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Photosensitized Electron Transfer Oxidation of Sulfides: A Steady-State Study

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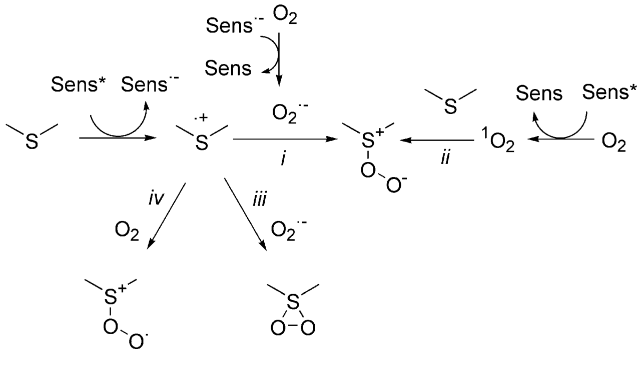
The photosensitized electron-transfer oxidation of a series of ethyl sulfides RSEt (**1**, R = $C_{12}H_{25}$; **2**, $PhCH_2CH_2$; **3**, $PhCH_2$; **4**, $PhCMe_2$; **5**, Ph_2CH) has been examined in acetonitrile and the product distribution discussed on the basis of the mechanisms proposed. In nitrogen-flushed solutions, cleaved alcohols and alkenes are formed, whereas under oxygen, in reactions that are 10–70 times faster, sulfoxides and cleaved aldehydes and ketones are formed in addition to the aforementioned products. Two sensitizers are compared, 9,10-dicyanoanthracene (DCA) and 2,4,6-triphenylpyrylium tetrafluoroborate ($TPP^+BF_4^-$), the former giving a higher proportion of the sulfoxide, the latter of cleaved carbonyls. The sulfoxidation is due to the contribution of the singlet oxygen path with DCA. Oxidative cleavage, on the other hand, occurs both with DCA and with TPP^+ which is known to produce neither singlet oxygen nor the superoxide anion. This process involves deprotonation from the α position of the sulfide radical cation, but the TPP^+ results suggest that $O_2^{\cdot-}$ is not necessarily involved and non-activated oxygen forms a weak adduct with the radical cation promoting α-hydrogen transfer, particularly with benzylic derivatives.

Introduction

Organic sulfides have an accessible oxidation potential and single-electron transfer (SET) oxidation plays an important role in the chemistry and biochemistry of these compounds.[1] Among the reactions involving such a mechanism, photosensitized ET (PET) oxygenation has an important place. PET has been the subject of a number of studies[2] and has been found to be an alternative to the well-known addition of singlet oxygen to sulfides, characterized by a larger range of applications (see below).[3] Such a difference in the scope of the reactions contrasts with the earlier proposal[4] that the same intermediate is involved in the two reactions. Thus, after the initial redox step, secondary electron transfer to oxygen from the sensitizer radical anion and combination of the sulfide radical cation with the resulting superoxide anion could generate a persulfoxide that is also the intermediate formed by the addition of $^1O_2$ to the sulfide (compare paths *i* and *ii* in Scheme 1). Recent in depth investigations with the support of experimental and computational evidence[5,6] ascertained that ET oxidations involve the sulfide radical cation, but demonstrated that at least in some cases the reaction does not exactly duplicate the chemistry observed with singlet oxygen, which suggests that a different intermediate is involved. A mechanism that has been found viable by computational analysis suggests that addition of superoxide gives a thiadioxirane rather than the open-chain persulfoxide as the first intermediate (path *iii*).[5] An alternative path, likewise computationally supported, explains the difference by the reaction of the sulfide radical cation with molecular oxygen rather than with superoxide (path *iv*).[6]



Scheme 1. Alternative paths for the photosensitized oxidation of sulfides.

Investigations are complicated by the fact that the same sensitizers may act both by generating singlet oxygen and by a PET path,[5–7] as well as by the dependence of the reactivity of the sulfides on the structure and conditions, such that it is possible that a shift to a different mechanism occurs under slightly different conditions. Furthermore, sulfide radical cations are known to undergo fragmentation processes that may be fast enough to compete with the reaction with oxygen.

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As a contribution to the current debate, our results with a number of representative sulfides are presented herein. These have been obtained by using two sensitizers, both in the presence and in the absence of oxygen. The chosen sensitizers, 9,10-dicyanoanthracene (DCA) and 2,4,6-triphenylpyrylium tetrafluoroborate (TPP$^+$ BF_4^-), were deemed to be suitable probes as both of them are powerful oxidants in the excited state, making ET from the sulfides efficient. However, in the ground state, DCA is reduced at a potential (–0.89 V vs. SCE in MeCN)[8] comparable to that of oxygen (–0.87 V),[9] with TPP$^+$ above it (–0.37 V),[10] so that reduction of oxygen according to Scheme 1 is feasible only with the former sensitizer.

Results

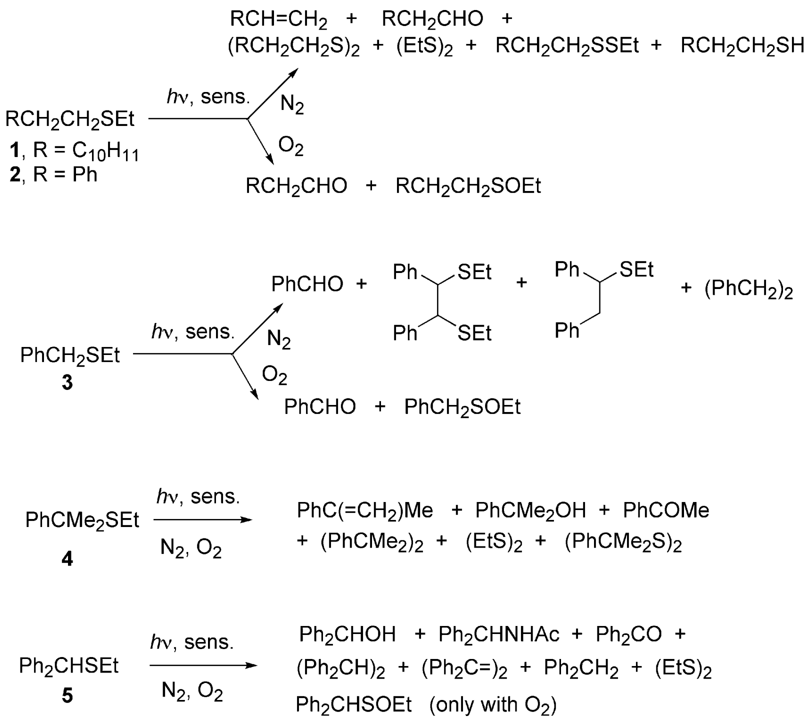
We wished to explore chemical paths that may be informative about the mechanism and chose a series of ethyl sulfides, RSEt, in which the R group was thought to be susceptible to some diagnostic reaction. Their sensitized photochemistry, both in the absence and in the presence of oxygen, was compared. The ethyl sulfides studied included the dodecyl (**1**), phenethyl (**2**), benzyl (**3**), cumyl (**4**) and benzhydryl (**5**) derivatives. Solutions in acetonitrile were irradiated in the presence of the above sensitizers under conditions in which only the latter absorbed. The results refer to a 20–30% conversion, for which further reactions of the primary products could be considered as less important.

Photosensitization of **1** with both DCA and TPP$^+$ required several hours in nitrogen-flushed solutions. The products formed were 1-dodecene, dodecanal, diethyl disulfide, ethyl dodecyl disulfide and dodecanethiol (see Scheme 2 and Table 1). In oxygen-equilibrated solutions, however, the sulfoxide was the main product (see Table 2).

The reaction of **2** was even slower under nitrogen, with the formation of styrene (and 2-phenylethanol) as well as three disulfides [diethyl, bis(phenethyl), phenethyl ethyl]. Under oxygen flushing, both cleaved products, phenylacetaldehyde and styrene (observed at low conversion, later itself oxidized), and the sulfoxide were formed in comparable yields.

Benzyl sulfide **3** gave 1,2-diphenyl-1,2-bis(ethylthio)ethane, 1,2-diphenylethyl ethyl sulfide and benzaldehyde with DCA as the sensitizer under nitrogen. This reaction was somewhat more closely examined and it was found that addition of methanol (10% volume) increased the yield of the bis(ethylthio)ethane, whereas addition of biphenyl (BP, 1 M) increased that of the diphenylethyl sulfide. Benzaldehyde was the only product formed with TPP$^+$ under nitrogen. On the other hand, benzaldehyde and the sulfoxide were formed with both sensitizers under oxygen, although in different yields.

The cumyl sulfide **4** was more reactive than **3** when photosensitized by either DCA or TPP$^+$ under nitrogen. The sensitization gave diethyl disulfide, but all of the phenyl-containing products were sulfur-free, namely, α-methylstyrene, cumyl alcohol, acetophenone and bicumyl.[11] The reaction in the presence of oxygen remained slow with DCA and the product distribution did not include, in contrast to the previous cases, the sulfoxide. The main products with both sensitizers were α-methylstyrene and acetophenone, along with some dicumyl disulfide in the case of DCA.



Scheme 2. Products formed upon photosensitization of sulfides **1**–**5** in nitrogen- and oxygen-equilibrated solutions.

Table 1. Products from the photosensitization of sulfides **1**–**5** in nitrogen-equilibrated acetonitrile solution.

Sulfide	Sensitizer	Products, % yield			
		From R^+	Carbonyl derivatives	Radical coupling products	Products involving α-deprotonation
$C_{12}H_{25}SEt$	DCA	$C_{10}H_{21}CH=CH_2$, 13	$C_{11}H_{23}CHO$, 6	$C_{12}H_{25}S_2Et$, 6	
	TPP^+		$C_{11}H_{23}CHO$, 44	$C_{12}H_{25}S_2Et$, 31 $C_{12}H_{25}SH$, 6	
PhC_2H_4SEt	DCA	$PhCH=CH_2$, 36[a]		$[PhC_2H_4S]_2$, 3 $PhC_2H_4S_2Et$, 4 EtS_2Et, 2	
	TPP^+	$PhCH=CH_2$, 38[a]		$[PhC_2H_4S]_2$, 16 $PhC_2H_4S_2Et$, 25 EtS_2Et, 20	
$PhCH_2SEt$	DCA		PhCHO, 35		$[PhCH(SEt)]_2$, 17 $PhCH(SEt)CH_2Ph$, 2
	DCA[b]		PhCHO, 23		$[PhCH(SEt)]_2$, 5 $PhCH(SEt)CH_2Ph$, 24 $[PhCH_2]_2$, 1
	DCA[c]		PhCHO, 9		$[PhCH(SEt)]_2$, 29 $PhCH(SEt)CH_2Ph$, 2
	TPP^+		PhCHO, 54		
$PhCMe_2SEt$	DCA	$PhC(=CH_2)Me$, 11 $PhCMe_2OH$, 20	PhCOMe, 3	$[PhCMe_2]_2$, 4 EtS_2Et, 9	
	TPP^+	$PhC(=CH_2)Me$, 5 $PhCMe_2OH$, 40	PhCOMe, 18	$[PhCMe_2]_2$, 2 EtS_2Et, 18	
Ph_2CHSEt	DCA	$Ph_2CHNHAc$, 21[d] Ph_2CHOH, 35	Ph_2CO, 39	$[Ph_2CH]_2$, 15 $[Ph_2C=]_2$, 6 Ph_2CH_2, 12 EtS_2Et, 10	
	TPP^+	$Ph_2CHNHAc$, 8 Ph_2CHOH, 26	Ph_2CO, 22	$[Ph_2CH]_2$, 15 $[Ph_2C=]_2$, 6 Ph_2CH_2, 12 EtS_2Et, 9	

[a] Including some 2-phenylethanol. [b] In the presence of BP (M). [c] In the presence of 10% methanol (v/v). [d] 10% $Ph_2CHNHAc$ + 11% Ph_2CHNH_2.

Table 2. Products from the photosensitization of sulfides **1**–**5** in oxygen-equilibrated acetonitrile.

Sulfide	Sensitizer	Products, % yield	
		Fragmentation	Conserving the skeleton
$C_{12}H_{25}SEt$	DCA	$C_{11}H_{23}CHO$, 8	$C_{12}H_{25}SOEt$, 40
	TPP^+	$C_{11}H_{23}CHO$, 21	$C_{12}H_{25}SOEt$, 50
PhC_2H_4SEt	DCA	$PhCH=CH_2$, 30[a] $PhCH_2CHO$, 23	PhC_2H_4SOEt, 44
	TPP^+	$PhCH=CH_2$, 50[a] $PhCH_2CHO$, 19	PhC_2H_4SOEt, 30
$PhCH_2SEt$	DCA	PhCHO, 26	$PhCH_2SOEt$, 47
	TPP^+	PhCHO, 29	$PhCH_2SOEt$, 53
$PhCMe_2SEt$	DCA	$PhC(=CH_2)Me$, 5[a] PhCOMe, 20 $[PhCMe_2S]_2$, 5	
	TPP^+	$PhC(=CH_2)Me$, 5[a] PhCOMe, 28 $[PhCMe_2S]_2$, tr	
Ph_2CHSEt	DCA	$Ph_2CHNHAc$, 22 Ph_2CHOH, 10 Ph_2CO, 53	$Ph_2CHSOEt$, 12 Ph_2CHSO_2Et, 2
	TPP^+	$Ph_2CHNHAc$, 11 Ph_2CHOH, 3 Ph_2CO, 87	$Ph_2CHSOEt$, 1

[a] Further oxidized during the course of the reaction.

As for benzhydryl sulfide **5**, this again gave diethyl disulfide as the only sulfur-containing product under nitrogen, along with benzhydrol, benzophenone, benzhydrylamine (and the corresponding acetamide) as well as diphenylmethane, tetraphenylethane and tetraphenylethylene. Under oxygen, the main products were again the acetamide and benzophenone, with a 2% yield of the sulfone and 12% of the sulfoxide in the case of DCA, but only 1% of the sulfoxide with TPP^+.

The efficiency of the photosensitization of sulfides **1**–**5** is documented in Table 3 in which the rates of consumption [$\mu mol\,min^{-1}$] of the sulfides are compared, which are proportional to the rate constants. It appears that the reaction is 10–70 times more efficient under oxygen than under ni-

Table 3. Amount of photoreacted sulfides [$\mu mol\,min^{-1}$] in acetonitrile under nitrogen and under oxygen.[a]

Sulfide	Sensitizer	Under N_2	Under O_2	
				C–S bond cleavage [%]
$C_{12}H_{25}SEt$	DCA	0.036	2.21	16
	TPP^+	0.011	0.23	35
PhC_2H_4SEt	DCA	0.047	1.43	55
	TPP^+	0.045	0.97	69
$PhCH_2SEt$	DCA	0.052	2.38	35
	TPP^+	0.040	0.49	37
$PhCMe_2SEt$	DCA	0.10	0.06	100
	TPP^+	0.084	0.73	100
Ph_2CHSEt	DCA	0.031	0.85	85
	TPP^+	0.056	0.36	100

[a] Normalized at equal adsorbed light flux.

trogen (the only exception is **4** with DCA) and that, at equal absorbed flux, DCA is more effective than TPP^+ (except with **4**). Further important evidence is the quenching of the sensitizers' fluorescence by the above sulfides: all these compounds were effective quenchers, with rate constants $k_f > 5 \times 10^9$ $\text{M}^{-1}\,\text{s}^{-1}$.

Discussion

Sulfide Radical Cations: Primary Processes

The sulfides quench the fluorescence of both the aromatic nitrile DCA and the phenylium salt TPP^+ at rates close to diffusion control and the electron transfer from these donors, both aliphatic and aromatic, to the singlet excited state of both DCA and TPP^+ is thermoneutral or exoergonic.[12] Thus, photosensitization generates a radical-ion pair (with DCA) or a radical-ion/radical pair in the case of TPP^+, for which the ground state of the sensitizer is a cation; see Equations (1) and (2).

$$^1\text{DCA} + R_2S \rightarrow \text{DCA}^{\cdot-} + R_2S^{\cdot+} \tag{1}$$

$$^1\text{TPP}^+ + R_2S \rightarrow \text{TPP}^{\cdot} + R_2S^{\cdot+} \tag{2}$$

In many of the known photoinduced electron-transfer processes, the largely exothermic back electron transfer (BET) competes with the chemical reaction of the radical ions. The present case is no exception and, despite efficient initial ET, the chemically unproductive back electron transfer shown in Equation (3) greatly diminishes the reaction efficiency.

$$\text{DCA}^{\cdot-}\ (\text{or TPP}^{\cdot}) + R_2S^{\cdot+} \rightarrow \text{DCA}\ (\text{or TPP}^+) + R_2S \tag{3}$$

However, some chemical reaction does occur, more significantly in the case of the benzyl sulfides **3**–**5**. Such reactions can be rationalized as involving a fragmentation of the sulfide radical cation, namely, either cleavage of the carbon–sulfur bond [Equation (4)] or deprotonation from the α position [Equation (5)].

$$R_2S^{\cdot+} \rightarrow R^+ + RS^{\cdot} \tag{4}$$

$$RCH_2SR^{\cdot+} \rightarrow RCH^{\cdot}SR + H^+ \tag{5}$$

The likelihood of such fragmentations can be evaluated by means of a thermochemical cycle. Abstraction of an electron weakens a σ bond and the free energy change for radical cation cleavage [$RX^{\cdot+} \rightarrow R^+ + X^{\cdot}$; Equation (6)] differs from that of the neutral species by the difference between the oxidation potential of the molecule and that of the radical corresponding to the cation formed.

$$\Delta G(RX^{\cdot+}) = \Delta G(RX) - [E^{\circ}(RX) - E^{\circ}(R^{\cdot})] \tag{6}$$

In the case of sulfide radical cations, if cleavage of the C–S bond occurs, it will give an alkyl cation [Equation (4)] and not an alkyl radical [Equation (7)] as the latter intermediates are oxidized at a less positive potential than alkylthiyl radicals.[13]

$$R_2S^{\cdot+} \rightarrow R^{\cdot} + RS^+ \tag{7}$$

In this work, asymmetric sulfides of the general structure RSEt have been considered. With compounds **1** and **2**, in which R is a non-stabilized alkyl radical, both alkyl cations may be formed, whereas with derivatives **3**–**5**, in which R is a (α-substituted) benzyl group, a regioselective process should take place [Equation (8)].

$$RSEt^{\cdot+} \rightarrow R^+ + EtS^{\cdot} \tag{8}$$

Evaluation of the thermochemistry of the process shown in Equation (8) according to Equation (6) shows that it is a strongly endoergonic process for dialkyl sulfides **1** and **2** (bond dissociation free energy, BDFE = 45 kcal mol^{-1}, Table 4), whereas the lowering of the C–S bond energy and the easier oxidation of the radicals make fragmentation of the benzyl sulfide radical cations less endoergonic (BDFE of 28 kcal mol^{-1} for $\mathbf{3}^{\cdot+}$ and 13.5 kcal mol for both $\mathbf{4}^{\cdot+}$ and $\mathbf{5}^{\cdot+}$).[13]

Deprotonation [Equation (5)] from benzyl sulfides has actually been detected[14] and thus is expected to occur in compounds **3** and **5** [see Equation (9)], for which ΔG_{C-H} is zero or slightly negative.[15] Deprotonation following oxidation is a common process both for benzylic derivatives

Table 4. Thermodynamic parameters for the fragmentation of the radical cations of sulfides **1**–**5**.

Sulfide (RSEt)	E_{OX} [V] (vs. SCE)	BDE (RSEt) [kcal mol^{-1}]	E° ($R^{\cdot}$) [V] (vs. SCE)	BDE ($RSEt^{\cdot+}$) [kcal mol^{-1}]	BDFE [kcal mol^{-1}][a]
$C_{12}H_{25}SEt$	1.65[b]	70[c]	1.00[d]	54 (69.2)	45
PhC_2H_4SEt	1.65[b]	69.5[e]	1.00[d]	53.5 (72.2)	45
$PhCH_2SEt$	1.60[f]	56[c]	0.73[g]	38 (51.4)	28
$PhCMe_2SEt$	1.60[d]	57[h]	0.16[g]	23.5 (39.6)	13.5
Ph_2CHSEt	1.34[d]	53.5[i]	0.53[g]	25.5 (39.0)	13.5

[a] Calculated by subtracting an entropic correction ($T\Delta S^{\circ}$) of 13 kcal mol^{-1}, corresponding to the entropy change associated with the C–S homolysis in methyl ethyl sulfide, $\Delta S^{\circ}(\text{MeS–Et}) = S^{\circ}(\text{MeSEt}) - S^{\circ}(\text{MeS}^{\cdot}) - S^{\circ}(\text{Et}^{\cdot})$, as calculated from literature values, see ref.[32] [b] Value assumed to be equal with that of diethyl sulfide. [c] See ref.[33] [d] Value estimated from the IP, see ref.[13] [e] Based on the hypothesis that β-phenyl substitution has a minor effect (ca. 0.5 kcal mol^{-1}) on the BDE, as is the case, for example, with the iodide, see ref.[34] [f] Assumed to be equal to that of the corresponding methyl benzyl sulfide, see ref.[35] [g] See ref.[36] [h] Based upon the hypothesis that α,α-dimethyl substitution lowers the BDE by about 1.3 kcal mol^{-1}, as it does with benzyl chlorides, see ref.[37] [i] Based on the hypothesis that α-phenyl substitution lowers the BDE by 4.5 kcal mol^{-1}, as it does with alkanes, see ref.[38]

and sulfides, and this is a particular instance of such general cases. Reference to previous work[16] suggests, however, that, although thermodynamically favoured, deprotonation may be a slow reaction and that anyway its rate is largely dependent on the structure of the radical cation (stereoelectronic factor) and on the protic acceptance by the solvent or by additives present.

$$\mathrm{PhCHRSEt^{\cdot+} \rightarrow PhC^{\cdot}RSEt + H^{+}} \tag{9}$$

Photosensitized Reaction in the Absence of Oxygen

The experiments in the absence of oxygen were aimed at ascertaining whether fragmentation of sulfide radical cations was a viable path under the conditions used. At least with benzyl sulfides **3**–**5**, the extent of the reaction is sufficient to identify the paths followed. C–S bond fragmentation; (path *a*, Scheme 3) leads to benzyl cations that are stabilized by weakly nucleophilic acetonitrile. This allows subsequent water addition, leading to the products actually isolated, a benzyl alcohol from **4** and *N*-benzylacetamide from **5** (Ritter addition, path *a'*). In the case of **4**, α-methylstyrene is also formed and may result from deprotonation of the benzyl cation (*a''*) or by dehydration of the alcohol.[11]

Furthermore, since the redox equilibrium between benzyl radicals and cations lies at a moderately positive potential and a strongly reducing agent is present, the sensitizer radical anion,[17a] yet another process may occur, namely, the reduction of benzyl cations to radicals [Equation (10), path *a'''* in Scheme 2].

$$\mathrm{PhCRR'^{+} + A^{\cdot-} \rightarrow PhCRR'^{\cdot} + A} \tag{10}$$

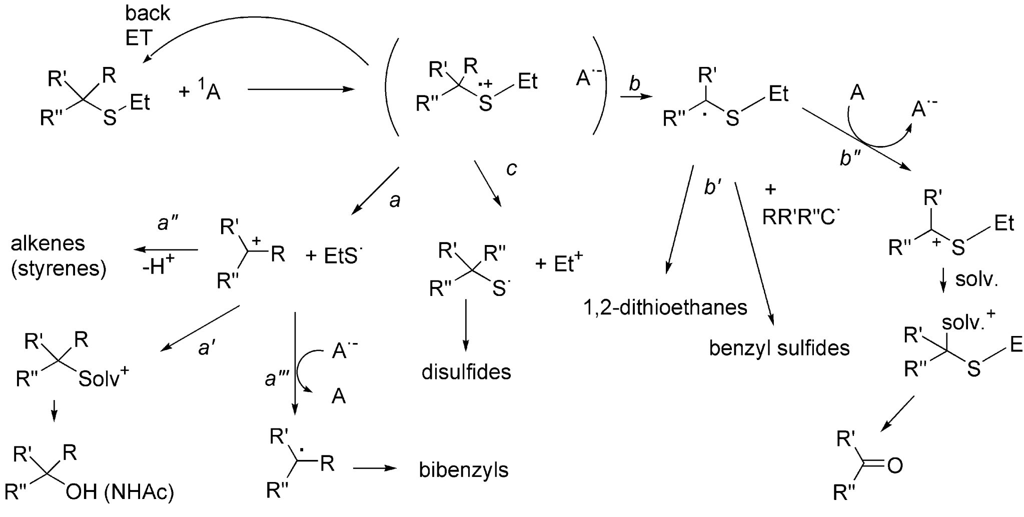
This process is thermodynamically allowed for the three benzyl cations considered with both $\mathrm{DCA^{\cdot-}}$ and with $\mathrm{TPP^{\cdot}}$. Thus, benzyl radicals are formed by this path, but not by direct fragmentation, as seen above [Equation (7)]. These radicals either couple to give bibenzyls, which are indeed observed with sulfides **3**–**5** (although not with **3** and $\mathrm{TPP^+}$), or disproportionate, as observed in the case of **5**, with the formation of diphenylmethane and diphenylethylene.

Deprotonation [Equation (9), path *b* in Scheme 3] competes with C–S bond cleavage in the case of sulfide **5** and is practically the only process available to sulfide **3**, for which path *a* is strongly endoergonic. The resulting (α-thio)benzyl radicals are rather persistent species and undergo coupling (path *b'*, accompanied by cross coupling with benzyl radicals arising from path *a'''* in the case of **3**) or are oxidized by the ground-state sensitizer (path *b''*).[17b] This is a thermodynamically favoured process, which is important particularly with $\mathrm{TPP^+}$, a better ground-state oxidant than DCA, and leads to the observed ketones as the final products by hydrolysis of the thioacetals. As demonstrated in the case of **3**, prolonging the lifetime of the radical cation (through secondary electron transfer to biphenyl) favours C–S bond cleavage (higher yield of 1,2-diphenylethyl ethyl sulfide, see Table 1), whereas methanol acts as a base, favouring deprotonation [higher yield of the bis(methylthio)diphenylethane].

With compounds **1** and **2**, both paths *a* and *c* are endoergonic to such a degree that fragmentation of either one of the C–S bonds is insignificant, and to the small extent to which it does occur, it is unselective, forming both the ethyl cation (path *c* in Scheme 3) or the other alkyl cation (paths *a*), as well as the thiyl radicals. In nitrogen-flushed solutions the products are the alkenes from the alkyl cations and the disulfides from the thiyl radicals. The small amount of dodecanaldehyde formed from **1** is probably due to residual traces of oxygen.

Reactions in the Presence of Oxygen

Equilibration with oxygen has a varied effect, in particular in the case of DCA, for which it ranges from efficient sulfoxidation versus virtually no reaction in the case of dodecyl sulfide **1** to almost no difference between reactions under $\mathrm{O_2}$ and $\mathrm{N_2}$ in the case of cumyl sulfide **4** (Table 2



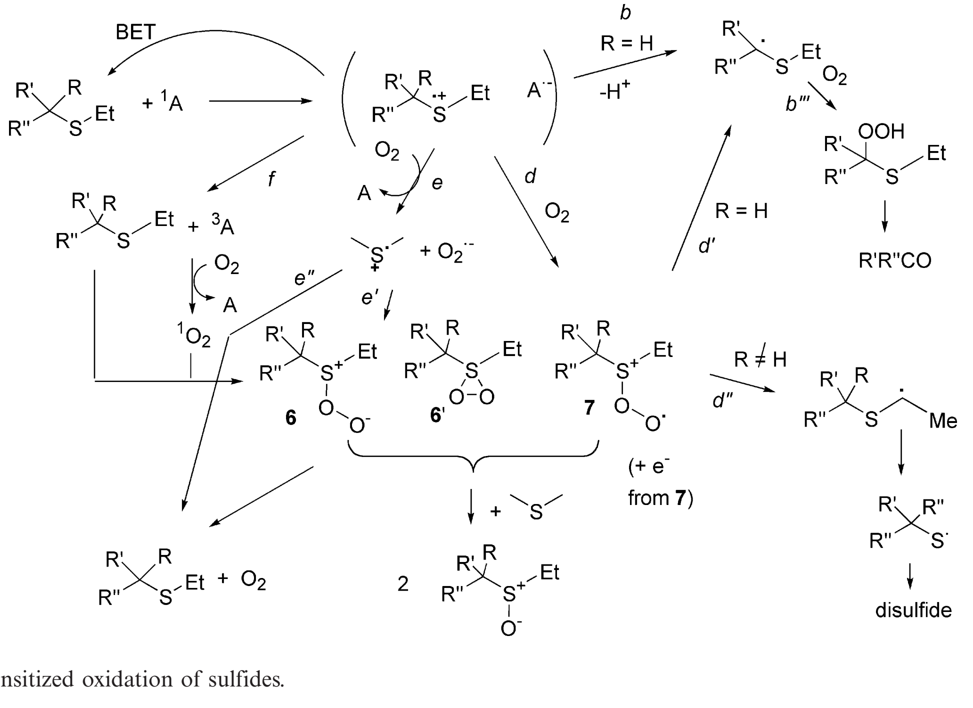
Scheme 3. Photosensitized reactions of sulfides.

and Table 3). The sulfoxidation of **1** clearly involves singlet oxygen with persulfoxide **6** as the key intermediate, as previously demonstrated for diethyl and dibutyl sulfide with DCA.[18,19] In fact, with sulfides in the 0.01–0.05 M concentration range, both direct oxygen sensitization with ^{1}DCA (with a limiting quantum yield of 2) and the formation of ^{3}DCA after ET quenching by sulfides occur and lead to singlet oxygen (path *f*, Scheme 4).[5,6] Consistent with this idea, TPP$^+$ that does not form $^1O_2$ remains an inefficient sensitizer of **1**. DCA-sensitized oxidation under O_2 is also efficient with phenethyl and benzyl sulfides **2** and **3**, for which sulfoxidation is accompanied by C–S bond cleavage. With these compounds, the latter process also occurs in dye-sensitized oxygenation, although to a lesser extent.[18] When TPP$^+$ is the sensitizer, the reaction is less efficient (but more than with **1**) and gives a larger proportion of the aldehyde. Oxidative cleavage of benzhydryl sulfide **5** is the predominating process with DCA (6:1 with respect to sulfoxidation) and virtually the exclusive reaction with TPP$^+$.

Thus, in the DCA reaction part of the process occurs by the singlet oxygen path and part by the PET mechanism. The quite efficient reaction of benzyl sulfide **3** compared with the absence of O_2-induced oxidation with the cumyl sulfide **4** (see below) and the importance of the oxidative C–S bond cleavage with the former compound suggest that the presence of an easily abstracted (benzylic) hydrogen is determining. It may be recalled that the reaction of **3** with $^1O_2$ had been shown to involve two intermediates, namely a first formed "loose" complex (giving benzaldehyde) that evolved to a "tight" complex and then to the sulfoxide.[18a,20] It may be that an intermediate similar to the "loose" complex is involved in the non-$^1O_2$ path. This may be the previously proposed[5] thiadioxirane **6′**, resulting from superoxide addition (path *e′*), but it is different from the persulfoxide.

Addition of $O_2^{\cdot -}$ to a sulfide radical cation has been demonstrated to occur (in the case of thianthrene),[21a] but how efficient it is is doubtful as the highly exoergonic back electron transfer (path *e′′*, ΔH = –64 kcal mol^{-1} for $Me_2S^{\cdot +}$) should compete favourably.[5,6] Furthermore, the fact that oxidative C–S bond cleavage is also observed, although with a lower efficiency, with TPP$^+$, which does not form $O_2^{\cdot -}$, leaves room for an alternative hypothesis that non-activated O_2 is involved. One possibility is that deprotonation is a reversible process under these conditions and only trapping by oxygen of the benzyl radical leads to an irreversible reaction (path *b′′′*). Another one is that oxygen forms a complex with the radical cation; it was previously calculated that the dimethyl sulfide radical cation formed a loose dipole complex with oxygen ($Me_2S^{+\cdot}OO^{\cdot}$, d_{S-O} = 2.6 Å, path *d*).[6,21b] Reasonably, when a benzylic rather than a methyl hydrogen is present, the complex $R_2S^{+\cdot}OO^{\cdot}$ may undergo intramolecular hydrogen abstraction, a process that finally leads to C–S bond cleavage (path *d′*). Thus, it may be that reaction via **7** becomes significant when a convenient chemical path from it is available, such as the abstraction of benzylic hydrogen. Some interaction with the benzene ring may also be involved as benzylic deprotonation has also been invoked for the TPP$^+$-sensitized oxidative cleavage of benzyl ethers[22] and alcohols[23] in the presence of oxygen.

The case of cumyl sulfide **4** is contrasting. With DCA, introducing oxygen changes little the product distribution (see below) and halves the efficiency. This is in accord with the fact that this hindered sulfide does not react significantly either with $^1O_2$ [as confirmed by the inefficient Rose Bengal (RB) sensitization][18a] or with $O_2^{\cdot -}$. More precisely, an indication of a minor reaction with singlet oxygen is given by the formation of 5% dicumyl disulfide (only with DCA), obtained also in the RB oxidation,[18a] but not with



Scheme 4. Photosensitized oxidation of sulfides.

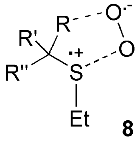
TPP^+. As discussed above, this does not result from the fragmentation of the radical cation, which occurs in the opposite direction, but rather from persulfoxide **6**, as intramolecular abstraction in this case necessarily involves the methylene of the ethyl group (path *d''*). The conversion of these hydroperoxides to thiols, oxidized under the reaction conditions to the observed disulfide, has been previously commented.[20]

The main process is fragmentation to give the cumyl cation, and styrene from this (and by further oxidation, acetophenone). In contrast to what was observed with the other sulfides, for which TPP^+ is a less efficient sensitizer than DCA, the oxidation under O_2 of **4**, which has no α-hydrogen atoms, is markedly more efficient with TPP^+. This suggests a generalization about the relative rates of reaction. Thus, BET with DCA (involving oppositely charged species) is more efficient than with TPP^+ (for which neutral $TPP^{\cdot}$ is involved)[24,25] so that with the latter sensitizer the sulfide radical cation is longer lived and C–S bond fragmentation is expected to be more efficient, as indeed is observed with **4**. However, with **3** and **5**, for which hydrogen abstraction is the key step, the fast BET with DCA is compensated for by a more efficient reaction, reasonably, due to the formation of superoxide under these conditions. With **1** and **2**, on the other hand, it is the contribution of $^1O_2$ that makes DCA more efficient.

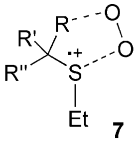
Conclusions

The sulfides examined in this work undergo both sulfoxidation and oxidative cleavage under oxygen. The results confirm that in DCA-sensitized oxidation, the singlet oxygen path makes a contribution and is the main path with simple aliphatic sulfides such as **1**. In the other cases, a different (PET) mechanism operates, which is the only one with TPP^+. PET leads to some sulfoxidation (with non-hindered sulfides), as well as C–S bond fragmentation (forming an alkyl cation only with heavily substituted sulfides such as **4** and **5**) and oxidative cleavage to aldehydes and ketones. The last process involves deprotonation from the α position, as shown by the increased efficiency when this position is further activated (benzylic). Comparison with the reactions carried out under N_2 (10–70 times less efficient) supports the view that it is not the sulfide radical cation that cleaves directly, but that oxygen must interact in a determining way. This may involve combination of the sulfide radical cation with the superoxide anion that is generated when using DCA[5,28] to form intermediate **6′**. However, TPP^+ sensitization leads to the same reactions, although with a lower efficiency (from1/2.5 to 1/5), and, as $O_2^{\cdot-}$ is not formed here, **6′** is not the intermediate. The intermediate may rather be a dipole complex formed with O_2 (**7**). Recalling that $^1O_2$ and benzyl sulfides first form a "loose" complex (precursor of benzaldehyde) and then a "tight" complex (precursor of the sulfoxide), one may suggest that interaction with O_2 via **7** would be similar to the "loose" complex and play a role when an easily abstracted hydrogen that is easily abstracted is available. Having a longer S···O distance, **7** is less affected by the steric hindrance of substituents on the sulfide moiety, which in contrast strongly decreases both the dye-sensitized sulfoxidation and the multi-path DCA oxidation, explaining the restricted range of the rates with TPP^+ in comparison with the large range with DCA (see Table 3).

Speculating further, and justified by the fact that calculations are at the moment available only for low-molecular-weight sulfides and by the similar product distribution with DCA and TPP^+, it can be suggested that the complexes formed with $O_2^{\cdot-}$ and O_2, neither of which is significantly stabilized, as far as is known for simple cases such as $Me_2S^{+\cdot}OO^{\cdot(-)}$,[21b] are barely significant minima on the path leading to the products. When an activated α-hydrogen atom is present, interaction with it is probably as important as that with the sulfur atom (formulae **7** and **8**: R = H, R′ = Ph) and partition between decay to the components, C–S bond cleavage to yield an alkyl cation and hydrogen transfer finally leading to carbonyl derivatives depends on the sulfide structure in the same way.



8



7

R = or ≠ H

Experimental Section

Materials: The sulfides were prepared according to literature methods[29] or were commercial products. The sensitizers were of commercial origin, but TPP^+ was washed with water and dried before use in order to eliminate traces of acids.

Photoreactions: The photoreactions were carried out by using 0.01–0.05 M solutions (2 mL) of the sulfide in the presence of DCA or TPP^+ (1×10^{-3} M) in acetonitrile. The solutions were placed in rubber-stopped Pyrex tubes (∅ = 1 cm). These were exposed to four phosphor-coated 15-W lamps with the centre of emission at 400 nm while a stream of dry oxygen was passed into the solution (previously saturated with oxygen) through a needle. The flux impinging on the tubes was around 1×10^{-6} Einstein $min^{-1} cm^{-2}$, as determined by using the DCA-sensitized oxidation of 1,1-diphenylethylene as the actinometer.[30]

The products were determined by GC on the basis of calibration curves in the presence of dodecane as the internal standard or by HPLC with biphenyl as the internal standard. The products were identified by comparison of their chromatographic characteristics and mass spectra with those of authentic samples, either of commercial origin or prepared according to published procedures (in particular, sulfoxides and disulfides),[31] or, in some cases, on the basis of the mass spectral characteristics.

2-Phenylethyl Ethyl Disulfide: MS: *m*/*z* (%) = 198 (19) $[M]^+$, 137 (4), 105 (100), 91 (16), 77 (12), 65 (7).

1,2-Bis(ethylthio)-1,2-diphenylethane: MS: *m*/*z* (%) = 151 (100) $[M/2]^+$, 122 (21), 90 (11), 77 (9).

1,2-Diphenylethyl Ethyl Sulfide: MS: *m*/*z* (%) = 242 (5) $[M]^+$, 182 (14), 151 (100), 91 (6), 77 (4).

Fluorescence: The fluorescence of DCA and TPP$^+$ was measured in a Perkin–Elmer spectrofluorimeter in 1 cm cuvettes with four optical faces and quenching by sulfides **1**–**5** was determined by the usual Stern–Volmer treatment. In addition to the known singlet lifetime of these compound, this allowed values of $k > 5 \times 10^9$ M^{-1} s^{-1} to be assigned to all of the sulfides tested.

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[1] J. Drabowicz, P. Kielbasinski, M. Mikolajczyk in *Synthesis of Sulfones, Sulfoxides and Cyclic Sulfides* (Eds.: S. Patai, Z. Rappoport), Wiley, Chichester, **1994**, p. 195; E. G. Mata, *Phosphorus Sulfur Silicon Relat. Elem.* **1996**, *117*, 231; J. W. Chu, B. L. Trout, *J. Am. Chem. Soc.* **2004**, *126*, 900; A. K. Das, *Coord. Chem. Rev.* **2004**, *248*, 81; M. C. Carreño, *Chem. Rev.* **1995**, *95*, 1717; A. L. Baumstark, *Bioorg. Chem.* **1986**, *14*, 326; P. Filipiak, G. L. Hug, I. Charmichael, A. Korzeniowska-Sobczuk, K. Bobrowoski, B. Marciniak, *J. Phys. Chem. A* **2004**, *108*, 6503; M. L. Huang, A. Rauk, *J. Phys. Chem.* **2004**, *108*, 6222.

[2] a) E. Baciocchi, C. Crescenzi, O. Lanzalunga, *Tetrahedron* **1997**, *53*, 4469; b) J. Eriksen, C. S. Foote, T. L. Parker, *J. Am. Chem. Soc.* **1977**, *99*, 6455; c) N. Soggiu, H. Cardy, J. L. Habib, J. P. Soumillon, *J. Photochem. Photobiol. A* **1999**, *124*, 1; d) e) Y. Che, W. Ma, Y. Ren, C. Chen, X. Zhang, J. Zhao, L. Zang, *J. Phys. Chem. B* **2005**, *109*, 8270; f) S. Lacombe, H. Cardy, M. Simon, A. Khoukh, J. P. Soumillon, M. Ayadim, *Photochem. Photobiol. Sci.* **2002**, *1*, 347; g) T. Pigot, T. Arbitre, M. Hervé, S. Lacombe, *Tetrahedron Lett.* **2004**, *45*, 4047; h) V. Latour, T. Pigot, M. Simon, H. Cardy, S. Lacombe, *Photochem. Photobiol. Sci.* **2005**, *4*, 221; K. Bobrowski, B. Marciniak, G. L. Hug, *J. Photochem. Photobiol. A* **1994**, *81*, 159; S. Inbar, H. Linschitz, S. G. Cohen, *J. Am. Chem. Soc.* **1982**, *104*, 1679; J. C. Ronfard-Haret, R. V. Bensasson, J. C. Gramain, *Chem. Phys. Lett.* **1983**, *96*, 31; W. Adam, J. E. Arguello, A. B. Penenory, *J. Org. Chem.* **1998**, *63*, 3905; E. Bosch, J. K. Kochi, *J. Org. Chem.* **1995**, *60*, 3172; V. Iliev, D. Tomova, *Catal. Commun.* **2002**, *3*, 287; M. Alvaro, E. Carbonell, H. Garcia, *Appl. Catal. B* **2004**, *51*, 195.

[3] E. L. Clennan, *Acc. Chem. Res.* **2001**, *34*, 875; E. L. Clennan, *Sulfur Rep.* **1996**, *19*, 171; E. L. Clennan, C. Liao, *Tetrahedron* **2006**, *62*, 10724; E. L. Clennan, S. E. Hightower, A. Greer, *J. Am. Chem. Soc.* **2005**, *127*, 11819.

[4] T. Akasaka, W. Ando, *Tetrahedron Lett.* **1985**, *26*, 5049.

[5] E. Baciocchi, T. Del Giacco, F. Elisei, M. F. Gerini, M. Guerra, A. Lapi, P. Liberali, *J. Am. Chem. Soc.* **2003**, *125*, 16444; E. Baiocchi, T. Del Giacco, P. Giombolini, O. Lanzalunga, *Tetrahedron* **2006**, *62*, 6566; Y. Che, W. Ma, Y. Ren, C. Chen, X. Zhang, J. Zhao, L. Zang, *J. Phys. Chem. B* **2005**, *109*, 8270.

[6] S. M. Bonesi, I. Manet, M. Freccero, M. Fagnoni, A. Albini, *Chem. Eur. J.* **2006**, *12*, 4844.

[7] a) D. C. Dobrowolski, P. R. Ogilby, C. S. Foote, *J. Phys. Chem.* **1983**, *87*, 2261; b) R. S. Davidson, J. E. Pratt, *Tetrahedron* **1984**, *40*, 999; c) L. E. Manring, C. L. Gu, C. S. Foote, *J. Phys. Chem.* **1983**, *87*, 40; d) A. P. Darmanyan, *Chem. Phys. Lett.* **1984**, *110*, 89; e) W. Abraham, A. Glänzel, R. Stösser, U. W. Grummt, H. Köppel, *J. Photochem. Photobiol.* **1990**, *51*, 350.

[8] D. T. Breslin, M. A. Fox, *J. Am. Chem. Soc.* **1993**, *115*, 11716.

[9] a) R. D. Egland, F. Marken, E. M. Southern, *Anal. Chem.* **2002**, *74*, 1590; b) M. A. Fox, M. Chanon (Eds.), *Photoinduced Electron Transfer*, Elsevier, Amsterdam, **1988**, p. 475.

[10] a) F. D. Saeva, G. R. Olin, *J. Am. Chem. Soc.* **1980**, *102*, 299; b) R. Akaba, H. Sakuragi, K. Tokumaru, *J. Chem. Soc. Perkin Trans. 2* **1991**, 291; c) M. A. Miranda, H. Garcia, *Chem. Rev.* **1994**, *94*, 1063; d) K. D. Warzecha, M. Demuth, H. Görner, *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 1523; e) M. V. Baldovi, H. Garcia, M. A. Miranda, J. Primo, J. Soto, F. Vargas, *Tetrahedron* **1995**, *51*, 8113.

[11] In a previous study of the *N*-methylquinolinium photosensitization of sulfide **4**, α-methylstyrene and 1-phenylethanol were also found. The percentage of the two compounds varied during irradiation, reasonably, owing to dehydration promoted by the acidity formed during the irradiation (see ref.[5b]).

[12] a) ΔG_{ET} for electron transfer from the sulfides considered to singlet-excited DCA and TPP$^+$, calculated by the Weller equation, $\Delta G°_{\mathrm{ET}} = 23.06[E°(\mathrm{D/D}^{\cdot+}) - E°(\mathrm{A}^{\cdot-}/\mathrm{A})] - E_{\mathrm{exc}} - e^2/\varepsilon a$ (ref.[9b]), ranges between +11 and –25 kcal mol^{-1}, based on the reported redox potentials (see ref.[10] and the notes to Table 4). In the case of TPP$^+$ the $-e^2/\varepsilon a$ term is disregarded as no charge separation is involved. b) D. Rehm, A. Weller, *Isr. J. Chem.* **1970**, *8*, 259.

[13] As an example of the ionization potential of the ethyl radical, values between 8.11 and 8.24 eV have been reported, see: a) B. Ruscic, J. Berkowitz, L. A. Curtiss, J. A. Pople, *J. Chem. Phys.* **1989**, *91*, 114; b) J. Wang, L. Wei, B. Yang, R. Yang, C. Huang, X. Shan, L. Sheng, Y. Zhang, F. Qi, C. Yao, Q. Li, Q. Ji, *Chem. Res. Chin. Univ.* **2006**, *22*, 375; the ionization potential for EtS$^{\cdot}$ is 9.08 eff, see: c) M. Ge, J. Wang, X. Zhu, Z. Sun, D. Wang, *J. Chem. Phys.* **2000**, *113*, 1866; the oxidation potentials of these radicals, $E°(\mathrm{EtS}^{\cdot}) = 1.85$ V and $E°(\mathrm{Et}^{\cdot}) \approx 1.00$ V vs. SCE were estimated from the measured IP by the Miller equation, not taking into account the solvation energy which may heavily affect the result.

[14] M. Ioele, S. Steenken, E. Baciocchi, *J. Phys. Chem. A* **1997**, *101*, 2979; E. Baciocchi, M. F. Gerini, O. Lanzalunga, A. Lapi, M. G. Lo Piparo, *Org. Biomol. Chem.* **2003**, *1*, 422.

[15] The C–H BDE has been measured as 82.4 kcal/mol for $\mathrm{Ph_2CHSPh}$, see: F. G. Bordwell, X. Zhang, J. P. Cheng, *J. Org. Chem.* **1991**, *56*, 3216; lower values were proposed for related derivatives, see: E. Baciocchi, C. Rol, E. Scamosci, G. V. Sebastiani, *J. Org. Chem.* **1991**, *56*, 5498. In related compounds it was found that the C–H energy changes by ≤1 kcal/mol when an EtS is substituted for a PhS group: F. G. Bordwell, X. M. Zhang, *J. Am. Chem. Soc.* **1994**, *116*, 973. Thus, in the first instance, we assume a value of 83 kcal mol^{-1} ($E°(\mathrm{H}^{\cdot}) = -2.01$ V vs. SCE): D. M. Wayner, V. D. Parker, *Acc. Chem. Res.* **1993**, *26*, 287. These values give *BDE* = 5.8 kcal mol^{-1} for $\mathbf{5}^{\cdot+}$ and 4.8 kcal mol^{-1} for $\mathbf{3}^{\cdot+}$ and thus *BDFE* reasonably negative for both radical cations.

[16] See, for example: a) M. Freccero, A. Pratt, A. Albini, C. Long, *J. Am. Chem. Soc.* **1998**, *120*, 284; b) E. Baciocchi, M. Bietti, O. Lanzalunga, *J. Phys. Org. Chem.* **2006**, *19*, 467.

[17] a) In the case of the benzyl cation, $\Delta G = 23.06[E°(\mathrm{A}^{\cdot-}) - E°(\mathrm{PhCH_2}^+)] = -37.3$ kcal mol^{-1} with DCA and –25.4 kcal mol^{-1} with TPP$^+$, with $\mathrm{PhCMe_2}^+$ –24.2 and –28.8 kcal mol^{-1}, and with $\mathrm{Ph_2CH^+}$ 28.8 and 16.1 kcal mol^{-1}. b) The oxidation potential of α-thioalkyl radicals should not be significantly different to those of α-hydroxyalkyl radicals (e.g., $\mathrm{Me_2C^{\cdot}OH} = -0.61$ V vs. SCE, a value affected by a large uncertainty), which would make oxidation, at least by TPP$^+$, viable, see: T. Lund, D. D. M. Wayner, M. Jonsson, A. G. Larsen, K. Daasbjerg, *J. Am. Chem. Soc.* **2001**, *123*, 12590.

[18] a) S. M. Bonesi, M. Fagnoni, S. Monti, A. Albini, *Tetrahedron* **2006**, *62*, 10716; b) S. M. Bonesi, M. Mella, N. d'Alessandro, G. G. Aloisi, M. Vanossi, A. Albini, *J. Org. Chem.* **1998**, *63*, 9946.

[19] J. J. Liang, C. L. Gu, M. L. Kacher, C. S. Foote, *J. Am. Chem. Soc.* **1983**, *105*, 4717; E. L. Clennan, A. Greer, *J. Org. Chem.* **1996**, *61*, 4793; F. Jensen, A. Greer, E. L. Clennan, *J. Am. Chem. Soc.* **1998**, *120*, 4439; E. L. Clennan, D. Wang, C. Clifton, M. F. Chen, *J. Am. Chem. Soc.* **1997**, *119*, 9081.

[20] A. Toutchine, D. Aebischer, E. L. Clennan, *J. Am. Chem. Soc.* **2001**, *123*, 4996.

[21] a) W. Ando, Y. Kabe, S. Kobayashi, C. Takyu, A. Yamagishi, H. Inaba, *J. Am. Chem. Soc.* **1980**, *102*, 4526. b) The interaction of this adduct with a $\mathrm{Me_2S}$ molecule leads to a covalently bound radical cation, $\mathrm{Me_2S^+{-}OO{-}S^{\cdot}Me_2}$, through a strongly exoergonic process and to the sulfoxide derived from it. Calculations show that the $\mathrm{Me_2S^{+\cdot}O_2^{\cdot}}$ complex is somewhat destabilized with respect to the reagents ($\Delta H = +6$ kcal mol^{-1}), but similarly intermediates **6** and **6′** are also destabilized with re-

spect to R_2S + $^1O_2$ by about the same amount,[5,6] although in every case subsequent paths from such intermediates to the sulfoxide are strongly exothermic.

[22] T. Del Giacco, L. Lipparoni, M. Ranchella, C. Rol, G. V. Sebastiani, *J. Chem. Soc. Perkin Trans. 2* **2001**, 1802.

[23] B. Branchi, M. Bietti, G. Ercolani, M. A. Izquierdo, M. A. Miranda, *J. Org. Chem.* **2004**, *69*, 8874.

[24] Flash photolysis experiments with the Ph_2S/TPP^+ system showed no oxygen quenching of either the sulfide radical cation or of $TPP^·$[6] (whereas the lifetimes of both $R_2S^{·+}$ and $DCA^{·-}$ was shortened in the corresponding experiments with DCA because of ET to O_2 from the latter and reaction with $O_2^{·-}$ of the former, path *e*). This proves that the rate constant for the reaction of both intermediates is $k_{O2} < 1 \times 10^6$ M^{-1} s^{-1}, but does not preclude this process having a role in steady-state experiments. Indeed, the reaction rate of $R_2S^{·+}$ with oxygen depends linearly on the intermediate concentration and thus on the intensity of the absorbed light flux, *k*[Intermediate][O_2], rather than on the square of the flux as the reaction with superoxide, *k*[Intermediate]^2. Thus, interaction with O_2 is more competitive at the low flux of steady-state irradiation than in flash experiments.

[25] There is some literature evidence that a further transient is involved in the reoxidation of the $TPP^·$ radical and it may well be that this is less efficient in BET than $TPP^·$, $DCA^{·-}$ or $O_2^{·-}$. Actually, it is known that $TPP^·$ is reoxidized to TPP^+ by reaction with oxygen,[26] the reoxidation probably involves dimerization to TPP-TPP and SET to TPP-$TPP^{·+}$ which cleaves to $TPP^·$ + TPP^+.[10d] That $TPP^·$ ultimately gives back reoxidized TPP^+ is also indicated by the fact that this sensitizer is only partially consumed when used in solution and not at all when using the silica-absorbed or zeolited-encapsulated materials.[27]

[26] D. Jacobi, W. Abraham, U. Pischel, L. Grubert, R. Stösser, W. Schnabbel, *J. Chem. Soc. Perkin Trans. 2* **1999**, 1695.

[27] M. Alvaro, E. Carbonell, H. Garcia, *Appl. Catal., B* **2004**, *51*, 195.

[28] a) C. H. Tung, J. Q. Guan, *J. Am. Chem. Soc.* **1998**, *120*, 11874; b) M. Kojima, A. Ishida, S. Takamuku, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2211; c) T. Tamai, N. Ichinose, T. Tanaka, T. Sasuga, I. Hashida, K. Mizuno, *J. Org. Chem.* **1998**, *63*, 3204; d) W. Adam, W. Haas, B. B. Lohray, *J. Am. Chem. Soc.* **1991**, *113*, 6202; e) F. D. Lewis, M. Kojima, *J. Am. Chem. Soc.* **1988**, *110*, 8664.

[29] a) E. A. Fehnel, M. Cormack, *J. Am. Chem. Soc.* **1949**, *71*, 84; b) C. G. Skrettas, M. Mischa-Skrettas, *J. Am. Chem. Soc.* **1979**, *44*, 714.

[30] J. Erikson, C. S. Foote, *J. Am. Chem. Soc.* **1980**, *102*, 6083.

[31] a) A. Cerniani, G. Modena, P. G. Todesco, *Gazz. Chim. Ital.* **1960**, *90*, 3; b) J. F. Carson, F. F. Wong, *J. Org. Chem.* **1959**, *24*, 175.

[32] a) J. P. McCullough, H. L. Finke, W. N. Hubbard, S. S. Todd, J. F. Messerly, D. R. Doublin, G. Waddington, *J. Phys. Chem.* **1961**, *65*, 784; b) A. J. Colussi, S. W. Benson, *Int. J. Chem. Kinet.* **1977**, *9*, 295.

[33] D. H. Fine, J. B. Westmore, *J. Chem. Soc. D* **1969**, 273.

[34] E. T. Denisov, *Russ. J. Phys. Chem. (Engl. Transl.)* **1995**, *69*, 396.

[35] T. Koizumi, T. Fuchigami, T. Nonaka *Bull. Chem. Soc. Jpn.* **1989**, *62*, *219.*

[36] D. M. Wayner, A. Houmam, *Acta Chem. Scand.* **1998**, *52*, 377.

[37] S. P. Verevkin, E. L. Krasnykh, J. S. Wright, *Phys. Chem. Chem. Phys.* **2003**, *5*, 2605.

[38] M. J. Rossi, D. F. McMillen, D. M. Golden, *J. Phys. Chem.* **1984**, *88*, 5031.

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