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Organic sulfides photooxidation using sensitizers covalently grafted on silica: towards a more efficient and selective solar photochemistry

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Abstract

A visible light sensitized oxidation of organic sulfides using a derivative of 9,10 dicyanonoanthracene (DCA) covalently grafted on silica (DCAC–Si) is studied. The reaction is more efficient than the corresponding homogeneous reaction and some improvement in the rate of product formation is noticed. These observations are discussed. In the case of di *n*-butylsulfide, the sulfoxide/(sulfone + disulfide) selectivity is increased. Diphenyl sulfide leads selectively and efficiently to diphenylsulfoxide. Advantages of the process, using reusable sensitizer and solar light are emphasized. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Photooxidation; Photoinduced electron transfer; Fluorescence quenching; Sulfides; Dicyanoanthracene; Grafted silica

1. Introduction

Photooxidation of sulfur compounds has been extensively investigated and different mechanisms have been described depending on the reaction conditions.

Unsensitized irradiation of disulfides or sulfides in the presence of oxygen and at short wavelengths leads to the formation of sulfonic acids as major products either in the gas phase [1–6] or in solvents such as alcohols or wet acetonitrile [7,8]. In these cases, the photochemical cleavage of the S–S or C–S bond was found to be followed by the addition of ground state triplet oxygen on the thiyl radicals [9].

$$\text{RSSR or RSR} \xrightarrow{h\nu} \text{RS}^{\cdot} \xrightarrow{^{3}\text{O}_2} \text{RS-O-O}^{\cdot} \dashrightarrow \text{RSO}_3\text{H} \qquad (1)$$

The sensitized photooxidation of sulfides has been most often studied with singlet oxygen sensitizers [10–16] and the major reaction products are sulfoxides with minor amount of sulfones. The complex mechanism of singlet oxygen addition is still of current interest [17–23] and different intermediates (peroxysulfoxide *A*, thiadioxirane *E*, S-hydroperoxysulfonium ylides *B*, ...) have been proposed on the basis of experimental and theoretical arguments (Scheme 1). The main features of the last proposed mechanism [17] may be summarized as follows:

- the first reaction intermediate, which gives rise to the intermediates *B* and *E*, is the peroxysulfoxide *A*, also responsible for oxidizing sulfoxides thus leading to mixtures of sulfoxide **2** and sulfone **3**.
- the behavior of the peroxysulfoxide *A* is strongly solvent dependent. Its stabilization in protic solvent such as methanol, with eventual formation of an electrophile sulfurane structure *D*, could account for the limitation of the quenching pathway and for the reduced amount of sulfone in those solvents [10,16].
- according to Clennan's calculated energetic data, the electrophile intermediate susceptible to sulfide attack is more probably a S-hydroperoxysulfonium ylide, *B* rather than a thiadioxirane *E*, although both possible intermediates were predicted by theoretical calculations. The reaction of *B* or *E* with sulfides gives sulfoxides, while the intramolecular rearrangement of *B*, leading to *C*, could give sulfones.

The oxidation of sulfur compounds with electron transfer photosensitizers has been less investigated [24–29]: a priori, the formation of a sulfur containing cation-radical and of superoxide anion (Scheme 2) can account for the formation of sulfoxides and sulfones through a peroxysulfoxide intermediate *A*, already proposed when using singlet oxygen

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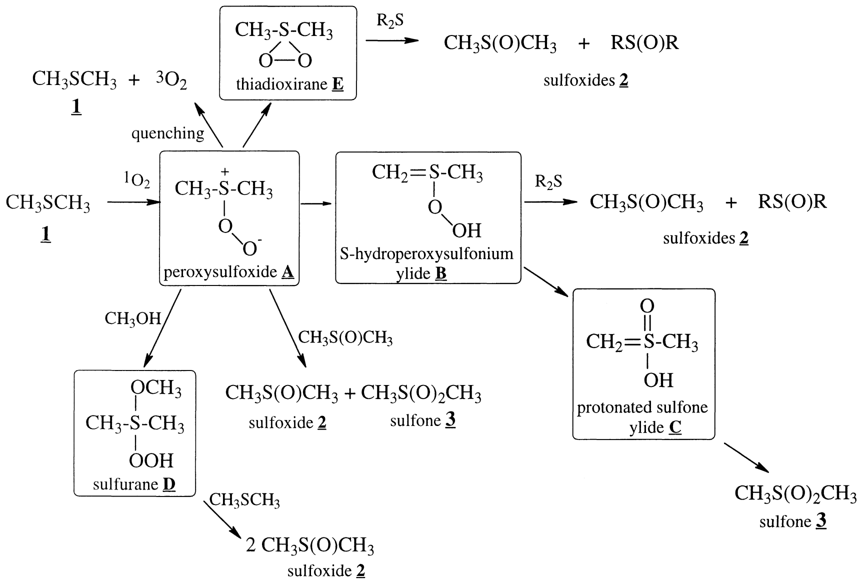
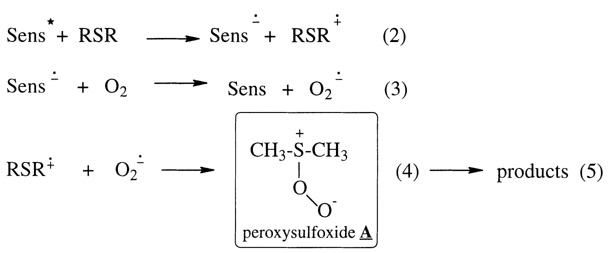


Scheme 1 from [17].

sensitizers. The efficiency of steps 2 and 3 is strongly dependent upon the redox properties of the excited photosensitizer (Sens*) and of the sulfide RSR.

The use of grafted photosensitizers, either in the case of energy transfer [30–33] or in the less investigated case of electron transfer [34–40], is a way to circumvent problems arising from the poor solubility of the sensitizers in some reaction media and to improve the ease of their separation from the reaction products. Moreover, if the photosensitizers are properly regenerated, their grafted form may easily be recycled. The properties of photoreactive molecules adsorbed on silica have been mentioned in recent papers [41–44], but the photosensitizing behavior of species chemically linked to the support were examined only in a few cases [30–40]. Some modulation of the reactivity of the grafted sensitizer by comparison with the soluble one has been shown [39,40] and may be expected in many other cases.

In this paper, the oxidation of di *n*-butylsulfide and diphenylsulfide (the latter known as unreactive versus singlet oxygen [24]) using 9,10-dicyanoanthracene as a Photoinduced Electron Transfer sensitizer is studied. Comparison is made between homogeneous (sensitizer and substrates in solution) and heterogeneous (sensitizer covalently linked to silica and substrate in solution) systems.



Scheme 2.

The electron transfer sensitizers used (Scheme 3) are 9,10-dicyanoanthracene (DCA) or a derivative of 9,10-dicyanoanthracene grafted in variable amounts on silica (DCAC–Si). For completeness, the soluble derivative of DCA bearing a carbamate moiety was also studied in solution (DCAC). Some comparison was also made with a known singlet oxygen sensitizer, 5,10,15,20-tetraphenylporphine (TPP) [45].

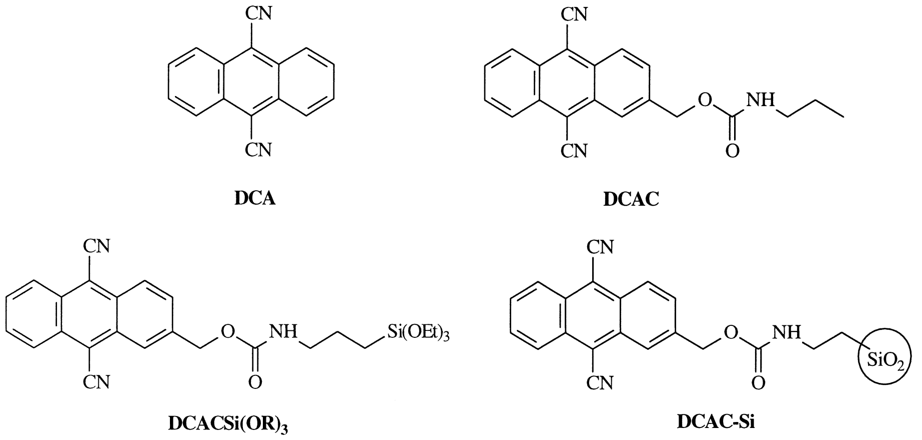
2. Experimental

2.1. Methods

Photochemical experiments (2.5 h unless otherwise stated) were run by external irradiation either in a Rayonet photoreactor equipped with four 25 watts lamps (RPR 4190 Å), or under solar irradiation. The reacting mixtures were continuously bubbled with oxygen during the irradiation. Product analysis was performed by GC (Fisons 8000 with a FID detector, Supelco SPB35 megabore column, 1 : 50 m, i.d.: 0.54 mm) or by GC-MS (HP5973, SPB35 column, 1 : 60 m, i.d.: 0.23 mm). Fluorescence measurements were made on a AMINCO 48000S system working in ratio mode. UV spectra were made on a Cary 5 Varian spectrometer. Grafted silicas were studied with the Varian reflectance accessory (Praying Mantis).

2.2. Products

Acetonitrile (Standa, HPLC quality) was used as received without any drying procedure. DCA was purchased from Kodak. Two DCAC–Si grafted silicas, with variable loading



Scheme 3.

of sensitizer were synthesized according to well known procedures from a triethoxysilyl precursor (DCAC–Si(OR)$_3$) (see Scheme 3). The synthesis of DCAC and of the alkoxysilylated precursor will be reported elsewhere [46]. DCA and DCAC concentrations in homogeneous solutions were calculated in order to have the same light absorption in both cases. In heterogeneous solutions, 10 mg of the grafted sensitizers were used in each case. For each experiment with grafted silicas, the solution before and after irradiation was checked for traces of leaking sensitizer. Under irradiation without sulfide for 2.5 h, grafted silicas are not completely stable: some DCA chromophore was detected by its characteristics UV absorption in the remaining liquid after centrifugation: a maximum of 28% in the case of the most densely loaded silica (DCAC–Si-2) and 23% for the less grafted DCAC–Si-1. In the presence of sulfides, i.e., under the photooxidation conditions, the unhooked sensitizer amounted to 26% in the case of the most densely loaded silica DCAC-Si-2, and decreased to 5% for the less loaded DCAC–Si-1. It would appear that the introduced sulfide concentration is able to prevent, probably by a competitive deactivation process, the photochemical degradation of the less grafted silica DCAC–Si-1.

2.3. Analysis of grafted silicas

Taking into account the amount of used alkoxysilylated precursor (DCAC–Si(OR)$_3$ for the synthesis of the grafted silicas, their maximum loading are 2.19 10^{-4} and 4.06 10^{-4} mol g^{-1}, respectively for DCAC–Si-1 and DCAC–Si-2. For these low sensitizer concentrations and owing to the possible traces of solvent adsorbed on silica, hardly desorbed after synthesis, microanalysis may be rather inaccurate.

Accordingly, in this study, the DCAC–Si loading was determined by UV-Visible Diffuse Reflectance Spectroscopy. Quantitative measurements could be made by this method using the Kubelka–Munk function

$$F(R) = (1 - R)^2/2R = K/S,$$

where K and S are the absorption and scattering coefficients [47]. For an ideal diffuser where the radiation has the same intensity in all directions, $K = 2\varepsilon C$ (ε is the Naperian absorption coefficient, C is the concentration). From these equations a liner correlation of the *F(R)* function with the concentration is expected for a constant scattering coefficient.

In a first step, a calibration curve was built by absorbing known amounts of the DCAC–Si(OR)$_3$ on silica: *F(R)* is shown to be practically a linear function of the concentration at several wavelengths (427, 403, 381 and 363 nm), up to about 10^{-5} mol g^{-1} (Fig. 1 at a selected 403 nm wavelength). The *F(R)* of the grafted silicas reported on this curve then gave an estimate of the amount of grafted sensitizer provided that no spectral deformation is observed (Fig. 2). Moreover, fluorescence spectra of the adsorbed or grafted silicas did not indicate the presence of excimer [46]. The results are as follows (values between brackets refer to microanalysis results): DCAC–Si-1: 2.9 10^{-6} mole g^{-1} (4.3 10^{-5} mol g^{-1}), DCAC–Si-2: 6.1 10^{-6} mol g^{-1} (6.4 10^{-5} mol g^{-1}. As stated previously, microanalysis results overestimate by about one order of magnitude the sensitizer concentrations.

According to the UV reflectance measurements, 10 mg of the grafted silicas (amount used in the heterogeneous photolyses) correspond to 0.03 and 0.06 µmol of sensitizer for

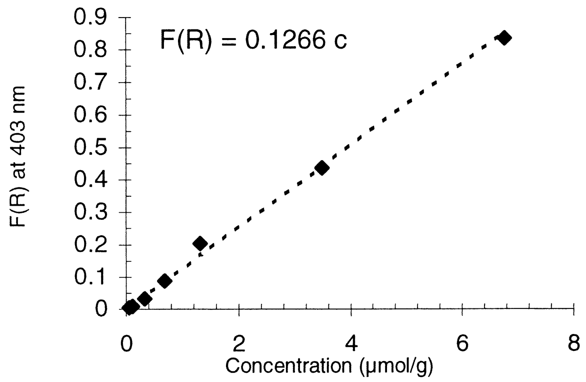


Fig. 1. Correlation between the remission function *F(R)* at 403 nm and the concentration of DCACSi(OR)$_3$ adsorbed on silica.

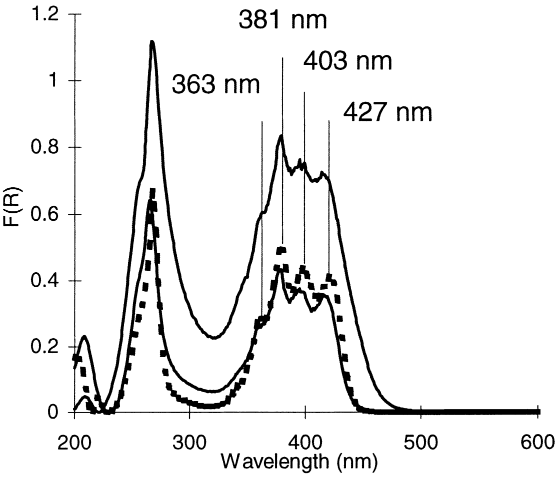


Fig. 2. Diffuse reflectance spectra of DCAC–Si-1 (lower full line spectrum), DCAC–Si-2 (upper full line) and one adsorbed sample (dotted line) recorded with the Praying Mantis accessory.

DCAC–Si-1 and -2, respectively. This must be compared with 0.38 µmol of DCA or 0.425 µmol of DCAC in homogeneous media.

3. Results and discussion

3.1. Fluorescence quenching experiments

An exergonic value between −23 and −29 kJ/mol^{-1} (depending on the solvent electrostatic interaction term, calculated either at a distance of 7 or 3 Å) for the Photoinduced Electron Transfer (PET) from an alkyl sulfide to DCA singlet state (Step 2 in Scheme 2) may be calculated from the following redox potentials [48] (versus SCE in acetonitrile) and photophysical values (namely the 0–0 excitation energy of DCA) [49]:

$$E^{\circ}_{(\mathrm{DCA/DCA^{-}})} = -0.98V \quad E^{\circ}_{(\mathrm{RSR^{\cdot+}/RSR})} = 1.79V$$
$$E_{00(\mathrm{DCA})} = 284\mathrm{kJ/mol^{-1}}$$

It is worth noting that the DCA triplet state is located at 175 kJ/mol^{-1} rendering electron transfer to the T_1 state highly endergonic [49].

The efficiency of the photoinduced electron transfer between sulfides and DCA is evidenced by DCA fluorescence quenching experiments (Table 1). The quenching constants of excited DCA by organic sulfides (between 1.2 10^{10} and 1.8 10^{10} l mol^{-1} s^{-1}), show diffusion controlled values in homogeneous solution and these values can only be explained by the previously cited exergonic electron transfer mechanism, the energy transfer being excluded since DCA is strongly bathochromic versus the considered sulfides.

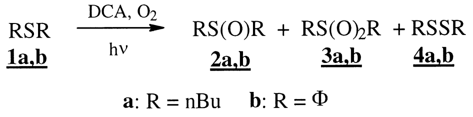
When comparing the DCA reduction potential with values reported for oxygen (−0.94 [50] or −0.82 V [37]), the formation of the superoxide anion by the electron transfer from DCA radical anion to ground state oxygen, regenerating the starting DCA (Step 3 in Scheme 2) appears almost isoergonic.

The mechanism of Scheme 2 is thus strongly supported, leading after the proposed PET from sulfide to the excited state of singlet DCA, to the ions $\mathrm{RSR^{\cdot+}}$ and $\mathrm{O_2^{-}}$. Therefore, further formation of the peroxysulfoxide intermediate *A* on the way to sulfoxide and sulfone according to Scheme 1 is very likely. Such a mechanism was recently studied in aqueous solutions by Schönreich and al [51]: the rate constant between dimethylsulfide radical-cation $\mathrm{CH_3SCH_3^{\cdot+}}$ and superoxide $\mathrm{O_2^{\cdot-}}$ was derived as 2.3 ± 1.2. 10^{11} mol^{-1} l s^{-1}, in agreement with a collapse of the ions to intermediate *A* (Step 4 in Scheme 2).

The fluorescence quenching constants of grafted DCAC–Si-1 and -2 by sulfides are 2–3 times smaller when compared with the same constants in homogeneous solutions (Table 1). The decrease of the quenching rate constants is probably due to the encounter limitation between the anchored sensitizer and the sulfide and related to a reduced rate of diffusion: nevertheless, the diffusional control of the electron transfer quenching probably remains operative in this heterogeneous case as already noticed elsewhere [46].

3.2. Photochemical results

The obtained photooxidation products, according to Equation 2 are listed in Table 2.


$$\underset{\underline{\mathbf{1a,b}}}{\mathrm{RSR}} \xrightarrow[h\nu]{\mathrm{DCA,\ O_2}} \underset{\underline{\mathbf{2a,b}}}{\mathrm{RS(O)R}} + \underset{\underline{\mathbf{3a,b}}}{\mathrm{RS(O)_2R}} + \underset{\underline{\mathbf{4a,b}}}{\mathrm{RSSR}} \qquad (2)$$
$$\mathbf{a}: \mathrm{R = nBu} \quad \mathbf{b}: \mathrm{R} = \Phi$$

Fluorescence quenching experiments have clearly proven the efficiency of the PET between DCA singlet state and

Table 1
Stern–Volmer and quenching constants of singlet excited DCA and DCAC–Si by sulfides RSR in acetonitrile (τ_f = 13 ns)[49]

Sulfide	DCA		DCAC-Si-1(2.9 10^{-6} mol g^{-1})		DCAC-Si-2(6.14 10^{-6} mol g^{-1})	
	K_{sv}(l mol^{-1})	k_q (s^{-1} mol^{-1} l)	K_{sv} (l mol^{-1})	k_q (s^{-1} mol^{-1} l)	K_{sv} (l mol^{-1})	k_q (s^{-1} mol^{-1} l)
R = Me	227	1.75×10^{10}	–	–	–	–
R = nBu	163	1.25×10^{10}	73	0.56×10^{10}	70	0.54×10^{10}
R = tBu	154	1.18×10^{10}	–	–	–	–
R = Φ	210	1.61×10^{10}	79	0.61×10^{10}	77	0.59×10^{10}

Table 2
Results of the sensitized photooxidations of di *n*-butylsulfide *1a* and diphenyl sulfide *1b* in oxygen saturated acetonitrile

Entry	Sensitizer[a]	Source[b]	Yields[c]						Selectivity[d]		Recovery[e]
			1a	*1b*	*2a*	*2b*	*3a*	*4a*	*3a*	*4a*	
1	DCA (7.6)	*A*	39		47		10	3	17	5	99
2	DCAC (8.5)	*A*	50		39		7	4	14	8	100
3	TPP (7.5)	*A*	0		88		5	7	5	7	100
4	DCAC-Si-1 (0.58)	*A*	39		58		1	1	2	2	99
5	DCAC-Si-2 (1.23)	*A*	49		47		1	2	2	4	99
6	DCA (7.6)	*B*	59		28		5	2	14	6	94
7	DCAC (8.5)	*B*	64		23		2	3	7	11	92
8	DCAC-Si-1 (0.58)	*B*	55		42		0	1	0	2	98
9	DCA (7.6)	*A*		22		68					90
10	DCAC (8.5)	*A*		32		58					90
11	TPP (7.5)	*A*		96		0					96
12	DCAC-Si-1 (0.58)	*A*		86		12					98
13	DCAC-Si-2 (1.23)	*A*		80		18					98

[a] Sensitizers concentrations in mol $l^{-1} \times 10^5$ (between brackets). Heterogeneous sensitizers used as a suspension of 10 mg of powdered silica in the 5 ml volume of irradiated solution, ‘Equivalent’ of concentration is given in those cases. Sulfide concentration: 6×10^{-2} mol l^{-1} in each experiment.

[b] $A = 4 \times 420$ nm RPR lamps in Rayonet reactory $B =$ solar irradiation without light concentrator; 2 h30 of irradiation.

[c] In percent, versus engaged sulfide.

[d] Defined as the ratio between the product *3a* or *4a* versus the sum *2a* + *3a* + *4a*.

[e] In percent, summing remaining sulfide and products.

sulfides **la,b**. Since DCA is also known as a singlet oxygen sensitizer [52–55], we investigated, for the purpose of comparison, a singlet oxygen oxidation of both sulfides sensitized by 5,10,15,20-tetraphenylporphine [13,45].

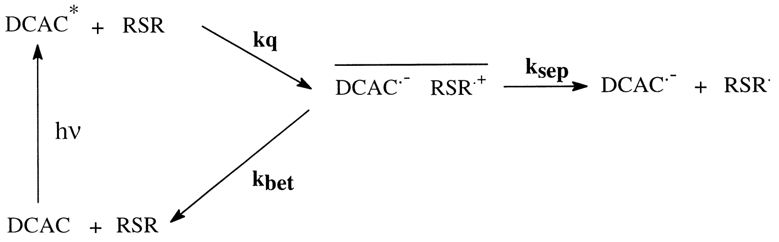
Comparing, in the case of diphenylsulfide, runs 11 with 9 or 10, a striking difference is observed showing that TPP is inefficient while DCA or DCAC lead to good sulfoxide yields, thus ruling out singlet oxygen participation in the latter cases. Since it was shown elsewhere [56] that ground state $^3O_2$ is not reactive versus sulfide radical-cations, we may conclude that the oxygen active species in the case of DCA or DCAC is oxygen superoxide. When the di n-butylsulfide case is considered, the comparison between runs 3 and 1 or 2 is less conclusive. However, since we are working under conditions where 90% DCA singlet states are intercepted by the sulfide, according to the Stern–Volmer constants of Table 1, the contribution of singlet oxygen is not expected to be important. In this case too, runs 1 and 2 probably correspond to superoxide reactions, as already proposed by other workers [24–26,28,57], while run 3 is a singlet oxygen reaction.

For di *n*-butylsulfide, the comparison of runs 1 or 2 with runs 4 or 5 shows that the reaction conversion is the same either in homogeneous or heterogeneous photoreactions despite a weaker (from 6 to 15 times) sensitizer ‘concentration’ in the latter case. Even if the absorbances are not directly comparable under homogeneous and heterogeneous conditions, it must be recognized that grafted DCAC is more efficient than DCA in solution. This cannot be related to the sensitizers singlet states quenching since k_q was shown to decrease when going from homogeneous to heterogeneous system. This indicates that the phenomenon responsible for the reaction improvement must take place later than the PET step. In these reactions, the PET first step (k_q) (Scheme 4) is not determining alone the reaction efficiency: the first radical ion pair created from the excited DCAC* quenching still needs to separate efficiently (k_{sep}) instead of recombining through a back electron transfer (k_{bet}) to the initial ground state.

The separation yield of the geminate radical pair may be a factor affected by the silica surface. A stabilization of the radical ion pair by the polar surface of the silica may also be responsible for a decrease of back electron transfer (k_{bet}) and the increase of the efficiency of the heterogeneous sentitizer. This will not affect the quenching constants but will lead to an increase of the reaction quantum yields. An alternative explanation, for the dibutylsulfoxide efficient formation may be some stabilization of the peroxysulfoxide (like *A*) by the surface silanols as will be discussed later.

For diphenylsulfide, no clear cut efficiency enhancement is observed in heterogeneous medium when taking the reduced amount of sensitizer into account (compare runs 9 or 10 with 12 or 13). This could result from the inherent stabilization, due to resonance effects, of the radical-cation $\Phi S\Phi^{\cdot+}$ or of the peroxysulfoxide $\Phi S\Phi^{+}OO^{-}$, relative to the equivalent alkyl species. In this case, the additional stabilization arising from the surface silanols could be less noticeable.

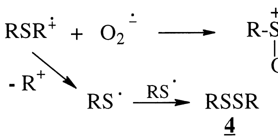
Another peculiar observation to be made concerns the comparison of runs 4 and 5 on the one hand, or runs 12 and 13 on the other hand: in both cases the loading of the grafted silicas increases by a factor of two and no corresponding increase of the rate is observed. Normally, and this was verified in homogeneous phase, with absorbances in the



Scheme 4.

vicinity of 0.1, doubling the concentration of sensitizer should result in doubling the reaction rate. This is not observed in the heterogeneous situation and we think that this is related to the fact that the surface effect decreases with the loading of the silicas. It is highly probable that when grafting a silica, the most accessible sites of the surface will be occupied at the beginning and the present observation suggests that these first sites should be more active. Accordingly, increasing the loading of silicas should not be an advantage.

The reaction selectivity also deserves comments. In homogeneous medium, diphenylsulfide leads very cleanly to sulfoxide without any sulfone or disulfide, while the di *n*-butylsulfide leads to mixtures of the three products. Mechanistically, the absence of diphenylsulfone may be reasonably explained if Scheme 1 is considered. One of the ways leading to sulfones and involving intermediates *B* and *C* cannot be followed in this case due to the absence of hydrogens α to the sulfur atom. The other pathway, where a sulfoxide must react with the peroxysulfoxide *A* is probably not operative (steric reasons ?). Alternatively, the formation of disulfide should imply, as already proposed by Ando [58], a C–S bond cleavage in the sulfide radical cation $RSR^{\cdot+}$ according to Equation 3. This is not expected in the case of diphenylsulfide since the formation of a phenyl cation is very unlikely.



(3)

When comparing the selectivities of homogeneous and heterogeneous di *n*-butyl sulfides photooxidations, some improvement is observed with the grafted sensitizers: less sulfone *3a* or disulfide *4a* are obtained versus enhanced yields in sulfoxide *2a* (runs 4 or 5 to be compared with runs 1 or 2, or under solar irradiation run 8 to be compared with runs 6 or 7). The surface effect, already mentioned to account for the enhanced efficiency of the grafted silica, can also explain this selectivity increase. Indeed, a parallel may be drawn between the results obtained here with DCAC–Si and the data reported on singlet oxygen oxidation in polar solvents like MeOH: in this solvent, a better efficiency and limited amounts of sulfone were registered [17] and the stabilization of the peroxysulfoxide *A* intermediate by the solvent or the actual formation of a sulfurane *D* was put forward. Such a stabilization can also be envisioned by the remaining silanol groups at the surface of silica. In other words, the peroxysulfoxide *A* could be trapped by the surface hydroxyl groups keeping this intermediate sufficiently active in order to react with a sulfide and give the sulfoxide while its reaction with a sulfoxide to give a sulfone should be more severely hindered.

A further argument favoring a surface effect on the selectivity of the reaction is a result obtained with biphenyl as a positive charge relaying cosensitizer. If biphenyl (BP) is added to the reaction medium in concentration of the order of 0.1 mol l^{-1} or more, the following steps are to be added to Scheme 2:

$$Sens^{\star} + BP \longrightarrow Sens^{\cdot-} + BP^{\cdot+} \qquad (2')$$

$$BP^{\cdot+} + RSR \longrightarrow BP + RSR^{\cdot+} \qquad (2'')$$

In such experiments performed with di *n*-butylsulfide, a product distribution closer to the one observed in homogeneous solution has been recorded (sulfone yields from 5 to 9% versus 0 to 1% in the absence of biphenyl with DCAD-Si-1 and 2). This implies that biphenyl has played the relaying game, giving an electron to the excited DCAC on the surface and transferring the charge to the sulfide in the surrounding solution, thus leading to a decreased sulfoxide selectivity. Biphenyl was not found to accelerate the reaction significantly as observed in the photocleavage of benzylic ethers [46], but this may be reasonable since the oxidation potentials of biphenyl (1.9 V [59]) and sulfide (1.79 V) are closer than in the former case.

We have to underline that the real selectivity of these heterogeneous photoreactions is probably higher than observed in this work, since some leaked sensitizer unhooked from the silica beads has to be taken into account. Finally it is worth noting that we are here working with a sensitizer efficiently regenerated and whose turnover may be estimated at 10^4 as a minimum in an experiment with a high sulfide conversion.

Another interesting result is related to the possible use of solar irradiation to perform the photooxidation. This has been checked in the case of the more reactive di *n*-butylsulfide. Under standard meteo conditions, within the same irradiation time, the photooxidation yield only decreases by about a factor 2. Moreover, as under irradiation with the 4190 Å lamps, a better efficiency and selectivity is observed in the heterogeneous case (performed with the less loaded silica DCA-Si-1) than in the homogeneous one (compare entries 8 with 6 or 7). The combined use of solar irradiation and of recyclable sensitizers renders this system attractive for the treatment of sulfur waste products. Further studies aimed at the optimization of the reaction conditions are in progress.

4. Conclusions

In this work, the PET mechanism of the DCA sensitized organic sulfides oxidation has been confirmed together with the role of the superoxide active species: the fluorescence quenching kinetics agrees only with such a mechanism.

Grafted photosensitizers appear to be more efficient for the sulfoxides formation than the corresponding homogeneous DCA sensitizers. Moreover the selectivity of sulfoxide/sulfone products is improved in the case of the di *n*-butyl sulfide. While the implications of these observations may not be accurately translated in mechanistic terms, it appears that the role of the silica surface on the geminate radical ion is probably one of the main factors and this may be accompanied by some stabilization of intermediates on the surface.

The efficiency of these solid photocatalysts under solar irradiation is demonstrated and their loading may be kept at a minimum. Their use in combination with oxygen (or even air) as the sole reagent and sun as a no cost energy source opens the way for some applications in the treatment of sulfur waste products.

DCA was already recognized as an efficient sensitizer in sulfides oxidation. A further step is here accomplished: the sensitizer may be used in a reusable form, easy to separate from the reaction medium, so that it may be taken as an environmental friendly reactant: no waste are expected.

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