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Sergio Mauricio Bonesi, Stefano Crespi, Daniele Merli, Ilse Manet, and Angelo Albini J. Org. Chem., Just Accepted Manuscript • DOI: 10.1021/acs.joc.7b01518 • Publication Date (Web): 04 Aug 2017 Downloaded from http://pubs.acs.org on August 4, 2017

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The Journal of Organic Chemistry is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Direct irradiaton of aryl sulfides. Homolytic fragmentation and sensitized S-oxidation.

Sergio M. Bonesi<sup>a,b,\*</sup>, Stefano Crespi<sup>b</sup>, Daniele Merli<sup>c</sup>, Ilse Manet<sup>d</sup> and Angelo Albini<sup>b</sup>

<sup>a</sup>Departamento de Química Orgánica, CIHIDECAR – CONICET, , 3<sup>er</sup> Piso, Pabellón 2, Ciudad Universitaria, FCEyN, University of Buenos Aires, Buenos Aires, 1428, Argentina. Phone/FAX:+541145763346.

<sup>b</sup>PhotoGreen Lab, Department of Chemistry, V.le Taramelli 12, 27100 Pavia, Italy. <sup>c</sup>Department of Chemistry, V.le Taramelli 12, 27100 Pavia, Italy. <sup>d</sup>ISOF-CNR, via Gobetti 101, 40129, Bologna, Italy.

**Abstract** The direct irradiation of diphenyl sulfide and *p*-substituted thioanisoles in the presence of oxygen was investigated by means of both steady state and laser flash photolysis experiments. Two competitive pathways took place from the triplet excited state of thioanisoles, C-S bond cleavage, finally leading to aryl sulfinic acid and sensitized oxidation leading to S-oxidation. Co-oxidation of dodecyl methyl sulfide occurred efficiently implying that an S-persulfoxide intermediate is involved during the sensitized oxidation. On the other hand, triplet state of diphenyl sulfide also showed competitive C-S bond cleavage giving phenyl sulfinic acid and ionization to diphenyl sulfide radical cation that in turn led to diphenyl sulfoxide. The rate constants of the above reactions were determined by time-resolved experiments.



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# Introduction

During the last years, our research group has been involved in the study of the photo oxidation of sulfides providing new insight into both the oxygen sensitization and electron transfer oxidation reactions of alkyl and aryl sulfides<sup>1</sup>, through steady-state and laser flash photolysis experiments. In the following, a rather unexpected observation is reported, that is that the direct irradiation (310 nm, with no added energy or electron transfer photosensitizer) of thioanisoles and diphenyl sulfide in oxygen saturated solutions caused C-S bond cleavage and formation of sulfinic acids, along with S-oxidation of sulfides giving sulfoxides as photoproducts (eq. 1).



Two processes appear to occur competitively via aryl sulfenyl radicals (ArS<sup>-</sup>) are the reasonable intermediates and further reaction with molecular oxygen gives the observed aryl sulfinic acids. In the literature, two mechanisms have been reported for the fragmentation of C-S bond. One involves the reaction of oxygen singlet of aryl methyl sulfides (benzyl, benzhydryl and cumyl aryl sulfides) and occurs efficiently from the S-persulfoxide intermediate through a Pummerer rearrangement affording carbonyl compounds (aldehydes and ketones) as photoproducts in aprotic solvents along with the corresponding sulfoxides and sulfones.<sup>2,1a,1b,1c</sup> The second one, involves an electron transfer process releasing aryl thiyl radical and alkyl cation as intermediates,<sup>3</sup> as demonstrated by Baciocchi and coworkers, who observed the C-S bond cleavage of aryl 1-methyl-1-arylmethyl sulfide radical cations under steady-state conditions and revealed such intermediates by laser flash photolysis experiments. However, we have earlier demonstrated that diethyl and diphenyl sulfide radical cations do not fragment the C-S bonds and the corresponding sulfoxides were obtained as

the photoproducts under electron transfer photosensitization of O<sub>2</sub>-saturated solutions.<sup>4</sup> On the other hand, irradiation (254 nm) of a series of alkyl ethyl sulfides (RSEt) under inert atmosphere, where the second S-bonded substituent R is an alkyl or benzyl group, underwent photo homolysis providing end photoproducts that arose from coupling or disproportionation of the alkyl and thivl radicals formed with high quantum yields (0.41 - 0.90).<sup>5</sup> To summarize, these reports show that C<sub>sp3</sub>-S bond of sulfides can fragments under different experimental conditions, viz., singlet oxygen sensitization via a sulfide radical cation and from the excited state (singlet or triplet) of a sulfide. Recently, Jiang and co-workers have studied the photochemistry of diphenylquinoxaline derivatives bearing phenyl thioethers as type I photo initiator in photopolymerization experiments and have shown that C<sub>sp2</sub>-S bond of the thioether moiety fragmented under direct irradiation (365 nm).<sup>6</sup> Notice that irradiation of diaryl sulfoxides is another interesting example of the easy fragmentation of a C<sub>sp2</sub>-S(O) bond. In fact, Jenks and co-workers have studied the photochemistry of diphenyl and ditolyl sulfoxides and  $\alpha$ -cleavage is the preferred fragmentation pathway.<sup>7</sup> Also, the C-S bond strength in Ph<sub>2</sub>S=O and related compounds has to be around 65 kcal.mol<sup>-1</sup> which is lower than the energies of the singlet ( $E_8 \approx 90 - 100 \text{ kcal.mol}^{-1}$ ) and triplet ( $E_T \approx 75 - 80 \text{ kcal.mol}^{-1}$ ) states. Therefore, the C<sub>sp2</sub>-S cleavage of these compounds is markedly exothermic regardless of the excited state involved.

On the other hand, photoinduced S-oxidation is commonly carried out by reaction with singlet oxygen generated by energy transfer from triplet sensitizers.<sup>8</sup> However, in some cases, it has been demonstrated that such interaction does not occur with unitary efficiency.<sup>9</sup> In other words, the "chemical" combination of the organic molecule (A) with oxygen is accompanied by purely "physical" decay (eq. 2) and further processes, such as the decay of the triplet sensitizer not accompanied by oxygen sensitization and electron transfer.



In general, aryl alkyl (as well as diaryl) sulfides appear to be less reactive towards singlet oxidation and have received less attention than dialkyl sulfides, though the singlet oxygenation of thioanisoles has been considered in mechanistic papers.<sup>10</sup> Addition of protic additives (alcohol and acids), zeolites and clays provides photo oxidation of sulfides more efficiently.<sup>11</sup> Likewise, S-oxidation of alkyl and aryl sulfides could be achieved under electron transfer sensitization in the presence of molecular oxygen and involved sulfide radical cation as the key intermediate.<sup>12</sup> Sulfoxides are generally the main products, but variable amounts of C–S bond cleavage products can also be obtained, depending on the substrate structure.

As it was reported above, we have studied the photochemistry of alkyl sulfides by direct irradiation with wavelength of 254 nm under Ar atmosphere<sup>5</sup> as well as photosensitized oxidation reactions under energy transfer<sup>1</sup> and electron transfer<sup>4</sup> conditions of dialkyl, arylalkyl and diaryl sulfides in different solvents and with different photosensitizers. However, according to our knowledge, the possibility of oxidation of sulfides by direct irradiation (310 nm) in the presence of oxygen was not previously investigated making this one of our reason to develop the study. Therefore, based on the preliminary reports mentioned above and considering that the direct irradiation of sulfides was not reported yet encouraged us to do more extensive work for which we chose a series of *p*-substituted thioanisoles and diphenyl sulfide as substrates, as reported below, and examined in terms of product distribution, chemical quenching and laser flash photolysis experiments.

## Results

*Photo oxidation of diphenyl sulfide.* Irradiation of diphenyl sulfide (Ph<sub>2</sub>S) in the presence of dyes, such as Rose Bengal (RB), under oxygen flushed solutions causes no chemical change. However, direct irradiation of diphenyl sulfide in acetonitrile with  $\lambda_{exc} = 310$  nm under oxygen atmosphere caused the generation of diphenyl sulfoxide (12.8 %) and phenyl sulfinic acid (32.0 %) when Ph<sub>2</sub>S is consumed in up to 55% yield. The course of the reaction in MeCN is detailed in Fig. 1, where it is apparent that C-S cleavage to form phenyl sulfinic acid is the main process.



Figure 1. Consumption of diphenylsulfide (black circles) and formation of phenylsulfinic acid (red triangles) and diphenylsulfoxide (blue triangles) with reaction time.

The UV-visible spectra of diphenyl sulfide show two absorption bands located at 296 and 320 nm. The first weak absorption band was assigned to the  ${}^{1}L_{b}$  state while strong absorption band was assigned to the  ${}^{1}L_{a}$  state by comparison with reported data.<sup>13</sup> Diphenyl sulfide is suitable compound that can absorb the incident light (310 nm) because a maximal overlapping between the  ${}^{1}L_{b}$  band and the incident light takes place as it was verified when the recorded UV-visible absorption spectra of a solution of thioanisole in MeCN and the emission spectra of the lamps used (310 nm) were overlaid each other.

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The photo oxidation of diphenyl sulfide also occurs in methanol and dichloromethane, a polar protic and an aprotic solvents, respectively, providing the same product distribution. Noteworthy, in any experiment diphenyl sulfone was not formed even at high sulfide conversion. The quantum yields of formation of diphenyl sulfoxide (Ph<sub>2</sub>SO) ( $\phi_{Ph_2SO}$ , see Table 1) were also measured and in aprotic solvents the quantum yields are quite similar while in protic solvents, such as methanol, the value is halved.

It is known from the literature that dye photo oxidation of dialkyl and alkylaryl sulfides generates sulfoxides at a noticeably enhanced rate in aprotic solvents in the presence of acids.<sup>10c,11d</sup> On the contrary, addition of cesium carbonate to the reaction mixture suppressed the formation of sulfoxide (even after a further period in the darkness) as can be seen in Table 1. Likewise, no significant oxidation was detected when diphenyl sulfide was treated with hydrogen peroxide in acetic acid in the darkness.

Solvent	Sensitizer or Additives	Conv. (%)	$[Ph_2SO]_1 / \mu mol min^{-1}$	$\phi_{Ph2SO}^{b}$
МеОН	RB (visible light)	0	0	
MeCN		23.0	0.070 (0.120 $\mu mol.min^{-1}$ of $H^{+})$	0.048
МеОН		34.4	0.039	0.026
DCM		30.7	0.062	0.041
MeCN	CH <sub>3</sub> COOH (2.5x10 <sup>-3</sup> M)	24.1	0.096	
MeCN	CH <sub>3</sub> COOH (7.5x10 <sup>-3</sup> M)	11.9	0.073	
MeCN	ClCH <sub>2</sub> COOH (5.0x10 <sup>-3</sup> M)	20.3	0.060	
MeCN	34.5 mg Cs <sub>2</sub> CO <sub>3</sub>	25.0	0	
MeCN	34.5 mg Cs <sub>2</sub> CO <sub>3</sub> / $hv + 20$ min in the darkness	25.0	0	

Table 1. Direct photo oxidation of diphenylsulfide.<sup>a</sup>

<sup>a</sup> Sulfide concentration: 0.010 M. RB = Rose Bengal. <sup>b</sup>Actinometer: KI (0.6 M), KIO<sub>3</sub> (0.1 M) and Na<sub>2</sub>B<sub>2</sub>O<sub>7</sub>.10H<sub>2</sub>O (0.01 M) in water;  $\phi(I_3^-) = 0.38$ ;  $\lambda_{exc} = 310$  nm.<sup>14</sup> Error:  $\pm 0.001$ .

The role of oxygenated intermediates has been investigated through their oxygen-transfer properties.<sup>15</sup> In the present case, dodecyl methyl sulfide was chosen as an adequate oxygen acceptor because it neither absorbs nor reacts at the excitation wavelength (310 nm). Thus, co-irradiation of diphenyl sulfide (0.010 M) and dodecyl methyl sulfide (0.010 M) in oxygen saturated MeCN solution caused oxidation of both sulfides (Scheme 1). Under these conditions, dodecyl methyl sulfide was co-oxidized to the corresponding sulfoxide and sulfone supporting that Foote's mechanism via singlet oxygen and persulfoxide is operating.



Scheme 1. Co-irradiation of diphenyl sulfide and dodecyl methyl sulfide at 310 nm.

*Time-resolved spectroscopy of diphenyl sulfide*. Irradiation of diphenyl sulfide in acetonitrile solution with a 266 nm laser pulse under nitrogen atmosphere provides transient absorption spectra (see fig. 2(a)) showing five characteristic absorption bands located at 300, 340, 460, 600 and 740 nm. Comparison with literature shows that two transient species are responsible for these bands, viz. diphenyl sulfide radical cation and phenyl thiyl radical, with the bands located at 340, 600 and 740 nm attributed to the former, and those at 300 and 460 nm to the latter one.<sup>16, 4</sup> Quenching of the Ph<sub>2</sub>S<sup>+</sup> radical cation was obtained by addition of triethylamine which is easily oxidized ( $E_{ox}(Et_3N)$ ): 0.69 V<sup>17a</sup> vs  $E_{ox}(Ph_2S)$ : 1.43 V<sup>17b</sup> (vs. SCE)). In fact, in fig. 2(b), the bands belonging to the radical cation disappear completely while those of the phenyl thiyl radical remain. This quenching experiment demonstrated that both transient intermediates are simultaneously formed after the laser pulse by two different pathways from the triplet state of diphenyl sulfide: (i) ionization of Ph<sub>2</sub>S giving the Ph<sub>2</sub>S<sup>+</sup> and the electron and, (ii) C-S cleavage providing radical PhS<sup>-</sup>. As reported in the literature, diphenyl sulfide showed a minimal fluorescence emission but a phosphorescence

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quantum yield of 0.45. The  $\phi_p/\phi_f$  ratio was also reported and the fluorescence quantum yield was easily estimated as 0.004.<sup>18</sup> Then, we suggest that intersystem crossing to the triplet state of diphenyl sulfide was largely predominating taking into account the reported  $\phi_f$  and  $\phi_p$  values and hence, the ionization process as well as the C-S bond cleavage observed after the laser pulse is more likely to proceed from the triplet excited state.

Further, the transient decay traces of both intermediates,  $Ph_2S^+$  and  $PhS^-$ , were also recorded at 740 and 460 nm, respectively, where overlapping was minimal, under N<sub>2</sub> and O<sub>2</sub> atmospheres and are shown in fig. 3. Both transients showed nice second-order decays under N<sub>2</sub>-saturated acetonitrile solutions and from the slopes of the linear regression of the reciprocal of the concentration of the transients vs. time plots the bimolecular rate constants,  $k_{BET}$  and  $k_{recomb}$ , of 10<sup>10</sup> M<sup>-1</sup>.s<sup>-1</sup> were obtained (see Table 2).



**Figure 2. (a)** Transient absorption spectra recorded after a laser pulse (9  $\mu$ s;  $\lambda_{exc}$ : 266 nm) of N<sub>2</sub>saturated acetonitrile solution of diphenyl sulfide (6.03x10<sup>-4</sup> M). (b) Overlay of transient absorption spectra recorded at 9  $\mu$ s after a laser pulse ( $\lambda_{exc}$ : 266 nm) of N<sub>2</sub>-saturated acetonitrile solution of diphenyl sulfide (6.03x10<sup>-4</sup> M) in the absence and in the presence of trimethylamine (0.024 M).

The rate constant  $k_{\text{BET}}$  was attributed, for the case of diphenyl sulfide radical cation, to the backelectron transfer process between this transient and the ejected electron. Likewise, for the case of phenyl sulfide radical, the rate constant  $k_{\text{Recomb}}$  represented the recombination process of the radicals formed after the C-S fragmentation in the solvent cage.

On the other hand, the decay traces of transients  $Ph_2S^{+}$  and  $PhS^{-}$  showed a pseudo-first order decay under oxygen atmosphere indicating that both transients reacts efficiently with molecular oxygen. After fitting analysis of the data the pseudo-first rate constants were obtained and a second-order rate constant of  $10^6 - 10^7 \text{ M}^{-1}\text{s}^{-1}$  was calculated by considering the concentration of O<sub>2</sub> solubilized in each of the solvents used (see Table 2).



**Figure 3.** Decay traces of  $Ph_2S^+$  after a laser pulse ( $\lambda_{exc}$ : 266 nm) of acetonitrile solutions of  $Ph_2S$  (6.03 × 10<sup>-4</sup> M) recorded at: (a) 740 nm and (b) 450 nm under N<sub>2</sub> and O<sub>2</sub> atmospheres.

		N <sub>2</sub>	O <sub>2</sub>
$Ph_2S^{++}$ ( $\epsilon_{740} = 5600 M^{-1}.s^{-1}$ )	$\lambda_{abs}/nm$	$k_{\rm BET} / {\rm M}^{-1}.{\rm s}^{-1}$	$k_{\rm ox} / {\rm M}^{-1}.{\rm s}^{-1}$
MeCN	340; 740	$1.01 \times 10^{10}$	3.23x10 <sup>7</sup>
МеОН	344; 720	$1.24 \times 10^{10}$	1.04x10 <sup>7</sup>
		N <sub>2</sub>	O <sub>2</sub>
PhS <sup>-</sup> ( $\epsilon_{450} = 1800 \text{ M}^{-1}.\text{s}^{-1}$ )		$k_{\text{Recomb}} / \text{M}^{-1}.\text{s}^{-1}$	$k'_{\rm ox} / {\rm M}^{-1}.{\rm s}^{-1}$
MeCN	296; 450	$1.01 \times 10^{10}$	$1.94 \text{x} 10^7$
МеОН	304; 448	$1.67 \times 10^{10}$	8.69x10 <sup>6</sup>

Table 2. Spectroscopic data and bimolecular rate constants of transients Ph<sub>2</sub>S<sup>.+</sup> and PhS<sup>. a</sup>

<sup>a</sup> Concentration of diphenyl sulfide:  $6.03 \times 10^{-4}$  M. The concentration of molecular oxygen was  $2.42 \times 10^{-3}$  M in MeCN and  $6.58 \times 10^{-3}$  M in MeOH.

*Direct photo oxidation of para-substituted thioanisoles.* The irradiation was extended to thioanisole and some of its *para-substituted derivatives*. As it was observed for diphenyl sulfide, thioanisole derivatives also show two typical absorption bands located around 260 and 300 nm. The first weak absorption band was assigned to the  ${}^{1}L_{b}$  state while strong absorption band was assigned to the  ${}^{1}L_{a}$ state by comparison with reported data.<sup>13</sup> The  ${}^{1}L_{b}$  band of thioanisoles overlaps with the incident light (310 nm) and the absorption process occurs efficiently promoting the photoreaction. The course of the reaction was monitored for thioanisole in MeCN under oxygen atmosphere (see fig. 4) and showed that acidity generation (formation of phenylsulfinic acid) was even more predominating over the oxidation (formation of phenyl methyl sulfoxide). A similar photochemical behavior was observed when the photoreaction of thioanisole was carried out in methanol and in dichloromethane under oxygen atmosphere. The results are collected in Table 3. The rate of formation of phenyl methyl sulfoxide in methanol is four times higher than in aprotic solvents (MeCN and dichloromethane), which showed quite similar values in the last two solvents. Noteworthy, the rate of formation of sulfoxide under direct irradiation of thioanisole in methanol shows the same order of magnitude of that obtained under Rose Bengal sensitized conditions indicating that proticity of the solvent enhances the formation of the sulfoxide.<sup>11d</sup>



Figure 4. Consumption of thioanisole (black circles) and formation of phenylsulfinic acid (red triangles) and phenyl methyl sulfoxide (blue triangles) vs irradiation time.

Solvent	Sensitizer or Additives	Conv. (%)	$[PhS(O)Me]_1 / \mu mol$	φ <sub>PhS(O)Me</sub> <sup>b</sup>
			min <sup>-1</sup>	
MeOH	RB (visible)	25.5	0.136	
MeCN		35.2	0.033	0.022
МеОН		30.5	0.189	0.124
DCM		48.5	0.045	0.019
MeCN	Acetone (8:2)	27.2	0.052	
MeCN	CICH <sub>2</sub> COOH (2.5x10 <sup>-3</sup> M)	25.7	0.174	
MeCN	CICH <sub>2</sub> COOH (5.0x10 <sup>-3</sup> M)	27.2	0.213	
MeCN	Cs <sub>2</sub> CO <sub>3</sub> (34 mg)	36.0	0	

Table 3. Direct photo oxidation of thioanisole.<sup>a</sup>

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<sup>a</sup> Sulfide concentration: 0.010 M. RB = Rose Bengal. <sup>b</sup>Actinometer: KI (0.6 M), KIO<sub>3</sub> (0.1 M) and Na<sub>2</sub>B<sub>2</sub>O<sub>7</sub>.10H<sub>2</sub>O (0.01 M) in water;  $\phi(I_3^-) = 0.38$ ;  $\lambda_{exc} = 310$  nm.<sup>14</sup>

As it is apparent in Table 3, direct irradiation of thioanisole in MeCN took place also in the presence of an external triplet energy sensitizer (acetone) and was accelerated by the addition of acids such as chloroacetic acid (compare the rate in the presence of acid ( $5x10^{-3}$  M), 0.213 µmol.min<sup>-1</sup> with that in neat MeCN, 0.033 µmol.min<sup>-1</sup>). On the other hand, no oxidation to sulfoxide took place in the presence of bases, but the cleavage to the phenyl sulfinate was maintained.

The direct irradiation of *para*-substituted thioanisoles was carried out under the same conditions and the results are collected in Table 4. As is apparent, the photo oxidation of these thioanisoles occurred in protic and aprotic solvents and a marked substituent effect was observed. Thus, electron-donating substituted thioanisoles made the photo oxidation faster. However, the C-S cleavage of thioanisoles to give the corresponding aryl sulfinic acids remaining competitive also in the presence of a base such as  $Cs_2CO_3$  where no photo oxidation took place (see for example in Table 4, *p*-methoxythioanisole in MeCN in the presence of  $Cs_2CO_3$ ).

R	Solvent	Conv. (%)	$[SO]_1 / \mu mol min^{-1}$	$\phi_{\rm SO}{}^{\rm c}$
MeO	MeCN	20.1	0.118	0.077
	MeCN <sup>b</sup>	22.3	0	
	DCM	25.2	0.119	0.078
	МеОН	25.9	0.055	0.036
Me	MeCN	26.7	0.123	0.080
	DCM	45.3	0.071	0.046
	МеОН	10.6	0.131	0.086

Table 4. Direct photo oxidation of *p*-substituted thioanisole derivatives.<sup>a</sup>

Н	MeCN	35.2	0.033	0.022
	MeCN <sup>b</sup>	36.0	0	
	DCM	48.5	0.045	0.024
	МеОН	30.5	0.189	0.124
CN	MeCN	21.1	0.041	0.017
	DCM	33.2	0.077	0.050
	МеОН	11.2	0.027	0.018
NO <sub>2</sub>	MeCN	8.0	0.010	0.007
	DCM	14.0	0.023	0.015
	MeOH	7.0	0.007	0.005

<sup>a</sup> Sulfides concentration: 0.010 M. SO = sulfoxides. <sup>b</sup> Carried out in the presence of Cs<sub>2</sub>CO<sub>3</sub> (34 mg). <sup>c</sup>Actinometer: KI (0.6 M), KIO<sub>3</sub> (0.1 M) and Na<sub>2</sub>B<sub>2</sub>O<sub>7</sub>.10H<sub>2</sub>O (0.01 M) in water;  $\phi(I_3^-) = 0.38$ ;  $\lambda_{exc} = 310 \text{ nm.}^{14}$ 

The co-photooxidation of thioanisole and *p*-methoxythioanisole in the presence of dodecyl methyl sulfide was likewise explored and gave results similar to those obtained for  $Ph_2S$  (see Scheme 2). Thus, a common intermediate is formed that oxidizes the oxygen acceptor dodecyl methyl sulfide.



Scheme 2. Co-irradiation of thioanisoles and dodecyl methyl sulfide.

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On the basis of the above data collected for thioanisole and *p*-substituted thioanisole, steady-state and time-resolved spectroscopies were further studied to shed some light on the reaction mechanism and, particularly, on the S-oxidation and C-S fragmentation pathways of these substrates.

Steady-state and time-resolved spectroscopy of thioanisoles. The oxidation pathway. The fluorescence emission spectra of thioanisoles were recorded in MeCN using a solution of 4chloroanisole as fluorescence actinometer. All the substrates showed a minimal fluorescence emission and the fluorescence quantum yields are collected in Table 5. With these molecules, intersystem crossing to the triplet excited state was in all case largely dominating. Time-resolved experiments were then carried out. In every case an emission spectrum identical to that obtained by using perinaphthenone, and attributed to the singlet oxygen phosphorescence, was obtained in MeCN. Comparison of the zero time intensity of the signal allowed measuring the production of singlet oxygen ( $\phi_A$ ) compiled in Table 5, which turned out to be around 0.15. Because the  $\phi_A$  values obtained for the thioanisole derivatives are less than unitary, a number of mechanisms have been considered for rationalizing this behavior that include chemical combination, energy transfer and fragmentation.

Table 5. Fluorescence quantum yield and singlet oxygen quantum yield ( $\phi_{\Delta}$ ) of thioanisole and *p*-substituted thioanisole derivatives measured in MeCN.

R	Atmosphere	$\phi_{\rm f}{}^a$	${\phi_\Delta}^b$
MeO	Ar	0.008	0.10
	O <sub>2</sub>	0.007	
Me	Ar	0.006	0.17
	O <sub>2</sub>	0.005	
Н	Ar	0.004	0.15

	O <sub>2</sub>	0.003	
CN	Ar	4x10 <sup>-4</sup>	0.16
	O <sub>2</sub>	3x10 <sup>-4</sup>	
NO <sub>2</sub>	Ar	Not detected	0.15

<sup>a</sup> Actinometer: acetonitrile solution of 4-chloroanisole under Ar atmosphere;  $\phi_f = 0.019^{19}$ ; Error:

 $\pm 0.002$ . <sup>b</sup> Values relative to acetonitrile solution of perinaphthenone;  $\phi_{\Delta} = 0.95^{20}$ ; Error:  $\pm 0.002$ .

Additionally, time-resolved experiments have been carried out using laser flash photolysis and the decay of the phosphorescence emission of singlet oxygen in the presence of the thioanisole derivatives was further analyzed in MeCN. Figure 5 shows typical decay traces of the emission of singlet oxygen in the presence of *p*-methoxythioanisole and *p*-cyanothioanisole, respectively. The decay of the singlet oxygen phosphorescence emission at 1230 nm in the presence of the thioanisoles was well fitted by a bi-exponential decay by using a laser pulse with an energy of *ca* 4 mJ and a  $\lambda_{exc} = 266$  nm, thus giving two observed lifetime values,  $\tau_d$  and  $\tau_{ox}$ , with the former much larger than the latter one.



Figure 5. Singlet oxygen phosphorescence emission ( $\lambda_{max}$ : 1230 nm) decay traces in the presence of: (a) *p*-methoxythioanisole and (b) *p*-cyanothioanisole.

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Two competitive pathways of deactivation of the singlet oxygen produced are attributed to the physical deactivation of the singlet oxygen ( $k_d$ ) and to the reaction between singlet oxygen and the nucleophilic sulfide ( $k_{ox}$ ) to give the corresponding sulfoxide, respectively. The spectroscopic data are collected in Table 6. The large values obtained were assigned to the physical deactivation of the singlet oxygen ( $\tau_d$ ) by comparison of the singlet oxygen decay value in the absence of sulfides, which is 86.9 µs in MeCN. Then, the small values collected in the table were attributed to the reaction between thioanisoles and singlet oxygen. In the same table the  $\tau_d/\tau_{ox}$  ratio which is equal to the ratio of  $k_{ox}$ .[ArSMe]/ $k_d$  was also included. The thus calculated values showed the expected trend of the substituent effect, electron-donating substituents enhance the oxidation rate constant while electron-withdrawing substituents lower it and rather favor the physical deactivation of singlet oxygen.

Table 6. Lifetimes ( $\tau_d$  and  $\tau_{ox}$ ) of singlet oxygen and  $\tau_{d/}\tau_{ox}$  ratio in the presence of thioanisole and *p*-substituted thioanisole derivatives measured in MeCN at room temperature.

R	$\tau_d{}^a$ / $\mu s$	$ au_{ox}{}^a$ / $\mu s$	$\tau_{d}/\tau_{ox}{}^{b}$
OMe	134.0	12.7	10.6
Me	115.0	18.2	6.3
Н	84.2	12.5	6.7
CN	79.2	16.1	4.9
$NO_2$	71.8	23.0	3.1

<sup>a</sup> Errors = ±0.1. <sup>b</sup> The ratio  $\tau_{d}/\tau_{ox}$  is equal to *the ratio*  $k_{ox}$ .[ArSMe]/ $k_{d}$ .

*The C-S fragmentation pathway of thioanisoles.* Laser flash photolysis of N<sub>2</sub>- and O<sub>2</sub>-saturated acetonitrile solutions of thioanisoles were carried out with a laser pulse of  $\lambda_{exc}$ : 266 nm and transient absorption spectra were obtained. The absorption spectra showed two characteristic bands

located around 295 - 310 nm and 450 - 530 nm as can be seen in fig. 6 for *p*-methoxy and *p*-methyl thioanisoles in MeCN under N<sub>2</sub> atmosphere.



Figure 6. Transient absorption spectra recorded after a laser pulse (9  $\mu$ s;  $\lambda_{exc}$ : 266 nm) of N<sub>2</sub>saturated acetonitrile solution of (a) *p*-methylthioanisole and (b) *p*-methoxythioanisole (6.03x10<sup>-4</sup> M).

Addition of radical cation scavengers such as triethylamine or NaN<sub>3</sub> caused no change of the transient absorption spectra and thus, the spectra can be assigned to aryl thiyl radicals (ArS<sup>-</sup>). Similar spectra have been obtained by laser flash photolysis and pulse radiolysis.<sup>21</sup> Therefore, C-S cleavage process is a competitive pathway for thioanisoles.

The transient decay traces of such radical were recorded under N<sub>2</sub> and O<sub>2</sub> atmospheres as shown in fig. 7 for *p*-methoxythioanisole and *p*-cyanothioanisole, respectively. Under N<sub>2</sub> the transient decay traces showed nice second-order decays from which, after linear regression fittings, bimolecular rate constants ( $k_{\text{recomb}}$ ) were obtained (rather independent of the substituent, 1 to 2x10<sup>10</sup> M<sup>-1</sup>.s<sup>-1</sup>) and are collected in Table 7. Such rates ( $k_{\text{Recomb}}$ ) were attributed to the recombination rate constants of the radicals formed after the C-S fragmentation from the triplet state of thioanisoles.

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Figure 7. Decay traces of aryl thiyl radical (ArS<sup>-</sup>) after a laser pulse ( $\lambda_{exc}$ : 266 nm) of acetonitrile solutions of thioanisoles (6.03 × 10<sup>-4</sup> M) recorded at: (a) 325 nm for *p*-methoxythioanisole and (b) 525 nm for *p*-cyanothioanisole under N<sub>2</sub> and O<sub>2</sub> atmospheres.

	N <sub>2</sub>	O <sub>2</sub>
Thiyl radicals	$k_{\text{recomb}} / \text{M}^{-1}.\text{s}^{-1}$	$k'_{\rm ox} / {\rm M}^{-1}.{\rm s}^{-1}$
p-MeOPhS <sup>-</sup>	9.82x10 <sup>9</sup>	$3.06 \times 10^7$
p-MePhS <sup>-</sup>	$2.06 \times 10^{10}$	$4.17 \text{x} 10^7$
PhS <sup>-</sup>	$1.39 \times 10^{10}$	$4.05 \times 10^7$
p-CNPhS <sup>-</sup>	9.31x10 <sup>9</sup>	3.29x10 <sup>7</sup>
<i>p</i> -NO <sub>2</sub> PhS <sup>-</sup>	$1.43 \times 10^{10}$	1.36x10 <sup>6</sup>

Table 7. Bimolecular rate constants of transient aryl thiyl radicals in MeCN.<sup>a</sup>

<sup>a</sup> Concentration of thioanisoles:  $6.03 \times 10^{-4}$  M. The concentration of molecular oxygen was  $2.42 \times 10^{-3}$  M in MeCN.

On the other hand, O<sub>2</sub>-saturated acetonitrile solutions of thioanisoles afforded pseudo-first order decay traces that, after fitting analysis, second-order rate constants ( $k'_{ox}$ ) of 10<sup>7</sup> M<sup>-1</sup>.s<sup>-1</sup> were calculated taking into account the concentration of O<sub>2</sub> dissolved in MeCN (2.42x10<sup>-3</sup> M). These

data are also collected in Table 7. The change in the kinetic profile of the decay traces from  $N_2$  to  $O_2$  atmospheres supports that aryl thiyl radicals react smoothly with molecular oxygen to give aryl sulfenyl peroxyl radicals in competition with recombination. Another feature observed when comparing the decay trace profiles obtained in  $N_2$ - and  $O_2$ -saturated solutions is that molecular oxygen diminishes the optical density at time-zero after the laser pulse from one fifth to one sixth fold indicating that molecular oxygen quenches efficiently the triplet excited state of the thioanisoles.

## Discussion

*Direct irradiation of diphenyl sulfide.* As hinted above diphenyl sulfide reacted efficiently upon direct irradiation (310 nm) in MeCN, MeOH and DCM under oxygen atmosphere. Steady-state and laser flash photolysis experiments reported above give credence to the mechanism shown in Scheme 3. Upon irradiation of Ph<sub>2</sub>S at 310 nm efficient population of the triplet state is achieved. Two main pathways compete with the physical deactivation ( $k_d$ ; Scheme 3) of the triplet state, viz. i) homolytic C-S bond fragmentation (*path (a)*) giving intermediate phenyl thiyl radical (PhS<sup>-</sup>) that finally evolves to phenyl sulfinic acid (main photoproduct under O<sub>2</sub>) and ii) ionization of diphenyl sulfide to diphenyl sulfide radical cation (Ph<sub>2</sub>S<sup>-+</sup>) (*path (b)*) evolving in the presence of molecular oxygen to Ph<sub>2</sub>SO. Laser flash photolysis experiments of N<sub>2</sub>- and O<sub>2</sub>-saturated acetonitrile solution of Ph<sub>2</sub>S with  $\lambda_{exc} = 266$  nm gave the transient absorption spectra of both intermediates, viz. PhS<sup>-</sup> and Ph<sub>2</sub>S<sup>++</sup>, which were formed simultaneously at 9 µs after the laser pulse (see fig. 2).



Scheme 3. Reaction mechanism proposed for direct irradiation of diphenyl sulfide.

Under N<sub>2</sub>, recombination of the radical gave back Ph<sub>2</sub>S (*path (e)*) with a second order rate constant  $(k_{\text{Recomb}})$  of  $1.01 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  in MeCN and  $1.67 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  in MeOH. Likewise, diphenyl sulfide radical cation formed by ionization of triplet Ph<sub>2</sub>S (*path (b)*) under N<sub>2</sub> decays by back-electron transfer process (*path (c)*) in both solvents, with a second order rate constant ( $k_{\text{BET}}$ ) of  $10^{10} \text{ M}^{-1} \text{ s}^{-1}$  (see Table 2).

On the other hand, laser experiments carried out under O<sub>2</sub> atmosphere showed that both transient species, PhS and Ph<sub>2</sub>S<sup>+</sup>, react smoothly with molecular oxygen with bimolecular rate constants ( $k_{ox}$  and  $k'_{ox}$ ) ranging from 10<sup>6</sup> to 10<sup>7</sup> M<sup>-1</sup>.s<sup>-1</sup> (see *path (f)* and *path (d)* in Scheme 3). In the case of phenyl thiyl radical (PhS<sup>-</sup>) reaction with molecular oxygen gives intermediate phenyl sulfenyl peroxyl radical (PhSOO<sup>-</sup>) that, in the presence of adventitious water in the solvent, evolves finally to the phenyl sulfinic acid which is the main photoproduct detected under steady-state experiments. Likewise, diphenyl sulfide radical cation (Ph<sub>2</sub>S<sup>+</sup>) reacts with molecular oxygen to provide the persulfoxide radical cation intermediate as shown in *path (d)* that finally evolves to diphenyl sulfoxide (Ph<sub>2</sub>S=O), the other photoproduct detected under steady-state experiments. Dialkyl and diaryl sulfides radical cation are prone to react with molecular oxygen as has been early demonstrated by laser flash photolysis forming the corresponding sulfoxides as photoproducts.<sup>4</sup> Other related Reactive Oxygen Species (ROS) such as singlet oxygen and superoxide ion, can be

involved in the overall processes, the superoxide ion may be formed by trapping the electron ejected from Ph<sub>2</sub>S. The fate of this anion has been the subject of some controversy in the case of sulfides, and both back electron transfer between  $O_2^{-}$  and  $R_2S^{+}$  as well as addition reaction of  $O_2^{-}$  with  $R_2S^{+}$ have been proposed.<sup>4,22</sup> The role of superoxide ion is more precisely indicated by the decay traces of Ph<sub>2</sub>S<sup>+</sup> measured at 740 nm under oxygen atmosphere which shows a pseudo-first order kinetics in all the solvents studied. If a direct reaction of  $O_2^{-}$  with Ph<sub>2</sub>S<sup>+</sup> was the primary oxidation pathway, second-order kinetics would be observed which is not the case in our experiments. Therefore,  $O_2^{-}$ has a role, but does not add to the diphenyl sulfide radical cation. A reasonable alternative is that  $O_2^{-}$  operates as electron carrier in the reduction of Ph<sub>2</sub>SO-O<sup>+</sup> (*path (g)*, Scheme 3) in the presence of a molecule of diphenyl sulfide to give diphenyl sulfoxide.

An active role of singlet oxygen has been previously excluded by Baciocchi for Nmethylquinolinium-mediated electron-transfer oxidation of sulfides,<sup>22</sup> because the reaction is faster than expected. In our case, a comparison between the bimolecular rate constant ( $k_{\rm r}$ ) between Ph<sub>2</sub>S and singlet oxygen ( $3.9 \times 10^4 \text{ M}^{-1}.\text{s}^{-1}$ )<sup>23</sup> and the values shown in Table 2, highlights that this process does not compete efficiently with the reaction of Ph<sub>2</sub>S<sup>-+</sup> and molecular oxygen. Furthermore, in our experimental conditions no Ph<sub>2</sub>SO<sub>2</sub> was formed, a photoproduct that was usually observed under singlet oxygen sensitization of sulfides<sup>1</sup>. Therefore, we excluded reaction of singlet oxygen with Ph<sub>2</sub>S from the reaction mechanism as a competitive oxidative pathway.

As far as we know, the homolytic fragmentation of the  $C_{sp2}$ -S bond from the triplet state of diphenyl sulfide is reported here for the first time. However, this kind of fragmentation has been recently reported by Jiang and co-workers<sup>6</sup> and has been also observed with aryl alkyl sulfoxides.<sup>7</sup> In the case of aryl alkyl sulfide radical cations the homolytic fragmentation of C-S bond occurs efficiently releasing aryl thiyl radicals and the corresponding carbocations<sup>8</sup> but the C-S bond of diphenyl sulfide radical cation does not fragment as it was early suggested.<sup>4</sup> In fact, our results confirms Ph<sub>2</sub>S<sup>.+</sup> behavior. Upon laser flash photolysis excitation of a N<sub>2</sub>-saturated solution of Ph<sub>2</sub>S in MeCN both PhS<sup>.</sup> and Ph<sub>2</sub>S<sup>.+</sup> transients are formed simultaneously but, addition of triethylamine as a radical

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 cation quencher to the solution, inhibits the formation of  $Ph_2S^{+}$  but not the formation of PhS<sup>-</sup>. Therefore, we can conclude that these results demonstrate that i)  $Ph_2S^{+}$  does not fragment to PhS<sup>-</sup> and Ph<sup>+</sup> and ii)  $C_{sp2}$ -S homolytic fragmentation occurs competitively from the triplet state of Ph<sub>2</sub>S and not from the  $Ph_2S^{+}$ .

Direct irradiation of thioanisoles. As in the case of diphenyl sulfide direct irradiation (310 nm) of thioanisoles provided aryl sulfinic acid as the main photoproduct along with the corresponding sulfoxides under oxygen atmosphere in MeOH, MeCN and DCM (see Table 4 and fig. 4). Based on steady-state and laser flash photolysis experiments described above we propose the reaction mechanism for the direct irradiation of the thioanisoles shown in Scheme 4. All the thioanisoles showed very low fluorescence quantum yields ( $\phi_f < 0.008$ ; see Table 5) and intersystem crossing to the triplet state in all cases predominated. Thus, direct excitation of these substrates at 310 nm populated efficiently the triplet state which is the photo reactive state involved in the photoreaction. In the case of thioanisoles, two distinctly and competitive pathways occurred: homolytic C-S fragmentation (path (a); Scheme 4) and singlet oxygen sensitization (path (b); Scheme 4). Irradiation of N<sub>2</sub>-saturated acetonitrile solutions of thioanisoles with a laser pulse (266 nm) afforded transients absorption spectra which were assigned to the aryl thiv radical demonstrating that C-S homolytic fragmentation occurred efficiently (see, for example, fig. 6 for the cases of p-methyl- and *p*-methoxythioanisoles). Noteworthy, no radical cation transients of thioanisoles were detected in laser experiments indicating that no ionization occurred after the laser pulse as it was observed for the case of diphenyl sulfide. This means that  $C_{sp3}$ -S cleavage in thioanisoles competes efficiently with the ionization process despite the fact that thioanisoles have oxidation potentials ranging between 1.13 to 1.70 V vs SCE<sup>10c</sup> and are susceptible to oxidation under laser flash photolysis conditions.



Scheme 4. Proposed reaction mechanism for direct irradiation of thioanisoles.

The absorption decay traces of the aryl thiyl radicals were also recorded in MeCN under N<sub>2</sub> atmosphere and showed clean second-order kinetics ( $k_{\text{Recomb}}$ ) of 10<sup>9</sup> to 10<sup>10</sup> M<sup>-1</sup>.s<sup>-1</sup> (see Table 7 and fig. 7) which were assigned to the recombination process of the radical species formed in-cage after the laser pulse (*path* (*c*); Scheme 4). When the same experiments were carried out under O<sub>2</sub>-saturated acetonitrile solutions a noticeable change in the decay traces of the transients were observed (see fig. 7). In fact, pseudo-first order kinetics was obtained for all the thioanisoles studied and bimolecular rate constants ( $k'_{ox}$ ) of 10<sup>7</sup> M<sup>-1</sup>.s<sup>-1</sup> were calculated using the concentration of dissolved molecular oxygen in MeCN of 2.42x10<sup>-3</sup> M (see Table 7). This behavior was easily attributed to the reaction of molecular oxygen with aryl thiyl radical (*path* (*d*); Scheme 4) giving phenyl sulfenyl peroxyl intermediate PhSOO<sup>-</sup> that evolve to the phenyl sulfinic acid in the presence of adventitious water in the solution. Noteworthy, pathways (*a*) and (*d*) and subsequently formation of phenyl sulfinic acid clearly describes the results obtained under steady-state and time-resolved experiments for the thioanisoles studied.

On the other hand, thioanisoles behaved as smooth singlet oxygen sensitizers when irradiated under oxygen atmosphere (*path (b)*; Scheme 4) with a production of singlet oxygen ( $\phi_{\Delta}$ ) of ca 0.10 - 0.15 (see Table 5). Two competitive pathways take place: i) physical deactivation of the singlet oxygen

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 $(k_d)$  to the ground state and, ii) reaction of <sup>1</sup>O<sub>2</sub> with nucleophilic thioanisoles to give the corresponding S-persulfoxide intermediates (path (e) in Scheme 4), as supported by the analysis of the decay curves of the phosphorescence emission of singlet oxygen with two distinct lifetime values,  $\tau_d$  and  $\tau_{ox}$  (Table 6). Thus,  $\tau_d$  described the physical decay of singlet oxygen while  $\tau_{ox}$  refers to the reaction between singlet oxygen and the nucleophilic thioanisoles ( $k_{ox}$  in *path (e)*; Scheme 4). S-persulfoxide intermediates were formed with thioanisoles. Reaction of the intermediate with a molecule of thioanisole afforded the corresponding thioanisole sulfoxides (path (f)). Formation of S-persulfoxide intermediate occurs during singlet oxygen photo sensitization of sulfides as have been reported in the literature.<sup>10, 14a, 24</sup> However, protonation of S-persulfoxide intermediate during the photoreaction takes place and the oxidant intermediate is more likely to be the Shydropersulfoxide intermediate (*path (h*) in Scheme 4). The catalytic effect of acids on the photosensitized oxidation of sulfides is well documented in the literature and the intermediate Shydropersulfoxide has been proposed.<sup>10c,11d</sup> This intermediate is also a good oxidant species that evolves to the corresponding sulfoxide releasing the acid catalyst, in our case, the phenyl sulfinic acid (*path (i*); Scheme 4). It is clearly that the acidity in all the solvents studied arises from the formation of phenylsulfinic acid during the irradiation. Thus, efficient protonation of the Spersulfoxide intermediate accelerates the oxidation process and promotes high regio selectivity in favor of the sulfoxide over the sulfone (compare the data in Table 3 of the rate of formation of sulfoxide in MeCN with the increasing amounts of ClCH<sub>2</sub>COOH). In fact, no sulfones were detected during direct irradiation of thioanisoles, a typical side product formed under singlet oxygen sensitization of sulfides.<sup>1, 23a</sup> Sulfone derivatives are formed from a S-hydroxypersulfonium ylide as it was early reported by Sawaki<sup>10b</sup> and later by us in the photosensitized oxidation of 4-substituted thioanisoles.<sup>10c</sup> However, this vlide that is formed during the irradiation is inhibited under the acidic condition of the photoreaction and sulfones are not formed which is in agreement with our observations. Therefore, we suggest that the formation of sulfoxides is more likely to proceed by the sequence of *path* (*h*) and *path* (*i*) (see Scheme 4) under acid catalysis than through *path* (*f*).

Further, the S-persulfoxide intermediate is a good oxidant species and is able to co-oxidize dodecyl methyl sulfide when is added to the reaction mixture. In fact, direct irradiation of a solution of the thioanisole in the presence of dodecyl methyl sulfide (RSMe in Scheme 4), which does not absorb at 310 nm, co-oxidation take place (*path (g)*) and both sulfoxides are formed in good yields (see Scheme 2).

## Conclusions

The photochemical reaction of diphenyl sulfide and *p*-substituted thioanisoles examined in the present paper take place, at least, through two competitive reaction mechanisms, S-C bond cleavage and S-oxidation occurring in polar and non-polar solvents. Photo homolytic fragmentation of  $C_{sp2}$ -S (for diphenyl sulfide) and  $C_{sp3}$ -S (for thioanisoles) give the corresponding aryl thiyl radicals (ArS') which are characterized by laser flash photolysis spectroscopy (see *path (a)* in Schemes 3 and 4). Under inert atmosphere the radicals recombine to the starting sulfides (*path (e)* in Scheme 3 and *path (c)* in Scheme 4) with rate constants of  $10^9 - 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . On the other hand, aryl thiyl radicals react with oxygen affording aryl sulfinic acids (*paths (d)* and (f) in Schemes 3 and 4, respectively) with rate constants of  $10^6 - 10^7 \text{ M}^{-1} \text{ s}^{-1}$  and these compounds are the main photoproducts formed during irradiation.

In the case of diphenyl sulfide ionization from the triplet state (*path (b)* in Scheme 3) gives  $Ph_2S^{+}$  that reacts smoothly with molecular oxygen (*path (d)*). This reaction occurs with bimolecular rate constants ( $k_{ox}$ ) of 10<sup>7</sup> M<sup>-1</sup>.s<sup>-1</sup> affording intermediate  $Ph_2SOO^{+}$  that finally evolves to  $Ph_2SO$  in the presence of  $Ph_2S$  and an electron donor, e.g. superoxide ion (*path (g)*). Besides, under inert atmosphere,  $Ph_2S^{+}$  turns back to  $Ph_2S$  by an electron transfer process (*path (c)*) with bimolecular rate constants of 10<sup>10</sup> M<sup>-1</sup>.s<sup>-1</sup>. Noteworthy, superoxide ion is formed during the irradiation of  $Ph_2S$  and operates as an electron carrier (see Scheme 3).

Oxidation of thioanisoles takes place by singlet oxygen sensitization (*path (b)* in Scheme 4) that arise from the triplet excited state of thioanisoles with  $\phi_{\Delta}$  of 0.10 - 0.15. Because thioanisoles are

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reactive with singlet oxygen, formation of the S-persulfoxide intermediates is the next reaction step (*path (e)*) that converts efficiently to the corresponding sulfoxides (*path (f)*). However, *paths (h)* and (*i*) (see Scheme 4) are the main pathways for the oxidation process under acid catalysis because phenyl sulfinic acid is the catalyst that is formed during the irradiation of thioanisoles. In fact, acid catalysis accelerates the sensitized oxidation reaction and favors the regioselectivity of the oxidation reaction giving exclusively the corresponding sulfoxides.

Finally, the finding that C-S fragmentation and S-sulfoxidation of diaryl and aryl alkyl sulfides are competitive pathways under direct irradiation (310 nm) sheds some light on the photochemistry of thioethers.

## **Experimental details**

**Materials** Thioanisoles, diphenyl sulfide, diphenyl sulfoxide, dodecyl methyl sulfide and benzene sulphynic acid, benzene sulphinic acid and perinaphthenone were commercial products. Sulfoxides and sulfones used as reference compounds were prepared via published procedures.<sup>25</sup> The dodecyl methyl sulfoxide was prepared via published procedures.<sup>26</sup>

**Photoreactions** The photoreactions were carried out by using 0.01 M solutions of the sulfides in different solvents (methanol, acetonitrile and dichloromethane). The solutions were contained in rubber stoppered, 1 cm diameter quartz tubes and a steam of dry oxygen saturated with the appropriate solvent was passed into the solution through a needle during 10 minutes. The quartz tubes were exposed to ten phosphor-coated 15 W lamps (Rayonet) emitting at 310 nm. The photooxidation reaction of diphenyl sulfides and thioanisole in the presence of Rose Bengal (in methanol) were carried out using 0.01 M solutions and were contained in rubber stoppered, 1 cm diameter Pyrex tubes. A steam of dry oxygen saturated with methanol was passed into the solution through a needle during 10 minutes. The solutions were irradiated with four visible 15 W lamps emitting at 528 nm. Co-oxidation experiments were carried out by using 0.01 M solutions of both sulfides according to the procedure above described.

The products were determined by GC on the basis of calibration curves in the presence of undecane as the internal standard. The identification of benzene sulphonic acid was based on the comparison of the retention time of an authentic commercial sample by ionic chromatography. Potentiometric acid titrations (NaOH 0.1M) have been followed by using an Orion mod. 250 potentiometer equipped with an Orion pH glass combined electrode mod 91-56. The titrations by using 0.1M NaOH have been performed on 10 mL photolyzed solutions in MeOH diluted with 100 mL water.

**Quenching Measurements** Rate constants for the quenching of singlet oxygen were obtained from the shorthening of the (O<sub>2</sub>)  ${}^{1}\Delta g$  emission lifetime at 1.27  $\mu m$  in the presence of known amounts of sulfides in aerated CDCl<sub>3</sub>. Singlet oxygen was generated by energy transfer to O<sub>2</sub> from the triplet state of perinaphthenone, populated by laser excitation (Nd:YAG laser, 532 nm). The near-IR luminescence of molecular oxygen was observed at 90° geometry through a 5 mm thick AR-coated silicon metal filter with wavelength pass >1.1  $\mu m$  and an interference filter at 1.27  $\mu m$  by means of a pre-amplified (low-impedance) Ge photodiode cooled at 77 K (time resolution 300 ns). Secondorder analysis of the emission decay was performed with the exclusion of the initial part of the signal, affected by scattered light, sensitizer fluorescence, and the formation profile of the emission signal itself. Comparison of the zero time intensity of the signal of the sulfides with that of the perinaphthone allowed measuring the production of singlet oxygen ( $\phi_{\Delta}$ ).

**Fluorescence quantum yield** UV and fluorescence spectra were recorded on a Jasco V-550 UV spectrophotometer and a PerkinElmer LS55 luminescence spectrometer, respectively. Fluorescence quantum yield ( $\phi_f$ ) were measured in acetonitrile and calculated by using 4-chloroanisole as fluorescence reference.<sup>19</sup>

**Chemical quantum yield** The light flux was determined by irradiation of an aqueous solution of KI (0.6 M), KIO<sub>3</sub> (0.1 M) and Na<sub>2</sub>B<sub>2</sub>O<sub>7</sub>.10H<sub>2</sub>O (0.01 M) and measuring the formation of I<sub>3</sub><sup>-</sup> by UV-visible spectroscopy after irradiation with ten phosphor-coated 15 W lamps (Rayonet) emitting at 310 nm ( $\phi$ (I<sub>3</sub><sup>-</sup>) = 0.38).<sup>14</sup>

## Acknowledgement

S.M.B is a research member of CONICET (Argentinean National Council of Research).

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