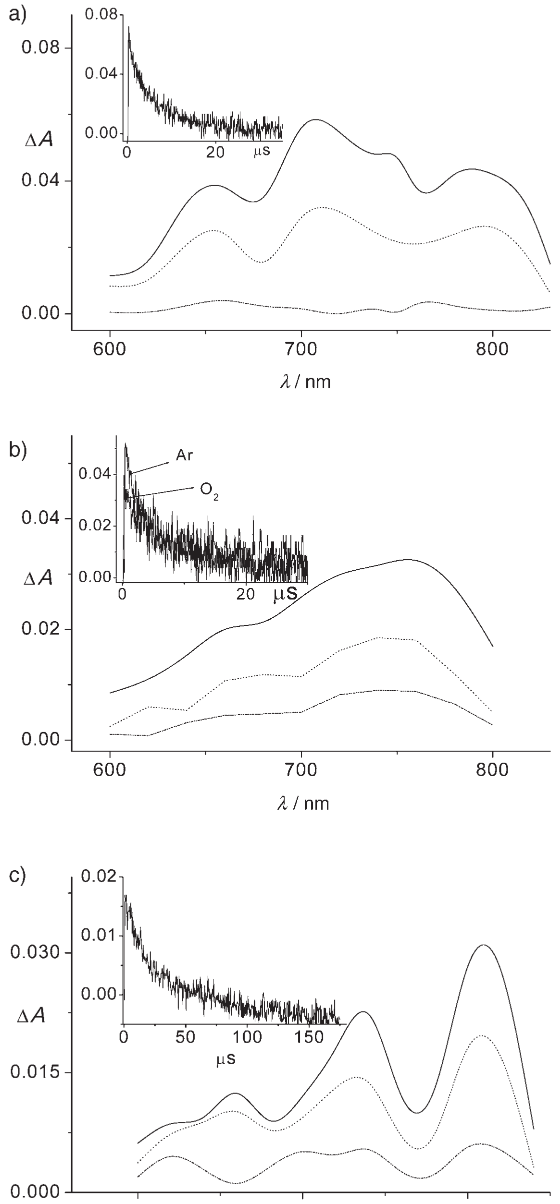


Figure 3. Transients observed on flashing a DCA solution in the presence of 0.02 M Ph_2S a) in Ar-equilibrated MeCN (1 (——), 3 (•••••), 30 μs (–•–•)), b) in oxygen-equilibrated MeCN (0.4 (——), 4 (•••••), 30 μs (–•–•)), and c) in Ar-equilibrated DCE (1 (——), 10 (•••••), 70 μs (–•–•)). Inset: decay of the absorbance at 750 and 550 nm in argon- and oxygen-equilibrated solutions.

In the case of TPP^+ and diethyl sulfide a transient absorption extending from 420 to 650 nm with λ_{max} = 530 nm was measured. The sulfide radical cation dimer, $TPP^{\bullet}$, and triplet excited TPP^{+} are known to absorb in the observed region with $\lambda_{max}=485$ (in water), 550, and 480 nm respectively.[16] The signal was much more intense in DCE than in CH_3CN and CH_3OH (Figure 4).

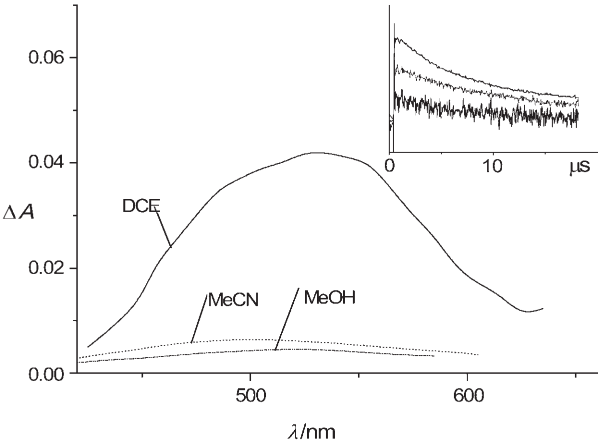


Figure 4. Transients observed 1 μs after flashing a TPP^{+} solution in the presence of 0.02 M Et_2S in DCE, MeCN, and MeOH. Inset: decay of the absorbance at 520 nm in the same solvents (MeCN, MeOH ×5).

With diphenyl sulfide, the transient absorption spectrum in both argon-saturated CH_3CN and DCE exhibited maxima at 540 and 760 nm attributable to $TPP^{\bullet}$ and to the sulfide radical cation, respectively (Figure 5a and b). The absorption was much more intense in DCE (Figure 5b) than in CH_3CN (Figure 5a) and very weak in CH_3OH. In DCE both maxima underwent second-order decay with rate constants that did not change on oxygen saturation, though the intensity of both bands was reduced. In CH_3CN the signal of the radical cation decay was little affected by O_2, while the 540 nm transient disappeared.

The molar absorption coefficients of several of the transients involved ($(Et_2S)_2^{\bullet+}$,[12] $DCA^{\bullet-}$,[14] ^3DCA,[15]) have been previously reported. We evaluated the molar absorption coefficients of the diphenyl sulfide radical cation and the $NMQ^{\bullet}$ and $TPP^{\bullet}$ radicals, assuming that ET to excited sensitizer from the sulfide occurred with unitary quantum yield in the NMQ^{+}/Ph_2S system in DCE, where the transient absorptions were most intense. The assumption was supported by the fact that experiments with NMQ^{+} solutions in DCE with increasing concentrations of both Et_2S and Ph_2S (up to 0.1 M) showed that the transient intensity did not grow further; the molar absorption coefficient thus evaluated for $Ph_2S^{\bullet+}$, $\varepsilon_{750}=5900\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$, was close to that obtained for other sulfide radical cations.[12,13] The reduced species $NMQ^{\bullet}$ and $TPP^{\bullet}$ were formed in equimolar amounts with respect to the sulfide radical cation, and the values $\varepsilon_{550}=2200$ and $5900\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$, respectively, were calculated. This is a higher value than that reported ($\varepsilon=2790\,\mathrm{M}^{-1}\,\mathrm{cm}^{-1}$) for $TPP^{\bullet}$ at 550 nm in CH_3CN.[16] Relative LFP formation quantum yields of the transients are compared with the quantum yields of sulfoxidation Φ_{SO} in Table 3. Second-order fitting of the observed decay afforded the rate constants k_2 of the observed transients from the experimental rate constants $k_{obs}=k_2/\varepsilon$ and the above ε data. These are reported in Table 4, both for argon- and for oxygen-saturated solutions.

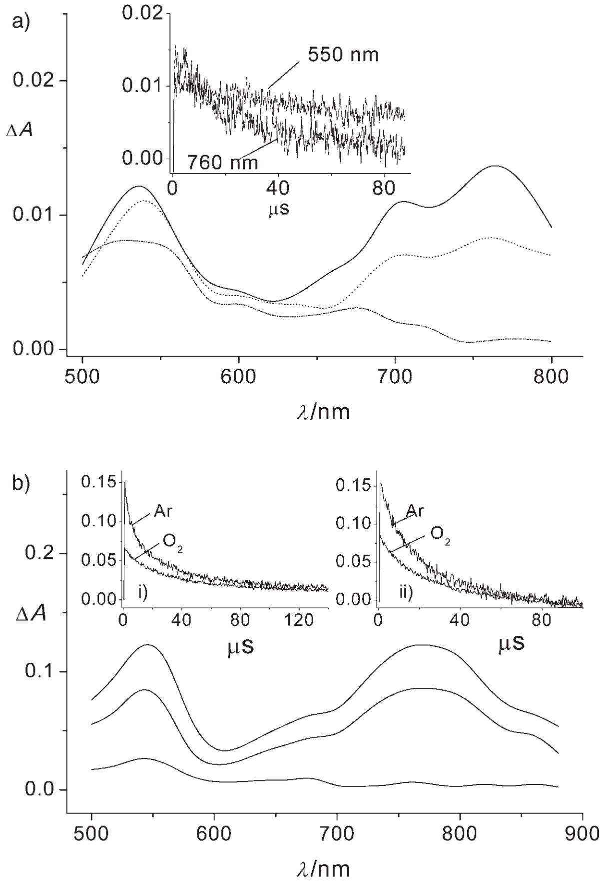


Figure 5. Transients observed on flashing a TPP^{+} solution in the presence of 0.02 M Ph_2S. Solvent: a) DCE (2 (——), 10 (•••••), 80 μs (–•–•)), b) MeCN (1 (——), 10 (•••••), 70 μs (–•–•)). Inset: decay of the absorbance at i) 760 and ii) 550 nm in argon- and oxygen-equilibrated solutions.

Calculations: Theoretical calculations were performed to rationalize the mechanism of the observed sulfoxidation. Since sulfide radical cations were formed, it was explored how these interact with molecular oxygen or the superoxide anion. The radical cation of dimethyl sulfide (**1**) was taken as model, and calculations were carried out at the B3LYP/6-31+G(2d,p) level of theory. The reactions considered are reported in Equations (7)–(10).

$$Me_2S^{\bullet+}\ (\mathbf{1}^{\bullet+}) + O_2^{\bullet-} \rightarrow Me_2S^{+}{-}O{-}O^{-} \tag{7}$$

$$\mathbf{1}^{\bullet+} + O_2^{\bullet-} \rightarrow Me_2\overline{S{-}O{-}O} \tag{8}$$

$$\mathbf{1}^{\bullet+} + O_2^{\bullet-} \rightarrow Me_2S + O_2 \tag{9}$$

$$\mathbf{1}^{\bullet+} + O_2 \rightarrow Me_2S^{+}{-}O{-}O^{\bullet} \tag{10}$$

The addition of $\mathbf{1}^{\cdot+}$ to the superoxide anion to give either the persulfoxide or the thiadioxirane [Eq. (7) and (8)] have been previously calculated by Baciocchi et al.[3d] at the same level of theory to be strongly exothermic processes: $\Delta H = -156.9\,\text{kcal}\,\text{mol}^{-1}$ in the gas phase (−47.8 in CH_3CN) and −158.6 (−48.6 in CH_3CN), respectively. Furthermore, the interaction between these two intermediates may also involve electron transfer [Eq. (9)]. We calculated that this process is even more exothermic, both in the gas phase ($\Delta H = -184.8\,\text{kcal}\,\text{mol}^{-1}$) and in acetonitrile solution ($-63.6\,\text{kcal}\,\text{mol}^{-1}$).[17]

For the reaction with molecular oxygen [Eq. (10)], Rauk et al.[18] previously calculated that $\mathbf{1}^{\cdot+}$ forms only weakly bound complexes. However, we felt that exploring in detail the potential energy surface (PES) of the reaction pathways involving **1** and $\mathbf{1}^{\cdot+}$ in the presence of oxygen was worthwhile.

The PES of the addition reaction of $\mathbf{1}^{\cdot+}$ to triplet oxygen at the B3LYP/6-31+G(2d,p) level of theory followed closely the B3LYP/6-311+G(d,p) hypersurface described by Rauk et al. In fact, it reached the same shallow minima: **1-OO**$^{\cdot+}$**(i)** with C_s symmetry and **1-OO**$^{\cdot+}$**(ii)**, both of which lie below $\mathbf{1}^{\cdot+}$ and triplet O_2 on the PES (by −4.0 and $-3.6\,\text{kcal}\,\text{mol}^{-1}$, respectively, in the gas phase; Table 5). The large S^1–O^2 distance (2.61 Å, see Figure 6) and the weak interaction between $\mathbf{1}^{\cdot+}$ and triplet O_2 suggested that the structures were ion-induced dipole complexes in equilibrium with free $\mathbf{1}^{\cdot+}$ and triplet O_2. Thermal contributions in the gas phase to the Gibbs free energy (ΔG) and solvation effects in acetonitrile computed by the PCM model ($\delta\Delta G_{\text{solv}}$) shifted the equilibrium toward the free reactants, which were roughly $10\,\text{kcal}\,\text{mol}^{-1}$ below the complexes in acetonitrile solution.

Table 5. Reaction energies ΔE[a] and reaction free energies ΔG in the gas phase and in acetonitrile solution for formation of the complexes **1-OO**$^{\cdot+}$**(i)** and **1-OO**$^{\cdot+}$**(ii)** starting from $\mathbf{1}^{\cdot+}$ and O_2, along with the solvation energies for each stationary point $\delta\Delta G_{\text{solv}}$ [in $\text{kcal}\,\text{mol}^{-1}$] in acetonitrile at the UB3LYP/6-31+G(2d,p) and PCM-UB3LYP/6-31+G(2d,p) levels of theory.

Stationary points	Gas phase		Acetonitrile solution		
	ΔE_{gas}[a]	ΔG_{gas}[b]	$\delta\Delta G_{\text{solv}}$	ΔE_{solv}	ΔG_{solv}
O_2(T)	–	–	1.8	–	–
1	–	–	0.9	–	–
$\mathbf{1}^{\cdot+}$	–	–	−48.2	-	–
1-OO$^{\cdot+}$**(i)**	−4.0	4.5	−39.4	6.4	11.5
1-OO$^{\cdot+}$**(ii)**	−3.6	4.2	−39.9	6.6	10.7

[a] Relative to free reactants: $\mathbf{1}^{\cdot+}$ and triplet O_2, −628.049443 Hartree. [b] For conversion from 1 atm standard state to $1\,\text{mol}\,\text{L}^{-1}$ standard state, the following contribution was added to the standard Gibbs free energy: $RT\ln R'T$, where R' is the value of R in $\text{L}\,\text{atm}\,\text{mol}^{-1}\,\text{K}$. For a reaction with A+B=C stoichiometry, the correction for $\Delta G^{\neq}$ is $RT\ln R'T$. At 298 K the corrections amount to $-1.90\,\text{kcal}\,\text{mol}^{-1}$ for $\Delta G^{\neq}$.

The interaction with a molecule of dimethyl sulfide made a new reaction pathway available for both of the loosely bonded complexes **1-OO**$^{\cdot+}$**(i)** and **1-OO**$^{\cdot+}$**(ii)** (Figure 6). Such a chemical pathway ended with the formation of a much more stable dimeric radical cation **P-1-OO-1**$^{\cdot+}$, which existed as three equilibrating conformers **P-1-OO-1**$^{\cdot+}$**(i)–(iii)**.

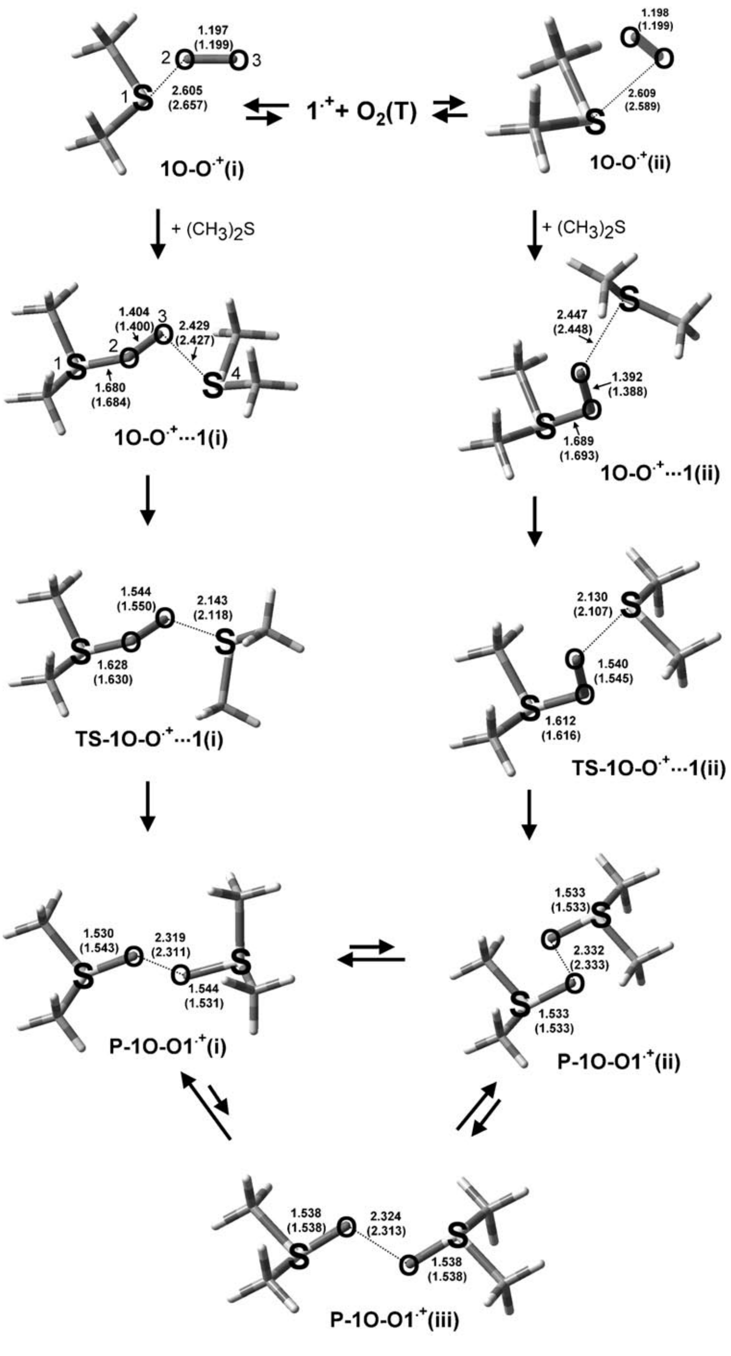


Figure 6. Structure of the stationary points (intermediates and transition structures) involved in the reaction of dimethyl sulfide radical cation ($\mathbf{1}^{\cdot+}$) with triplet oxygen.

In more detail, at the beginning of the reaction coordinate, two additional minima were located on the PES: **1-OO**$^{\cdot+}$**···1(i)** and **1-OO**$^{\cdot+}$**···1(ii)** (Figure 6). In such intermediates the S^4 atom (see Figure 6 for numbering) of the approaching dimethyl sulfide is 2.43–2.45 Å from the distal oxygen atom O^3.

The formation of the new intermediates **1-OO$^{\cdot+}$⋯1(i)** and **1-OO$^{\cdot+}$⋯1(ii)** starting from the complexes **1-OO$^{\cdot+}$** is an energetically favorable process. In fact, these two states were located −12.7 and −14.0 kcal mol^{-1} below free **1-OO$^{\cdot+}$(i)** and **1** on the PES, respectively (Table 6). The process was almost barrierless, since we were unable to locate a TS connecting them with complexes **1-OO$^{\cdot+}$**. To unambiguously prove that intermediate **1-OO$^{\cdot+}$⋯1(i)** is generated by nucleophilic addition of dimethyl sulfide to the ion-induced dipole complex **1-OO$^{\cdot+}$(i)**, we performed stepwise stretching of the O^3–S^4 distance in the intermediate **1-OO$^{\cdot+}$⋯1(i)** from 2.4 to 3.39 Å by a standard scan procedure and observed a parallel elongation of the S^1–O^2 bond in the intermediate up to 1.91 Å with concomitant increase in energy.

Table 6. Reaction energies ΔE[a] and reaction free energies ΔG in the gas phase and in acetonitrile solution for the reaction of the complex **1-OO$^{\cdot+}$** with **1**, along with the solvation energies for each stationary point $\delta\Delta G_{solv}$ [kcal mol^{-1}] in acetonitrile at the UB3LYP/6-31+G(2d,p) and PCM-UB3LYP/6-31+G(2d,p) levels of theory.[b]

Stationary points	Gas phase		Acetonitrile solution		
	ΔE_{gas}[a]	ΔG_{gas}	$\delta\Delta G_{solv}$	ΔE_{solv}	ΔG_{solv}
1-OO$^{\cdot+}$⋯1(i)	−12.7	−0.8	−27.2	−2.6	10.5
1-OO$^{\cdot+}$⋯1(ii)	−14.0	−1.7	−27.9	−4.2	9.0
TS-1-OO$^{\cdot+}$⋯1(i)	−8.8	3.0	−26.7	2.2	14.7
TS-1-OO$^{\cdot+}$⋯1(ii)	−10.2	1.8	−25.4	0.9	14.9
P-1-OO-1$^{\cdot+}$(i)	−56.9	−42.9	−25.1	−45.7	−29.6
P-1-OO-1$^{\cdot+}$(ii)	−55.1	−42.5	−24.2	−−43.6	−28.3
P-1-OO-1$^{\cdot+}$(iii)	−54.0	−41.6	−23.0	−41.5	−26.1

[a] Relative to the complex **1-OO$^{\cdot+}$(i)** and **1**: −1106.083589 Hartree. [b] See footnote [b] in Table 5

Up to this point the examination has been carried out in terms of energy on the PES. However, a balanced evaluation of the stabilities of intermediates **1-OO$^{\cdot+}$⋯1(i)** and **1-OO$^{\cdot+}$⋯1(ii)** relative to the complex **1-OO$^{\cdot+}$(i)** and dimethyl sulfide (**1**) should be based on free energy data (ΔG). When these were considered, it resulted that **1-OO$^{\cdot+}$-1(i)** and **1-OO$^{\cdot+}$-1(ii)** were again both more stable than the starting complexes **1-OO$^{\cdot+}$(i)** and **1** by −0.8 and −1.7 kcal mol^{-1}, respectively, in the gas phase. Taking into account solvation led to destabilization and placed these intermediates 9–10.5 kcal mol^{-1} above the complex **1OO$^{\cdot+}$(i)** and **1** (Table 6), a result due to the weaker solvation of the former radical cations (−27.2, −27.9 kcal mol^{-1}) with respect to the latter (−39.4, −39.9 kcal mol^{-1}).

Furthermore, **1-OO$^{\cdot+}$⋯1(i)** evolved along the reaction coordinate toward a covalently bonded intermediate **P-1-OO-1$^{\cdot+}$(i)**, which is much more stable than the original ion-induced dipole complex **1-OO$^{\cdot+}$(i)** and **1**, both in the gas phase ($\Delta G_{gas} = -42.9$ kcal mol^{-1}) and in acetonitrile solution ($\Delta G_{solv} = -29.6$ kcal mol^{-1}). This involved passing through transition structure **TS-1-OO$^{\cdot+}$⋯1(i)**. Similarly, **1-OO$^{\cdot+}$⋯1(ii)** evolved to intermediate **P-1-OO-1$^{\cdot+}$(ii)** ($\Delta G_{gas} = -40.8$ kcal mol^{-1}, $\Delta G_{solv} = -27.5$ kcal mol^{-1}), and also in this case the connecting **TS-1-OO$^{\cdot+}$⋯1(ii)** was located.

Internal reaction coordinate (IRCs) were calculated at the B3LYP/6-31+G(2d,p) level to connect both TSs **TS-1-OO$^{\cdot+}$** to the corresponding precomplexed reactants (**1-OO$^{\cdot+}$**) and products (**P-1-OO-1$^{\cdot+}$**).

The two final radical cations **P-1-OO-1$^{\cdot+}$(i)** and **P-1-OO-1$^{\cdot+}$(ii)** and a third form (see Figure 6) were interconverting conformers and were much more stable than the starting reactants both in the gas phase and in acetonitrile solution, and this afforded the driving force for arriving at such products through the equilibria in Figure 6. The stretched O–O bond length in the final adducts **P-1-OO-1$^{\cdot+}$** (2.31–2.33 Å) suggested this intermediate further evolved by breaking of the peroxo bond.

Discussion

Photosensitized sulfoxidation mechanism: Steady-state and laser flash photolysis results support that at least two different reaction paths are involved in the photosensitized oxidation of sulfides, depending on reagent, sensitizer, and solvent. Dialkyl sulfides are known to react with singlet oxygen to yield persulfoxide intermediates. Baciocchi et al.[3d] have supplied evidence that the DCA-sensitized oxidation of dibutyl sulfide in CH_3CN involves this reaction mechanism, since sulfoxidation is inhibited by DABCO, an efficient singlet-oxygen quencher, and cooxidation of Ph_2SO to the corresponding sulfone occurs on reaction with the nucleophilic persulfoxide intermediate [Eq. (11)]. The same conclusions apply to the oxidation of diethyl sulfide sensitized by DCA, and are supported by the diagnostic effect of the addition of Ph_2SO in the three solvents considered.

$$R_2S^+{-}O{-}O^- + Ph_2SO \rightarrow R_2SO + Ph_2SO_2 \qquad (11)$$

The extent of sulfoxidation in the presence of DCA depends on the solvent and increases by a factor three on going from DCE to CH_3CN and CH_3OH; this can be rationalized as arising from the more efficient conversion of the persulfoxide intermediate to the sulfoxide in protic solvents (by a factor of up to 20),[6] though the effect is attenuated, probably because of the different $^1O_2$ lifetimes in these solvents (ca. 50 μs for CH_3CN and $C_2H_4Cl_2$, 7 μs for CH_3OH),[19] which is relevant at the employed Et_2S concentration of 0.01 M. The fact that neither BQ nor DMB affects the DCA-sensitized oxidation confirms the $^1O_2$ mechanism.

The experiments on Et_2S in the presence of NMQ^+ or TPP^+ as sensitizer show that Ph_2SO cooxidation does not take place in any solvent, and sulfoxidation is inhibited in all cases by BQ, known as a quencher of $O_2^{\cdot-}$,[3d,20a–d] In fact, ET from $O_2^{\cdot-}$ to BQ is exoergonic ($E°(BQ/BQ^{\cdot-}) = -0.47$ and $E°(O_2/O_2^{\cdot-}) = -0.87$ V versus SCE).[20a,b] Moreover, the reactions are inhibited also by a small amount of DMB, which is expected to reduce the sulfide radical cation ($E°(Et_2S/Et_2S^{\cdot+}) = 1.65$ V and $E°(DMB/DMB^{\cdot+}) = 1.41$ V versus SCE).[20e,f] Further evidence comes also from the detection in laser flash photolysis of the dimeric sulfide radical cation $(Et_2S)_2^{\bullet +}$. For these reasons we can safely conclude that in the case of sensitization by TPP^+ and NMQ^+ an ET mechanism is involved in the sulfoxidation of Et_2S.

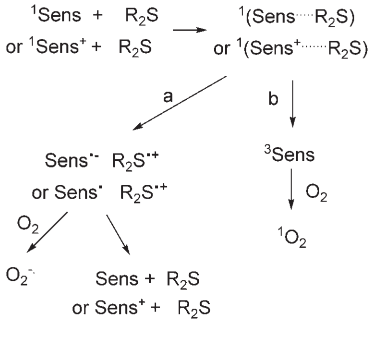
In the case of diphenyl sulfide there is no indication of the $^1O_2$ mechanism. Thus, no cooxidation of Ph_2SO to the sulfone has been observed. Further, sulfoxidation is in all cases inhibited both by BQ and by DMB, which are expected to reduce $Ph_2S^{\bullet +}$ ($E°(Ph_2S/Ph_2S^{\bullet +}) = 1.43$ V versus SCE).[20g] The sulfide radical cation in its monomeric form (no indication for a dimeric form, in accord with previous literature[13c]) is detected by laser flash photolysis along with the reduced sensitizer, and under oxygen the absorbance of the reduced sensitizer disappears partially or completely, while that of the sulfide radical cation persists. With NMQ^+ and TPP^+ the oxidation quantum yield shows little dependence on solvent (decreasing in CH_3OH for NMQ^+), while with DCA the reaction takes place in CH_3CN but is negligible in both DCE and CH_3OH.

Role of the photosensitizers: It is known that both DCA and NMQ^+ in the singlet excited state are capable of sensitizing singlet-oxygen formation with a limiting quantum yield of two, due to the near coincidence of the sensitizer singlet–triplet energy gap and the activation energy of singlet oxygen (24 and 21 kcal mol^{-1} for DCA and NMQ^+, respectively).[5d,e] Rate constants for quenching by oxygen in CH_3CN are $5.9 \times 10^9\,\text{M}^{-1}\text{s}^{-1}$ and $6.8 \times 10^9\,\text{M}^{-1}\text{s}^{-1}$ for ^{1}DCA and $^1NMQ^+$, respectively.[3d] Since rate constants of sensitizer quenching by sulfides via ET are $(1–3) \times 10^{10}$ at sulfide concentrations of 0.02 M, the contribution of quenching by oxygen is less than 15%. As $^1TPP^+$ is a poor singlet-oxygen sensitizer, we can conclude that oxygen quenching based on direct sensitization as in Equation (12) does not contribute significantly in any case studied.

$$^1\text{Sens} + O_2 \rightarrow {}^3\text{Sens} + {}^1O_2 \qquad (12)$$

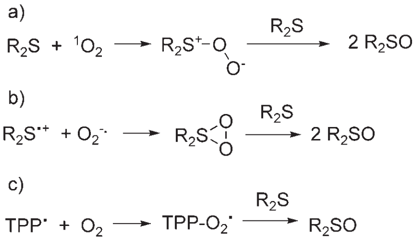
Another mechanism leading to singlet oxygen is sulfide-enhanced intersystem crossing (ISC) of ^{1}Sens to ^{3}Sens via the initial contact pair (Scheme 1, path b), followed by oxygen sensitization according to Equation (13).

$$^3\text{Sens} + O_2 \rightarrow \text{Sens} + {}^1O_2 \qquad (13)$$



Scheme 1. Sensibilization paths.

The triplet state is lower in energy than the radical ion pair only in the case of DCA.[21] Examination of Figure 3a and c shows that some DCA triplet is formed along with the radical anion in argon-saturated CH_3CN, and indeed in a less polar solvent such as DCE ($\varepsilon = 10.36$ versus 37.5 for CH_3CN and 32 for CH_3OH) path b completely substitutes path a leading to ^{3}DCA with a quantum yield of 0.7. Formation of ^{3}DCA has been previously reported for exciplexes in apolar solvents[22] and related to the charge-transfer character of such species.[22a] In conclusion, in the case of DCA, quenching by sulfide enhances ISC to ^{3}DCA and $^1O_2$ is formed mainly through path b Scheme 1, rather than by direct sensitization [Eqs. (12) and (13)]. With this sensitizer, diethyl sulfide is oxidized by singlet oxygen (Scheme 2, path a). Ph_2S, which scarcely reacts with $^1O_2$ ($k = 3.9 \times 10^4\,\text{M}^{-1}\text{s}^{-1}$),[6] is not oxidized in DCE, though LFP clearly demonstrates that efficient ISC to ^{3}DCA ($\Phi = 0.7$ and thus $^1O_2$ formation) takes place. Ph_2S is oxidized only in CH_3CN, where the ET mechanism plays a role.



Scheme 2. Oxygenation mechanisms.

In contrast to DCA, for the cationic sensitizers NMQ^+ and TPP^+ path a requires no charge separation. The formation of the $R_2S^{\bullet +}$/Sens$^\bullet$ pair is favored in the moderately polar solvent DCE, where the formation quantum yields of these transients are 4–8 times higher than in CH_3CN or CH_3OH, possibly because these more basic solvents specifically solvate Sens$^+$ cations, and significant solvent reorganization is required to form the radical ion pair. The formation quantum yield of the radical ions is higher for NMQ^+ than for TPP^+, in part due to incomplete quenching of the short-lived singlet of the latter sensitizer by the sulfide (compare $\tau = 2.7$ ns for $^1TPP^+$ with $\tau = 20$ ns for $^1NMQ^+$).[5d,e,8]

In most cases studied, the disappearance of the radical ions in the absence of oxygen is satisfactorily fitted by a second-order decay process, which is reasonably attributed to back electron transfer. This occurs at a diffusion-controlled rate with the aliphatic sulfide Et_2S, while with aromatic Ph_2S, back electron transfer from NMQ$^\bullet$ or TPP$^\bullet$ to the sulfide radical cation is slower in DCE than in CH_3CN (see Table 4), probably because of the above-mentioned preferential stabilization of Sens$^+$ in the former solvent.[23] In the presence of oxygen, both DCA$^{\bullet -}$ and NMQ$^\bullet$ are quenched (see the insets in Figures 2 and 3b) and most likely yield the superoxide anion. The free-energy change for reduction of oxygen is $\Delta G^\circ_{\mathrm{ET}} = -2.5$ kcal mol^{-1} for $DCA^{\cdot -}$ in CH_3CN and -0.8 kcal mol^{-1} for $NMQ^{\cdot}$ in CH_3CN ($+0.1$ kcal mol^{-1} in DCE). Under these conditions, the decay of $R_2S^{\cdot +}$ reasonably involves reaction with $O_2^{\cdot -}$ and is again well fit by a second-order rate law and diffusion control or close to it. When using TPP^+ the shape of the transient absorptions and the decay kinetics of both $TPP^{\cdot}$ and $R_2S^{\cdot +}$ are insensitive to the presence of oxygen (see the insets in Figure 5). As an example, $Ph_2S^{\cdot +}$ and $TPP^{\cdot}$ produced in DCE decay at the same rate (3.9 and 4.1×10^9 $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$) in the absence and in the presence of O_2. The superoxide anion is not appreciably formed with this sensitizer, in accord with the fact that ET from $TPP^{\cdot}$ is endothermic ($\Delta G^\circ_{\mathrm{ET}} = +10.2$ kcal mol^{-1} in CH_3CN). However, the initial absorbance intensity of the radical ions is somewhat lower in oxygenated solution (see Figure 5b), since part of the singlet excited TPP^+ decays through path b and triplet TPP^+ ($\tau = 10$ μs) can be quenched by oxygen in this case.[24]

ET sulfoxidation: As seen above, apart from the DCA/Et_2S system, all of the present sulfoxidations share the same characteristics, including quenching of the sensitizer singlet state by the sulfide. Thus, these reactions are safely recognized as ET-sensitized reactions, but the exact mechanism of the chemical process needs to be defined, also with respect to previous reports. An appealing rationalization is that the sulfide radical cation (or its dimer) adds to the superoxide anion and forms the same intermediate involved in singlet-oxygen reactions, the persulfoxide, and, after reaction with a second sulfide molecule, two sulfoxide molecules.

This analogy of the two paths for forming persulfoxide [Eqs. (2) and (14)] was suggested earlier.[25]

$$R_2S^{\cdot +} + O_2^{\cdot -} \rightarrow R_2S^{+}{-}O{-}O^{-} \qquad (14)$$

Extensive studies, mainly in water, later established that the reaction of the sulfide radical cation with $O_2^{\cdot -}$ is very fast ($(2.3 \pm 1.2) \times 10^{11}$ $\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ for $Me_2S^{\cdot +}$ in water), that the oxygen atom in sulfoxides arises from oxygen (under some conditions), and that persulfoxide is involved (e.g., SOD effect on sulfoxide formation).[26,27]

However, Baciocchi et al. recognized that NMQ^+-photosensitized oxidation in CH_3CN does not exhibit the diagnostic Ph_2SO cooxidation [Eq. (11)] and proposed that, although sulfoxidation involves reaction between $R_2S^{\cdot +}$ and $O_2^{\cdot -}$, the adduct formed is a thiadioxirane (path b in Scheme 2) rather than the persulfoxide formed in the $R_2S + {}^1O_2$ reaction (path a).[3d] The thiadioxirane is an electrophile and thus reacts with the sulfide as indicated, but not with Ph_2SO. Calculations showed that this intermediate is approximately isoenergetic with the persulfoxide but, in contrast to the latter, is separated from $R_2S + {}^1O_2$ by a sizeable barrier (ca. 10 kcal mol^{-1}). Thus, it is conceivable that it is formed when starting from the high-energy radical cation/superoxide pair,[3d] though not from $R_2S + {}^1O_2$ and, also in contrast to the persulfoxide, is sufficiently persistent to react with the sulfide according to Equation (3) (see below and Figure 7).

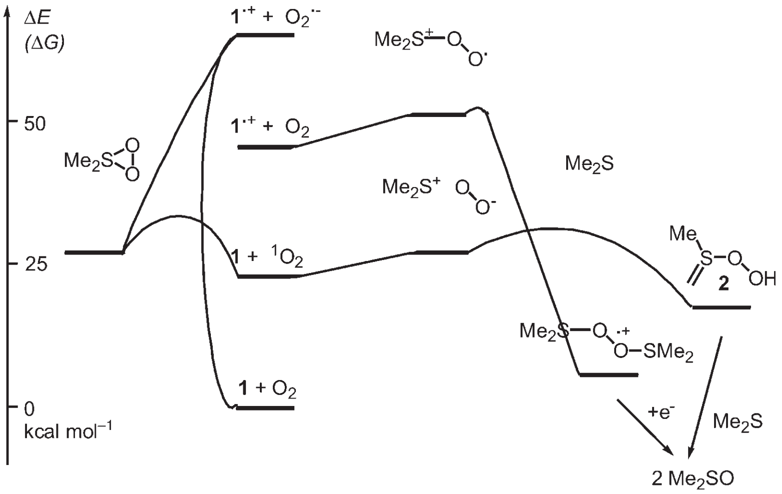


Figure 7. Energy profile for the reaction of dimethyl sulfide radical cation ($\mathbf{1}^{\cdot +}$) with oxygen. For the sake of clarity, not all of the located intermediates are shown. For comparison the singlet-oxygen oxidation of **1** via persulfoxide and rearrangement to **2** (right), as well as the possible processes from $\mathbf{1}^{\cdot +} + O_2^{\cdot -}$ (electron transfer and addition, left), are also shown.

The present evidence from flash photolysis experiments in various solvents and the inhibition of sulfoxidation by a small amount of dimethoxybenzene leave no doubt about the role of sulfide radical cation. However, reaction of $R_2S^{\cdot +}$ with the superoxide anion is not fully established, since sulfoxidation occurs when electron transfer from the reduced sensitizer to oxygen [Eq. (5)] is exoergonic (e.g., $DCA^{\cdot -}$), close to thermoneutral ($NMQ^{\cdot}$), or markedly endoergonic ($TPP^{\cdot}$).[28] Thus, it may be that some reactions occur via $R_2S^{\cdot +} + O_2^{\cdot -}$, while others do not.

If the $O_2^{\cdot -}$ mechanism applies to both DCA- (with Ph_2S) and NMQ^+-sensitized oxidations, the TPP^+-sensitized oxidation follows a different path. A possible explanation is the formation of peroxyl radicals TPP-OO$^{\cdot}$ from $TPP^{\cdot}$ (path c in Scheme 2) that oxidize the sulfides. This has analogy with the well-known oxygen transfer to aromatic and aliphatic sulfides by radicals of this type, for example, the cumylperoxyl radical or halogenated peroxyl radicals.[29] Indeed, electrochemical evidence indicates that $TPP^{\cdot}$ chemically reacts with molecular oxygen (on a long timescale).[8a] Thus, reaction via a TPP-OO$^{\cdot}$ radical is a possibility, but in such a case oxygen transfer should involve consumption of the sensitizer, since the alkoxyl radicals resulting from oxygen transfer ($TPP\text{-}OO^{\bullet}+R_2S \rightarrow TPP\text{-}O^{\bullet}+R_2SO$) would further react with irreversible degradation of the pyrylium ring. Experiments show that TPP^+ (2×10^{-3} M) does not react stoichiometrically and is only partially consumed when the sulfide (0.01 M in Table 1, but tested also at 0.03 M) is completely oxidized.[10] Furthermore, flash photolysis shows that decay of $Ph_2S^{\bullet+}/TPP^{\bullet}$ is not affected by oxygen and is identical to that of the $Ph_2S^{\bullet+}/NMQ^{\bullet}$ pair in DCE. This supports that back electron transfer to $TPP^{\bullet}$ remains the main path.[30] Finally, sulfide-enhanced ISC of $^1TPP^+$ is possible, and singlet oxygen generation by unquenched $^3TPP^+$ cannot be excluded but should not interfere with the decay of the radical ions and only lowers their initial absorbance intensity.

Alternatively, one can look for a hypothesis that would apply to all sulfoxidations not involving singlet oxygen. In this case, $O_2^{\bullet-}$ can have no role and the only remaining possibility is reaction of the sulfide radical cation with molecular oxygen. This has been generally excluded as a viable path,[26,31] though it does occur under "forced" conditions, such as high oxygen pressure,[32a] confinement in zeolites,[32b,c] and catalysis by amines or bases in water,[31d–f] cerium salts,[31h] and nitrogen dioxide.[31i] We thus examined whether such mechanisms may play a role.

Reaction with molecular oxygen: While addition of radical cation $\mathbf{1}^{\bullet+}$ to superoxide [Eq. (7) or (8)] is exothermic by about -48 kcal mol^{-1} in CH_3CN, electron transfer between the same species [Eq. (9)] is even more so (-64 kcal mol^{-1}, see Figure 7), which makes this process competitive with bond formation.

Although it has been demonstrated that superoxide adds to some neutral organic radicals (in water), rather than reducing them,[3] it is difficult to imagine that electron transfer would not be the main path when oppositely charged radical ions are involved, particularly in organic solvents. Indeed, flash photolysis provides evidence that $O_2^{\bullet-}$ is formed and reacts with the sulfide radical cation at a rate close to k_{diff}, as also found in previous studies. The high reaction rate is at least as well explained by Equation (9) as by Equations (7) and (8). Furthermore, the role of back electron transfer is supported by the fact that the yield of sulfoxidation may be considerably smaller than the yield of ion formation (particularly in a moderately polar solvent such as DCE, see Table 2).

As for combination with oxygen [Eq. (10)], calculations by Rauk,[18] confirmed in this work, support that $Me_2S^{\bullet+}$ does not form a covalent bond with molecular oxygen, but only loose dipole complexes (**1-OO**$^{\bullet+}$). These lie about 6 kcal mol^{-1} above the components, and taking into account the entropic contribution (which is, however, overestimated by the presently used methods)[34] brings them about 10 kcal mol^{-1} above the reagents. However, the ensuing reaction of this species with **1** opens an unexpected pathway leading, via the further complex **1-OO**$^{\bullet+}$**···1** and the transition state **TS-1-OO**$^{\bullet+}$**···1**, to the covalently bound radical cation **P-1-OO-1**$^{\bullet+}$ in a strongly exoergonic process. This intermediate is characterized by a somewhat elongated O–O bond in all of the conformers (see Figure 6) and radical character at the oxygen atom. Therefore, the essentially single-electron σ_{O-O} bond is expected to cleave either directly or on interaction with a sulfide molecule to yield the sulfoxide and regenerate $Me_2S^{\bullet+}$ [Eq. (15)].[35]

$$R_2S{-}O \overset{\cdot+}{-} O{-}SR_2 \rightarrow (R_2SO^{\cdot+} \cdots OSR_2) \xrightarrow{R_2S} 2\,R_2SO + R_2S^{\cdot+} \tag{15}$$

In this way, a radical cation chain process is initiated. Precedents for such mechanism are known, for example, in the ET oxidation of some arylalkenes[8a] and arylcyclopropanes.[36] Such a mechanism is in agreement with the quenching of the sulfide radical cation by a small amount of DMB (1.25×10^{-3} M). Electron transfer from $O_2^{\bullet-}$ or from the reduced sensitizers terminates the chain [Eq. (16)]. The length of the chain depends on structure and conditions (e.g., see the moderate effect of DMB with Et_2S in DCE, Table 1).

$$\begin{gathered} R_2S{-}O \overset{\cdot+}{-} O{-}SR_2 + O_2^{\cdot-}\ (TPP,\ BQ^-) \rightarrow \\ \text{Products} + O_2\ (TPP^+,\ BQ) \end{gathered} \tag{16}$$

The oxidation of sulfides is differentiated from the previously known cases by the inhibition by BQ, an effect not observed with alkenes and cyclopropanes[36] and indeed not expected if the only action of this additive is quenching of $O_2^{\bullet-}$, since the latter is not involved in chain propagation. We rather suggest that BQ terminates the chain [Eq. (17)], because the radical character of intermediate **P-1-OO-1**$^{\bullet+}$ makes it react with BQ in a way similar to that of O-centered radicals.[37]

$$R_2S{-}O \overset{\cdot+}{-} O{-}SR_2 + BQ \rightarrow \text{Products} \tag{17}$$

On passing from the loose ion-induced dipole complexes **1-OO**$^{\bullet+}$ to the final covalently bonded intermediates **P-1-OO-1**$^{\bullet+}$, the stationary points with the highest energies are the two TSs **TS-1-OO**$^{\bullet+}$**-1(i), (ii)**. Therefore these control the kinetics of the overall addition reaction. The potential energy (ΔE_{solv}, with no entropic contribution) of **TS-1-OO**$^{\bullet+}$**-1(ii)** in acetonitrile is quite similar to that of the complex between **1-OO**$^{\bullet+}$**(i)** and **1** (only 0.9 kcal mol^{-1} higher). With the inclusion of the non-potential-energy terms, the barrier, evaluated through the Gibbs free-energy data (ΔG_{solv}, Table 2), becomes 14.7 kcal mol^{-1} higher. This suggests that addition to a nucleophile such as dimethyl sulfide does not encounter any activation enthalpy, and that the activation energy must be ascribed entirely to entropic factors. In other words, the reaction could compete efficiently with any potential alternative bimolecular reaction.

Thus, reaction with oxygen is a definite possibility, and complex **1-OO**$^{\bullet+}$ may serve as the key electrophile in place of the thiadioxirane (see Scheme 2b), despite the low stability of this first-formed intermediate.

Interestingly, the energy profile of the oxidation via $1^{\bullet+} + O_2$ has a shape similar to that of the reaction of sulfides with singlet oxygen [Eq. (18), cf. Figure 7].

$$Me_2S + {}^1O_2 \rightarrow Me_2S^+{-}O{-}O^- \qquad (18)$$

In that case, the intermediate persulfoxide $\mathbf{1^+OO^-}$ (see Figure 7) has been calculated to be less stable than the reagents, with $\Delta H = 6.6$ and $\Delta G = 17.9\ \mathrm{kcal\,mol^{-1}}$[3d] (previous calculations had ΔH slightly negative, but this does not change the sense of the following reasoning).[38] Nevertheless, sulfoxidation via $^1O_2$ is actually initiated by this step, because rearrangement to hydroperoxysulfurane **2** ensues, and this intermediate reacts with **1** to give two molecules of sulfoxide (Figure 7). Protonation of $\mathbf{1^+OO^-}$ likewise allows oxygen transfer forming sulfoxide. Therefore, in both mechanisms [Eq. (10) and (18)] the initial interaction with oxygen lends no stabilization, and only the intervention of ensuing steps leads to stable products. This is the likely cause of the low quantum yield of both oxidations. Separation into the starting components both of zwitterion $\mathbf{1^+OO^-}$ and of the radical cation complex $\mathbf{1\text{-}OO^{\bullet+}}$ results in physical quenching rather than chemical reaction.

A difference between the two paths is that when rearrangement to **2** is precluded, as in diaryl or di-*tert*-alkyl sulfides, the singlet-oxygen path is not operative, while ET oxidation remains viable, because intermediate $\mathbf{1\text{-}OO^{\bullet+}}$ is per se an electrophile, contrary to the persulfoxide, which requires previous rearrangement to **2**. Presumably, the strongly electrophilic character of this intermediate also makes the following reaction with the sulfide less dependent on the steric hindrance or nucleophilicity of the latter compounds, another factor that has been found to slow down the singlet-oxygen reaction.[7] These characteristics suggest that ET sulfoxidation is essentially independent of the structure of the sulfide (provided of course that the initial sensitization is efficient), as is indeed observed. As an example, the presently considered sulfides Et_2S and Ph_2S differ by a factor of 10^3 in $^1O_2$ sulfoxidation rate,[6] but exhibit a similar reactivity in the ET process. Furthermore, alcohols favor the singlet oxygen path (because of partial protonation of $\mathbf{1^+OO^-}$) but disfavor the ET path (because hydrogen transfer to some of the radical intermediates may hinder the path to sulfoxide).[39] In this mechanism, in contrast to the $^1O_2$ reaction, there is no nucleophilic intermediate such as $\mathbf{1^+OO^-}$, and thus diphenyl sulfoxide is not cooxidized.

We explicitly note that we have no direct evidence for the reaction of the sulfide radical cation with oxygen. Flash photolysis rather supports reaction with superoxide, but obviously does not distinguish whether this is via a chemical or physical quenching channel. In the TPP^+ experiment, in which superoxide is not formed, the decay rate of the sulfide radical cation does not change in the presence of oxygen ($Ph_2S^{\bullet+}$ continues to react with $TPP^{\bullet}$, see Figure 5), while it does change when $O_2^{\bullet-}$ is formed, as when NMQ^+ is the sensitizer ($Ph_2S^{\bullet+}$ reacts faster with $O_2^{\bullet-}$ than with $DCA^{\bullet-}$ or $NMQ^{\bullet}$, see Figure 2). Furthermore, pulse radiolysis has previously indicated that in water the rate constant for the reaction of the dimethyl sulfide radical cation with triplet oxygen [see Eq. (10)] is less than $1\times10^6\ \mathrm{M^{-1}\,s^{-1}}$.[31a] However, care should be taken when extending conclusions from pulsed experiments to steady-state irradiation. The present flash experiments involve the absorption of about 1×10^{-8} Einstein across a small volume of solution ($6\times10^{-5}\ \mathrm{dm^3}$) in 20 ns. Under these conditions decay is dominated by second-order processes in which both of the species involved are transients, such as Equations (7)–(9). However, in steady-state reactions at low absorbed flux (ca. 1×10^{-6} Einstein in 2 cm^3 per minute, ca. 10^9 times less intense than in the previous case), the concentration of such transients is many orders of magnitude lower. It is therefore possible that the reaction with molecular oxygen, too slow to be detected on the flash photolysis timescale, is the actual mechanism of the observed sulfoxidation under steady-state irradiation (with low quantum yield and via a chain process), because the conspicuous reaction with $O_2^{\bullet-}$ leads only to physical decay.[40]

Conclusion

In conclusion, (hetero)aromatic molecules sensitize the photooxidation of sulfides through at least two mechanisms involving respectively 1) singlet oxygen and 2) the sulfide radical cation (ET sensitization). Path 1 is followed with neutral sensitizers such as DCA and aliphatic sulfides and has maximal efficiency in protic solvents; path 2 applies when cationic sensitizers are used with both aliphatic and aromatic sulfides, as well as to a neutral sensitizer such as DCA with an aryl sulfide in a polar medium. When the sensitizer has a reduction potential lower than or equal to −0.87 V versus SCE, superoxide is formed. Various tests show that with TPP^+, for which this condition does not apply, ET sensitization occurs in a way closely analogous to the other sensitizers. Although it is possible that two different paths are followed in the two cases, a unitary mechanism for ET sensitized sulfoxidation can be formulated and involves reaction of the sulfide radical cation with molecular oxygen, followed by electrophilic addition of the resulting intermediate to a molecule of sulfide. Calculations support that this path is viable, while interaction of the sulfide radical cation with superoxide mainly leads to chemically unproductive back electron transfer. The radical cation/molecular oxygen mechanism is similar to that operating with other singlet oxygen-resistant substrates, for example, in the ET oxidation of some alkenes and cyclopropanes.[36] The ET sensitized oxidation of sulfides is as clean as that via $^1O_2$, though less efficient than the best cases of sulfoxidation via $^1O_2$ (unhindered aliphatic sulfides in protic solvents). It is distinguished by its wide scope and insensitivity to substrate structure and conditions, facts that may make this method preparatively useful for sulfides resistant to singlet oxygen. Solvents of moderate polarity such as DCE are preferred in this case, in view of the good efficiency and enhanced stability of the photosensitizer. The finding that reaction of the sulfide radical cation with triplet oxygen is a viable path to sulfoxides has a bearing on the long-debated issues of the role of these intermediates and of the mechanism of (biological) oxidation of sulfides.[41]

Experimental Section

Materials: Diethyl sulfide, diphenyl sulfide, and TPP$^+$ were commercial products; TPP$^+$ was washed with water and dried before use to eliminate traces of acids. The sulfoxides and sulfones[42a] for comparison with the photoproducts, as well as DCA[42b] and NMQ$^+$,[42c] were prepared by published procedures.

Photoreactions: The photooxidations were carried out by using 0.01–0.1 M solutions (2 mL) of the sulfides in the presence of DCA, NMQ$^+$, or TPP$^+$ (5×10^{-4} to 1×10^{-3} M) in acetonitrile, methanol, or 1,2-dichlorethane. The solutions were contained in rubber-stoppered Pyrex tubes (∅ 1 cm). These were exposed to four phosphor-coated 15 W lamps with center of emission at 400 nm (for DCA and TPP$^+$) or 360 nm (for NMQ$^+$) while a steam of dry oxygen saturated with the appropriate solvent was passed into the solution through a needle.

The products were determined by GC on the basis of calibration curves in the presence of dodecane as internal standard and by HPLC with biphenyl as internal standard. The presence of possible side products such as disulfides or acids was checked by comparison with authentic samples. Experiments for quantum yield determination were limited to $\leq 10\%$ conversion and the DCA-sensitized oxidation of 1,1-diphenylethene was used for actinometry.[43] Experiments at a higher conversion ($>50\%$) were also carried out, and no significant difference in the product distribution was noted. In this case TPP$^+$ in CH_3OH CH_3OH was appreciably bleached and the addition of further amounts of the sensitizer was required in order to continue the oxidation.

Flash photolysis: Transient absorption spectroscopy was carried out by using a setup for nanosecond absorption measurements described previously.[44] The minimum response time of the detection system was about 2 ns. The laser beam from a JK-Lasers Nd-YAG, operated either at $\lambda =$ 266 or 355 nm, pulse width 20 ns FWHM, was focused on a 3-mm high and 10-mm wide rectangular area of the cell, and the first 2 mm in depth were analyzed at right-angle geometry. The incident pulse energies used were around 3 mJ per pulse. The bandwidth used for the transient absorption measurements was typically 2 nm (0.5 mm slit width). The spectra were reconstructed point by point from time profiles taken each 10 nm. The sample absorbance at 266 or 355 nm was typically 0.5–1 over 1 cm. Experiments were carried out after bubbling the solutions with a constant flux of either Ar or oxygen. The solution, in a flow cell of 1 cm optical path, was renewed after each laser shot. The temperature was 295 ± 2 K. Acquisition and processing of absorption signals were performed with a homemade program using Asyst 3.1 (Software Technologies, Inc.). Nonlinear fitting procedures by the least-squares method and χ^2 and distribution of residuals were used to judge the goodness of fit.

Calculations: All calculations were carried out by using the B2 version of the Gaussian 03 program package.[45] All the geometric structures of the located reactants and transition states were fully optimized both in the gas phase and in acetonitrile solution using the hybrid density functional UB3LYP with the 6-31+G(2d,p) basis set. The extension of the basis set is recommended to achieve better treatment of stationary points containing S atoms.[46]

Thermal contributions (δG), to activation free energy ($\Delta G^{\neq}$) were computed from UB3LYP/6-31+G(2d,p) structures in the gas phase, and harmonic frequencies by using the harmonic oscillator approximation and the standard expressions for an ideal gas in the canonical ensemble at 298.15 K and 1 atm.

The stationary points in the bulk solvent were optimized by the self-consistent reaction field (SCRF) method with PCM solvation model as implemented in the B.02 version of Gaussian 03. The cavity is composed of interlocking spheres centered on non-hydrogen atoms with radii obtained by the HF parameterization by Barone et al., known as united atom topological model (UAHF).[47] Such a model includes the nonelectrostatic terms (cavitation, dispersion, and repulsion energy) in addition to the classical electrostatic contribution.

We explicitly note that the energies resulting from PCM computations have the status of free energies, since they take implicitly into account thermal and entropic contributions by the solvent, but they do not include the thermal contributions (δG). The gas-phase thermal contribution of solute molecular motions was added to obtain the corresponding activation free energy in water ($\Delta G^{\neq}_{sol}$).

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[39] Bona fide photooxidations involving the addition of a radical cation and superoxide are *not* less efficient in MeOH. We checked that a typical such process, namely, the DCA-sensitized oxidation of stilbene, is somewhat faster in MeOH than in MeCN.

[40] As an example, assuming that the overall rate constant for the reaction with superoxide is $k_{7-9} = 2\times10^{10}$, while the constant for reaction with molecular oxygen is $k_{10} = 1\times10^{6}\,\text{M}^{-1}\text{s}^{-1}$ and taking into account that when ET is quantitative, for example, with NMQ^{+} in DCE, the end-of-pulse concentrations of $NMQ^{\bullet}$ and of the sulfide radical cation are $>1\times10^{-4}$ M, reaction according to Equations (7)–(9) would be 100 faster than Equation (10) in a flash photolysis experiment with 3 mJ (ca. 1×10^{-8} Einstein at 355 nm) absorbed flux per shot (in a volume of ca. 6×10^{-5} dm^{3}). However, it would be 100 slower in a preparative experiment with 0.5×10^{-6} Einstein min^{-1} of absorbed flux per cm^{3}.

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