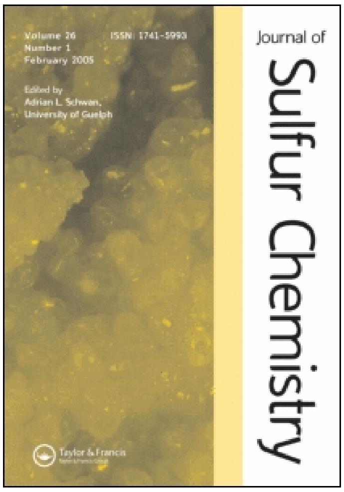

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Photosensitized electron transfer oxidation of sulfides: structure and medium effect

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Oxidation of a series of sulfides R′SR (R′, dodecyl, phenethyl, benzyl, cumyl, benzhydryl; R, ethyl, phenyl) under photoinduced electron transfer conditions (sensitizers: 9,10-dicyanoanthracene, triphenylpyrylium tetrafluoroborate) yields sulfoxides, products of trapping of the alkyl cation (for the benzhydryl and cumyl derivatives), and mainly aldehydes or ketones that result from α-deprotonation. The competing paths from the sulfide radical cation are discussed in this paper.

Keywords: sulfides; electron transfer; photochemistry; oxidation; fragmentation

1. Introduction

Thiols and thioethers have an accessible oxidation potential and single electron transfer (SET) from the sulfur atom by an organic or an inorganic species M^{n+1} is a common process. This may serve for an effective activation, yet occurring under mild and easy control conditions (Equation (1)). Indeed, SET has an important role in the chemistry and biochemistry of these compounds and in the preparation of sulfoxides under mild and enantioselective conditions (*1–18*).

$$R_2S + M^{n+} \longrightarrow R_2S^{+} + M^{(n-1)+} \qquad (1)$$

$$R_2S^{+} + M^{n+} \longrightarrow R_2S^{++} + M^{(n-1)+}. \qquad (2)$$

Furthermore, active intermediates have been generated in this way, *e.g.* SET oxidation by a chemical reagent or by a electrochemical process has shown to be a convenient method for the conversion of thioglycosides into O-glycosides and disaccharides via C–S bond cleavage and the reaction of the cation (*19, 20*).

A variation that enables further in controlling the reaction is based on photoinduced electron transfer (PET). In this case, the electron transfer step is allowed only via the excited state of the

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sensitizer (Equation (3)).

$$\begin{aligned} &\text{Sens} + h\nu \longrightarrow \text{Sens}^* \\ &\text{R}_2\text{S} \cdot + \text{Sens}^* \longrightarrow \text{R}_2\text{S}^+ + \text{Sens} \cdot^- \end{aligned} \tag{3}$$

In view of the short lifetime and small steady concentration of the latter, there is no competition by a second electron transfer step (Equation (2)), which may affect the course of the reaction when a highly oxidizing ground-state reagent is used, as in thermal methods. Therefore, PET is a method that can be classed among the ‘extreme energy’ methods, since it is based on high-energy intermediates such as radical ions, yet is characterized by the very mild, environmental-friendly conditions.

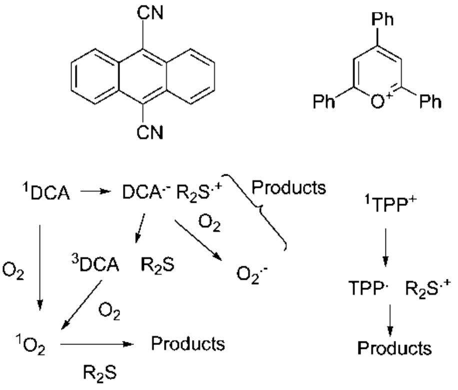
The accessible oxidation makes the process (Equation (3)) practically possible for all categories of PET sensitizers, such as electron-withdrawing substituted aromatics (*21, 22*), aromatic ketones (*23*), electron-poor heterocycles and salts (*21, 22, 24–26*), and titanium dioxide (*27*). Such sensitizers are used in oxidizing the sulfides in oxygen-equilibrated solution. Oxygen activation can also have a role, since the secondary electron transfer from the reduced sensitizer leads to the superoxide anion (Equation (4)). Furthermore, most of the above sensitizers are also able to promote oxygen to the singlet state (Equation (5)), a strong electrophile that reacts smoothly with aliphatic sulfides (*28–30*), and thus leads to the oxidation through a path that is different from the sulfide activation.

$$\text{Sens} \cdot^- + \text{O}_2 \longrightarrow \text{Sens} + \text{O} \cdot_2^- \tag{4}$$

$$\begin{aligned} &\text{Sens} + h\nu \longrightarrow \text{Sens}^* \\ &\text{Sens}^* + \text{O}_2 \longrightarrow \text{Sens} + {}^1\text{O}_2. \end{aligned} \tag{5}$$

Summing up, in principle, photosensitized oxidation of sulfides may involve activation of oxygen (Equation (5)), of the sulfide (Equation (3)) or of both species (Equations (3) and (4)).

The interest in these methods has led to an extensive investigation of both singlet oxygen reactions and, more recently, of PET-induced processes. As it will appear in the following, some details of the mechanistic picture has not been settled, however. In this frame, we present below some data, where two sensitizers are used: 9,10-dicyanoanthracene (DCA) and 2,4,6-triphenylpyrylium (TPP^+) tetrafluoroborate. Both are able to oxidize the sulfides, but as indicated in Scheme 1, these differ in two aspects: (i) in the former case, a radical ion pair; and in the latter, a radical/radical ion pair is formed; and (ii) their behaviour with oxygen. In fact, with DCA, there is a variety of



Scheme 1.

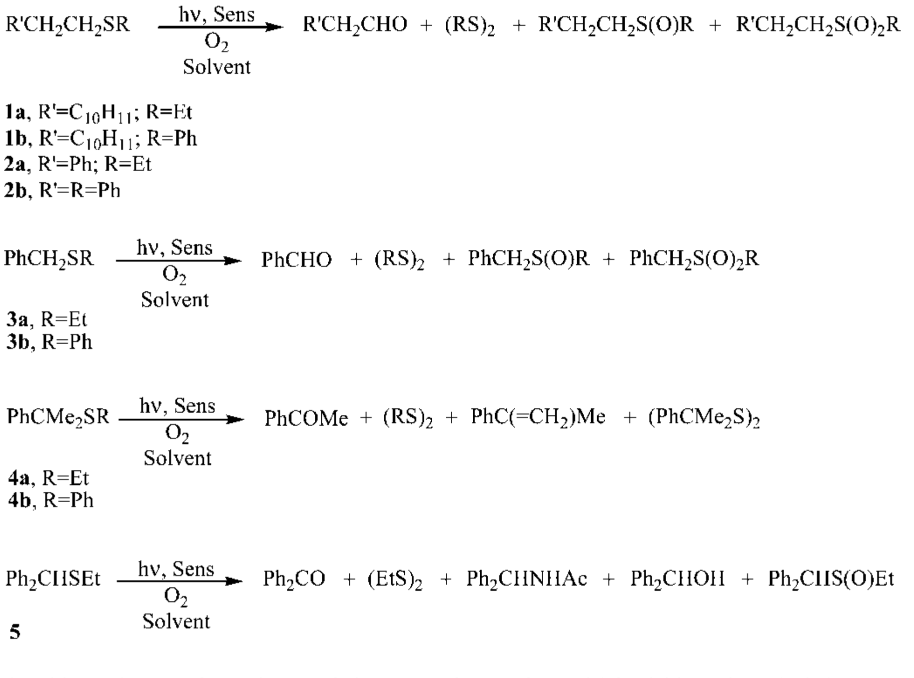
paths available. Singlet excited DCA accepts an electron from the sulfide, and secondary electron transfer gives superoxide (*28, 30, 31*) that may combine with the sulfide radical cation. The radical ion pair may, however, also undergo intersystem crossing to ^{3}DCA, and this gives singlet oxygen, possibly arising also via direct quenching of ^{1}DCA (*28, 30*). On the contrary, ^{1}TPP$^+$ is known as an inefficient oxygen sensitizer (^{3}TPP$^+$ may have a role at low sulfide concentration, but this does not change the situation), and TPP $\cdot$ is not sufficiently reducing to give superoxide (*32–35*) (see Scheme 1).

2. Results

As explained above, the two sensitizers have widely different properties. Furthermore, the competition between the different paths will be affected both by the structure of the sulfides, *e.g.* aryl sulfides react poorly with $^1O_2$, and by the medium. With the aim of contributing to determine the scope of sulfide photooxidation, we chose to compare the oxidation of a series of ethyl and of phenyl sulfides in a moderately polar (DCE, 1,2-dichloroethane), polar (MeCN), and protic (MeOH) solvents.

The results obtained by photosensitized oxidation (up to 20–30% conversion) are expressed in μmol/min (under normalized absorption conditions with the two sensitizers) in Tables 1 and 2, and the products identified are reported in Scheme 2.

The chemistry of the process can be summarized as follows. The sulfides are rather reactive under all of the conditions tested. The material balance is often good or very good, but there is a number of cases (involving the dodecyl sulfide and the cumyl sulfide), where the sum of the identified products is below 50%. The oxidation rate is higher for DCA for the ethyl sulfides, with



$$R'CH_2CH_2SR \xrightarrow[O_2\ \text{Solvent}]{h\nu,\ \text{Sens}} R'CH_2CHO + (RS)_2 + R'CH_2CH_2S(O)R + R'CH_2CH_2S(O)_2R$$

1a, $R'=C_{10}H_{11}$; R=Et
1b, $R'=C_{10}H_{11}$; R=Ph
2a, R'=Ph; R=Et
2b, R'=R=Ph

$$PhCH_2SR \xrightarrow[O_2\ \text{Solvent}]{h\nu,\ \text{Sens}} PhCHO + (RS)_2 + PhCH_2S(O)R + PhCH_2S(O)_2R$$

3a, R=Et
3b, R=Ph

$$PhCMe_2SR \xrightarrow[O_2\ \text{Solvent}]{h\nu,\ \text{Sens}} PhCOMe + (RS)_2 + PhC(=CH_2)Me + (PhCMe_2S)_2$$

4a, R=Et
4b, R=Ph

$$Ph_2CHSEt \xrightarrow[O_2\ \text{Solvent}]{h\nu,\ \text{Sens}} Ph_2CO + (EtS)_2 + Ph_2CHNHAc + Ph_2CHOH + Ph_2CHS(O)Et$$

5

Sensitizers (Sens): DCA and TPT^-; Solvents: MeCN, MeOH and 1,2-Dichloroethane (DCE)

Scheme 2.

Table 1. Photosensitized oxidation of alkyl ethyl sulfides **1–4a**, **5**.

			[µmol min^{-1}]		Products, % of Yield[b]	
Sulfide	Sens	Solvent[a]	Oxdative Cleavage	Sulfoxidation	Oxidative cleavage	Sulfoxidation
C$_{12}$H$_{25}$SEt, **1a**	DCA	MeOH		2.21	–	C$_{12}$H$_{25}$SOEt, 50
		MeCN	0.36	1.85	C$_{11}$H$_{23}$CHO, 8	C$_{12}$H$_{25}$SOEt, 40
		DCE	0.6	1.6	C$_{11}$H$_{23}$CHO, 10	C$_{12}$H$_{25}$SOEt, 27
	TPP$^+$	MeOH	0.2	0.37	C$_{11}$H$_{23}$CHO, 14	C$_{12}$H$_{25}$SOEt, 25
		MeCN	0.08	0.15	C$_{11}$H$_{23}$CHO, 21	C$_{12}$H$_{25}$SOEt, 50
		DCE	0.15	0.42	C$_{11}$H$_{23}$CHO, 21	C$_{12}$H$_{25}$SOEt, 60
PhC$_2$H$_4$SEt, **2a**	DCA	MeOH		1.18	–	PhC$_2$H$_4$SOEt, 73
		MeCN	0.79	0.64	PhCH$_2$CHO, 23; PhCH=CH$_2$, 30[c]	PhC$_2$H$_4$SOEt, 44
		DCE	0.15	0.52	PhCH$_2$CHO, 22	PhC$_2$H$_4$SOEt, 77
	TPP$^+$	MeOH	0.2	0.26	PhCH$_2$CHO, 11; PhCH=CH$_2$, 23[c]	PhC$_2$H$_4$SOEt, 66
		MeCN	0.67	0.3	PhCH$_2$CHO, 19; PhCH=CH$_2$, 50[c]	PhC$_2$H$_4$SOEt, 30
		DCE	0.085	0.135	PhCH$_2$CHO, 34	PhC$_2$H$_4$SOEt, 49
PhCH$_2$SEt, **3a**	DCA	MeOH	0.14	1.12	PhCHO, 11	PhCH$_2$SOEt, 73; PhCH$_2$SO$_2$Et, 13
		MeCN	0.83	1.55	PhCHO, 26	PhCH$_2$SOEt, 47
		DCE	0.55	0.4	PhCHO, 40	PhCH$_2$SOEt, 20; PhCH$_2$SO$_2$Et, 10
	TPP$^+$	MeOH	0.28	0.28	PhCHO, 32	PhCH$_2$SOEt, 32
		MeCN	0.18	0.32	PhCHO, 29	PhCH$_2$SOEt, 53
		DCE	0.38	0.86	PhCHO, 34	PhCH$_2$SOEt, 34; PhCH$_2$SO$_2$Et, 21
PhCMe$_2$SEt, **4a**	DCA	MeOH	0.085		PhCOMe, 40; [PhCMe$_2$S]$_2$, 1	–
		MeCN	0.06		PhC(=CH$_2$)Me, 5;[c] PhCOMe, 20; [PhCMe$_2$S]$_2$, 5	–
		DCE	0.27		PhC(=CH$_2$)Me, 10[c] PhCOMe, 26; [PhCMe$_2$S]$_2$, 13	–
	TPP$^+$	MeOH	0.09		PhC(=CH$_2$)Me, 9;[c] PhCOMe, 7	–
		MeCN	0.7		PhC(=CH$_2$)Me, 5;[c] PhCOMe, 28; [PhCMe$_2$S]$_2$, tr	–
		DCE	0.2		PhC(=CH$_2$)Me, 4;[c] PhCOMe, 10; [PhCMe$_2$S]$_2$, tr	–
Ph$_2$CHSEt, **5**	DCA	MeOH	0.044	0.15	Ph$_2$CO, 7	Ph$_2$CHSOEt, 22; Ph$_2$CHSO$_2$Et, 2
		MeCN	0.72	0.13	Ph$_2$CHOH, 10; Ph$_2$CO, 53; Ph$_2$CHNHAc, 22	Ph$_2$CHSOEt, 12; Ph$_2$CHSO$_2$Et, 2
		DCE	0.74	0.5	Ph$_2$CO, 61	Ph$_2$CHSOEt, 13; Ph$_2$CHSO$_2$Et, 27
	TPP$^+$	MeOH	0.26	0.11	Ph$_2$CO, 46; Ph$_2$CHOMe, 22	Ph$_2$CHSOEt, 15; Ph$_2$CHSO$_2$Et, 17.3
		MeCN	0.36	0.01	Ph$_2$CHOH, 3; Ph$_2$CO, 87; Ph$_2$CHNHAc, 11	Ph$_2$CHSOEt, 1
		DCE	0.95	0.23	Ph$_2$CO, 70	Ph$_2$CHSOEt, 10; Ph$_2$CHSO$_2$Et, 7

[a] The data in MeCN have been also reported in comparison with data in the absence of oxygen (*51*); [b] Percentage of yield on the cunsumed starting sulfide (20–30% of the starting amount); [c] Further oxidized during the course of the reaction.

Table 2. Photosensitized oxidation of alkyl phenyl sulfides **1–4b**.

			[μmol min^{-1}]		Products, % of Yield[a]	
Sulfide	Sens	Solvent	Oxdative Cleavage	Sulfoxidation	Oxidative cleavage	Sulfoxidation
$C_{12}H_{25}SPh$, **1b**	DCA	MeOH	0.19	0.07	$C_{11}H_{23}CHO$, 35; PhSSPh, 6	$C_{12}H_{25}SOPh$, 13
		MeCN	0.1	0.16	$C_{11}H_{23}CHO$, 42; PhSSPh, 9	$C_{12}H_{25}SOPh$, 64
		DCE	0.065	0.11	$C_{11}H_{23}CHO$, 64; PhSSPh, 10	$C_{12}H_{25}SOPh$, 10
	TPP^+	MeOH	0.35	0.49	$C_{11}H_{23}CHO$, 15; PhSSPh, 1	$C_{12}H_{25}SOPh$, 21
		MeCN	0.155	0.05	$C_{11}H_{23}CHO$, 48; PhSSPh, 13	$C_{12}H_{25}SOPh$, 15
		DCE	0.29	0.83	$C_{11}H_{23}CHO$, 25; PhSSPh, 4	$C_{12}H_{25}SOPh$, 71
PhC_2H_4SPh, **2b**	DCA	MeOH	0.21	–	$PhCH_2CHO$, 80; $PhSO_3H$, 20	–
		MeCN	0.3	–	$PhCH_2CHO$, 82; $PhSO_3H$, 9	–
		DCE	0.065	0.012	$PhCH_2CHO$, 44; $PhSO_3H$, 8; PhSSPh, 40	PhC_2H_4SOPh, 8
	TPP^+	MeOH	0.24	–	$PhCH_2CHO$, 75; $PhSO_3H$, 11; PhSSPh, 14	–
		MeCN	0.14	0.022	$PhCH_2CHO$, 44; PhSSPh, 6; $PhSO_3H$, 19	PhC_2H_4SOPh, 7
		DCE	0.36	0.03	$PhCH_2CHO$, 34; $PhSO_3H$, 4; PhSSPh, 59	PhC_2H_4SOPh, 3
$PhCH_2SPh$, **3b**	DCA	MeOH	0.04	0.35	PhCHO, 13; PhSSPh, 3	$PhCH_2SOPh$, 48; $PhCH_2SO_2Ph$, 2
		MeCN	0.93	–	PhCHO, 30; PhSSPh, 15	–
		DCE	0.025	0.006	PhCHO, 48; PhSSPh, 13	$PhCH_2SO_2Ph$, 13
	TPP^+	MeOH	0.13	–	PhCHO, 29; PhSSPh, 5	–
		MeCN	0.11	–	PhCHO, 20; PhSSPh, 13	–
		DCE	0.38	–	PhCHO, 30; PhSSPh, 23	–
$PhCMe_2SPh$, **4b**	DCA	MeOH	0.3	–	PhCOMe, 7; $[PhCMe_2S]_2$, 13; PhSSPh, 3; $PhCMe_2OMe$, 10	–
		MeCN	0.14	–	PhCOMe, 14; $[PhCMe_2S]_2$, 2; PhSSPh, 10	–
		DCE	0.014	–	PhCOMe, 24; $[PhCMe_2S]_2$, 3; PhSSPh, 47	–
	TPP^+	MeOH	0.125	–	PhCOMe, 6; $[PhCMe_2S]_2$, 17; PhSSPh, 2; $PhCMe_2OMe$, 17	–
		MeCN	0.11	–	PhCOMe, 28; $[PhCMe_2S]_2$, 5; PhSSPh, 33	
		DCE	0.19	–	PhCOMe, 26; $[PhCMe_2S]_2$, 3; PhSSPh, 43	–

[a] Percentage of yields calculated on the consumed sulfide (20–30% of the starting amount).

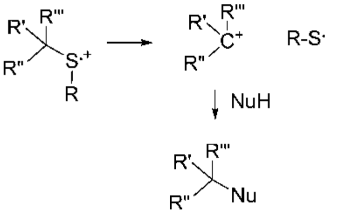
TPP^+ at most half as efficient, except for **4a** and **5**, where the DCA-induced reaction is slower, in particular, in methanol. In the phenyl series, the rates with both the sensitizers level down at one-fourth to one-half of the ethyl derivatives, with little medium effect except for the low values of the DCA reaction in DCE.

Two processes are observed: sulfoxidation and oxidative cleavage of the C–S bond. With the ethyl sulfides, the former is faster with DCA (with a solvent effect in the order MeOH>MeCN>DCE) than with TPP^+; with the phenyl sulfides, the sulfoxide is at most a minor product, and the distribution is less affected by the structure and the medium. More precisely, the oxidative cleavage gives an aldehyde (plus the diethyl, or respectively diphenyl, disulfide) with the dodecyl sulfides; the aldehyde and styrene with the phenethyl sulfide (in the ethyl series, only the aldehyde in the slow reaction of the phenyl series); the aldehyde from the benzyl sulfide (in this case, a large amount of sulfone, which under these conditions cannot arise by secondary oxidation of the sulfoxide, is also obtained); acetophenone, α-methylstyrene (from RSEt), or cumyl ethers (in MeOH from RSPh), and especially in the phenyl series, both possible disulfides, but no sulfoxides from the cumyl sulfides; benzophenone, benzhydrol (*N*-benzhydrylacetamide in MeCN), and remarkable amounts of sulfone from the benzhydryl sulfide.

3. Discussion

As for the mechanistic rationalization, a first element that can be appreciated is that there is some contribution of the $^1O_2$ path. This reaction, which is known to be efficient with dialkyl sulfides, leads mainly to the sulfoxide and is most effective in a protic medium, all characteristics that well fit with the trend of the above DCA photosensitization results (more sulfoxide in the Et series and in MeOH). As an example, the oxidation of **1a**, with the sulfoxide as the only product in MeOH (where the protonated persulfoxide is the intermediate), and a growing percentage of the aldehyde in aprotic solvents (where the persulfoxide is not stabilized) well corresponds to what expected for the $^1O_2$ path. Accordingly, the roughly constant overall reaction rate results from the balance between the lifetime of a singlet oxygen (short in MeOH) and the reactivity of the persulfoxide (high in MeOH). However, this mechanism does not explain clearly the DCA oxidation in all cases (in particular, sulfides that are quite resistant to $^1O_2$, such as cumyl and benzhydryl do react) and not at all the TPP^+ reaction. The paths different from sulfoxidation are fragmentations and can be discussed on the basis of the oxidation level of the fragments formed (Scheme 3).

Direct cleavage of the C–S bond in the sulfide radical cation to form an alkyl cation and a thiyl radical (Scheme 3) is a minor process. In fact, experiments under nitrogen that will be presented separately showed that little decomposition took place under those conditions, and furthermore, the present work shows that the products expected from the trapping of the alcohol cation are not observed except from **5** (small amount of the ether in alcohol, alcohol – from adventitious water – and the acetamide in MeCN) and from **4** (a little ether from **4b**, α-methylstyrene from **4a** that reasonably results from the deprotonation of the cumyl cation). In this process, oxygen is

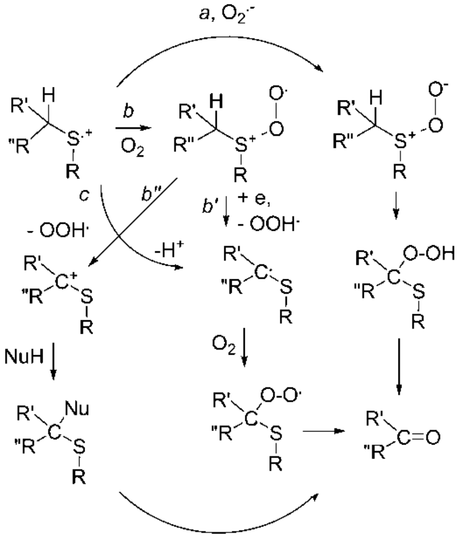


Scheme 3.

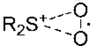
not involved in the key step (but only in a secondary reaction, *i.e.* the formation of acetophenone apparently resulting from the further oxygenation of α-methylstyrene), and DCA is not more efficient than TPP^+, indeed the most efficient reaction is that with TPP^+ in aprotic media.

Comparing the TPP^+-sensitized reaction with **4a** and **4b**, where this should be the only process occurring, one notices that passing from the ethyl to the phenyl series slows down the reaction, reasonably because the sulfide radical cation is stabilized by the substitution and thus fragmentation to yield the same (cumyl) cation is disfavored.

On the other hand, a larger scope cleavage leads to aldehydes or ketones, obtained in all cases. This path is symmetric with respect to sulfoxidation, contributing more with TPP^+ than with DCA, and with reversed solvent order, MeOH<MeCN<DCE for the ethyl series (again, smaller effects in the phenyl series). As mentioned above, experiments with the ethyl sulfides showed that these are less affected by photosensitization in the absence of oxygen. Thus, oxygen has a determining role in the fragmentation. With DCA, ET to oxygen is energetically allowed, and there is no reason to think that the thus formed superoxide anion does not add to the sulfide radical cation (path a in Scheme 4), (*29*) leading to the persulfoxide (the same intermediate of the singlet oxygen reaction) or to a ring-closed isomer, a thiadioxirane (*21*), and cleavage proceeds from such intermediates. This, however, applies only to the DCA case, since as mentioned above, TPP^+ does not reduce oxygen (or does it only at a slow rate), while this process occurs in both cases, with no large difference in the efficiency. Therefore, one may think that the radicalic character of R_2S^+ allows some interaction with the molecular oxygen (path *b*, a loose complex $Me_2S^+ \cdots$ O-O has indeed been computationally characterized) (*22*). This may lead to the reaction in different ways. Thus, it may afford some stabilization sufficient for promoting α-C–H deprotonation to give an α-alkylthio radical (path b′). Deprotonation directly from the sulfide radical cation (path c) appears unlikely in view of the poor reaction in the absence of oxygen; on the other hand, it may be more important when the superoxide anion is present, in view of the considerable basicity of such species (*36*). Trapping by oxygen of the latter species and decomposition of the peroxy radical or further oxidation to the cation, nucleophile (*e.g.* solvent) addition, and hydrolysis would give the carbonyl compounds. Alternatively, hydrogen transfer to the oxygen molecule yields directly the alkyl cation and hence the carbonyl function can be envisaged (path b″, Scheme 4).



Scheme 4.

As for the sulfone, it is interesting to note that this type of products forms in high proportion, sometimes in a yield higher than that of the sulfoxide, with the benzyl and benzhydryl sulfides, and in particular in apolar solvents. A high proportion of sulfone has also been obtained from the reaction of $^1O_2$ with benzyl and α-methylbenzyl sulfides in apolar solvents (*30*) reasonably resulting directly from the first adduct. Thus, it appears that the bulk around the sulfur atom favors the formation of sulfone, probably because this weakens a single-bonded intermediate, such as the persulfoxide, and enhances the tendency to bond with the second oxygen atom. What is true for the persulfoxide probably applies also to the radical cation oxygen complex, which may look more similar  to than to $R_2S^+ \cdots$O-O in this case, a difference that would explain the present results.

Finally, the formation of some styrene from **2a** (but not from the phenyl analogue **2b**) suggests that the phenyl moiety may contribute to the electron donation by the alkylthio (but not by the better donor arylthio) group, so that a different elimination takes place, probably after trapping by oxygen. The participation of the phenyl group to the donation in phenethyl sulfides has been studied by Baciocchi *et al.* (*15*).

4. Conclusion

In conclusion, the SET path to sulfide radical cations has been further documented. Cleavage to give carbocations is limited to highly stabilized cations (cumyl, benzhydryl), while a larger scope has cleavage to give carbonyls, a process that is initiated by deprotonation. The singlet oxygen path has a role with aliphatic sulfides using DCA as the sensitizer, particularly in a protic solution.

The advantages of the SET oxidation are lesser structure and condition dependence than the singlet oxygen path, although some limitations remain, *e.g.* phenyl sulfides are generally less reactive than the corresponding ethyl derivatives, reasonably because of the stabilization of the radical cation. The reaction gives at any rate a mixture of products and seems better suited for the elimination of undesired sulfur-containing pollutants, *e.g.* from fossil fuels (*27, 37*), from exhaust of meat rendering plants (*38*), and from industrial wastewater (*39*) rather than for preparative purposes. In such applications, the generality of the degradation and the moderate dependence on conditions, particularly with TPP^+, coupled with the fact that the reaction proceeds under oxygen, not requiring the addition of any chemical, give the character of a 'green' depollution method.

5. Experimental

5.1. *Materials*

The sensitizers 9,10-DCA and 2,4,6-TPP^+ were commercial products. TPP^+ was washed with water and dried before use in order to eliminate traces of acids. The sulfides **1a** (*40*), **1b**(*41*), **2a** and **2b** (*42*), **3a** and **3b** (*43*), and **5** (*44*) were prepared according to published procedures. Sulfides **4a** and **4b** were prepared from the condensation of α-methylstyrene with ethanethiol and thiophenol, respectively, under acid catalysis ($HClO_4$) according to the literature procedure (*45*). Diphenyldisulfide was prepared according to published procedure (*46*). Diphenylmethylacetamide was prepared by acetylation of the benzhydrylamine (*47*). 2-Methoxy-2-phenylpropane was prepared as reported in the literature (*48*). Other products (benzaldehyde, acetophenone, benzophenone, benzhydrol, styrene, α-methylstyrene, dodecanal, 3-phenylpropionaldehyde, and diethyldisulfide) and solvents were high-purity commercial samples and were used as received. Samples of the sulfoxides and sulfones for comparison with the products from the photosensitization reaction were prepared by 3-chloroperbenzoic acid and acetic acid – hydrogen peroxide oxidation following the general procedure described elsewhere (*49*).

5.2. *Photoreactions*

The photoreaction was carried out in Pyrex tubes by using 0.010–0.05 M solutions (2 mL) of the sulfides in the presence of DCA or TPP^+ (1×10^{-3} M) in the appropriate solvent. Then, 50 μL of an appropriate internal standard was added. The solutions were taken in rubber-stoppered Pyrex tubes. These were exposed to four 15 W phosphor-coated lamps (Applied Photophysics) centered at 410 nm, while a stream of dry oxygen saturated with the appropriate solvent was passed in the solution through a needle (temperature 20 ± 1 °C). The products were determined by HPLC [Suprasyl RP-18 chormatographic column, UV detector: λ: 230 or 260 nm, eluent: MeCN–H_2O (9:1) or (8:2) depending on the sulfide studied] on the basis of calibration curves with authentic samples in the presence of biphenyl as the internal standard or by GC (HP-1 chromatographic column, $100\,°C \times 2\,min - 10\,°C/min - 250\,°C \times 15\,min$) with cyclododecane as the internal standard. The products were identified by comparison of their chromatographic characteristics and mass spectra with those of the authentic samples.

The radiation intensity impinging on the tubes, measured by using the photosensitized oxidation of 1,2-diphenylethylene as the actinometer, was of ca. 1×10^{-6} Einstein cm^{-2} min^{-1} (*50*).

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