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# Substituent effects on the TiO<sub>2</sub> photosensitized oxidation reaction of benzyl thioethers and thiols in deaerated acetonitrile



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### ABSTRACT

The TiO<sub>2</sub> photosensitized oxidation of benzyl methyl sulfides (X-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SCH<sub>3</sub>) and benzyl thiols (X-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SH) has been investigated in Ar-saturated CH<sub>3</sub>CN. Steady-state irradiation produced benzaldehydes or dibenzylsulfides as oxidation products with sulfides and thiols, respectively. The results obtained through kinetic competitive experiments, aimed to evaluate the ring substituent effect on the reactivity, suggested the involvement of radical cation intermediates, formed by the favorable electron transfer from the substrate to the TiO<sub>2</sub> photogenerated hole, which reasonably deprotonate to give the final products. This process was poorly affected by the adsorption of the substrate at the TiO<sub>2</sub> surface, as demonstrated by similar results, both in terms of products and reactivity, collected for the homogeneous photooxidation of the same substrates sensitized by *N*-methoxyphenanthridinium hexafluorophosphate (MeOP<sup>+</sup>PF<sub>6</sub><sup>-</sup>). This behavior is likely due to the low hydrogen-bond acceptor ability of divalent sulfur systems. Density functional theory calculations pointed out that the most stable conformations of X-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SH<sup>+</sup> are characterized by having the C—S bond almost collinear with the  $\pi$  system of the aromatic ring and by a significant charge and spin delocalization involving both the phenyl ring and the sulfur atom.

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# 1. Introduction

Our research group has been involved for a long time in the mechanistic investigation of  $TiO_2$  (as powder, colloid or photoanode) sensitized photooxidation of organic compounds. In particular, with  $TiO_2$  as powder dispersed in deaerated CH<sub>3</sub>CN and in the presence of a sacrificial electron acceptor (Ag<sup>+</sup>), detailed studies have been performed, by product analysis and/or kinetic approach, on the photooxidation of several organic substrates, especially benzylic derivatives [1–8]. This investigation allowed us to collect information about the chemical properties of the radical cation intermediates in heterogeneous medium, produced through the electron transfer from the substrate to the photogenerated hole,  $(TiO_2)h^+$ .

In this context, we investigated some aspects concerning the reactivity of benzyl phenyl sulfide radical cations (having general formula  $Ar'SCH_2Ar^{+\bullet}$ ) [3]. These intermediates, generated by

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http://dx.doi.org/10.1016/j.jphotochem.2016.03.025 1010-6030/© 2016 Elsevier B.V. All rights reserved. photochemical oxidation of benzyl phenyl sulfides sensitized by  $TiO_2$  in the absence of oxygen, have been found to give: (i) benzaldehyde, through a deprotonation process, (ii) benzyl alcohol, with the involvement of C—S fragmentation, and (iii) sulfoxide through oxygen nucleophilic attack coming from the  $TiO_2$  surface. The competition among these three paths allowed us to gather information about the chemical properties of such radical cations, a deduction not able to be obtained in the presence of oxygen as electron trap, whereby sulfoxide was the principal product, owing to the efficient triplet oxygen trapping of sulfur centered radical cations [9–12].

Given the importance that the knowledge of the chemistry of sulfur radical cations may have both for the practical and theoretical aspects as well as for important biological implications [13], in this paper we have extended the study to radical cations produced by heterogeneous electron transfer oxidation of benzyl methyl sulfides (X-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SCH<sub>3</sub>: **1**, X = 4-OCH<sub>3</sub>; **2**, X = H; **3**, X = 4-CF<sub>3</sub>) and analogous benzyl thiols (X-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SH: **4**, X = 4-OCH<sub>3</sub>; **5**, X = H; **6**, X = 3-NO<sub>2</sub>) photosensitized by TiO<sub>2</sub> in deaerated CH<sub>3</sub>CN. In particular, the oxidation of the last class of compounds has important applications, especially in synthetic field, and has

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recently received remarkable attention [13], but so far only few papers are known about the oxidation of thiols occurring through an electron transfer mechanism [14,15].

The aim of this work is to assess the role of the substrate adsorption on TiO<sub>2</sub> surface on the reactivity of benzyl tioethers and thiols, in relation to the nature of the substituent on the aromatic ring, taking into account the high incidence of the adsorption found on the behavior of analogous benzyl methyl ethers and benzyl alcohols derivatives (X- $C_6H_4CH_2OCH_3$  and X- $C_6H_4CH_2OH$ , respectively, with various substituents) in the photooxidation by TiO<sub>2</sub> [4,5]. Accordingly, the results collected by product analysis and competitive experiments were compared with those obtained in homogeneous medium for the electron transfer oxidation of the same benzyl methyl sulfides (recently reported [16]) and benzyl thiols studied in this work photosensitized by MeOP<sup>+</sup>PF<sub>6</sub><sup>-</sup> in deaerated CH<sub>3</sub>CN.

DFT calculations at the B3LYP/6-311G(d,p) level of theory have been also carried out for  $4^{+\circ}$ ,  $5^{+\circ}$  and  $6^{+\circ}$ , in order to get information on the geometry of the radical cations and more importantly on their charge and spin distribution.

## 2. Experimental

GC analyses were carried out on an Agilent 6850 Series II gaschromatograph using a HP-1 capillary column. <sup>1</sup>H NMR spectra (CDCl<sub>3</sub> with TMS as internal standard) were run on a Bruker AC 200 (200 MHz) spectrometer. GC–MS analyses were performed on a Hewlett Packard 6890A gas-chromatograph (HP-Innovax capillary column) coupled with a MSD-HP 5973 mass selective detector (70 eV).  $E_p$  values were obtained with an Amel 552 potentiostat controlled by a programmable Amel 568 function generator.

## 2.1. Materials

Benzyl thiols **4–5** (purity > 97%), TiO<sub>2</sub> (anatase, Aldrich-99.9% and P-25, Degussa-99,5%, both dried at 110 °C) and CH<sub>3</sub>CN (HPLC grade) were commercial samples and were used as received. Benzyl methyl sulfides **1–3** were prepared by reaction of the corresponding benzyl thiols with CH<sub>3</sub>I in ethyl alcohol according to a literature procedure [17]. The sulfides were characterized as already described [16]. *N*-methoxyphenanthridinium hexafluor-ophosphate (MeOP<sup>+</sup>PF<sub>6</sub><sup>-</sup>) was prepared according to a literature procedure [18,19].

## 2.2. Photochemical oxidation

For the heterogeneous sensitized photooxidation, 10 ml of CH<sub>3</sub>CN containing the substrate (sulfide or thiol  $1.0 \times 10^{-2}$  M), TiO<sub>2</sub> and the scavenger (75 mg of anatase/Ag<sub>2</sub>SO<sub>4</sub>  $1.0 \times 10^{-2}$  M or 17 mg of P25/Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>  $1.0 \times 10^{-2}$  M with sulfide and thiol, respectively) were stirred for 30 min at room temperature in the dark. The mixture was then externally irradiated in an Applied Photophysics multilamp apparatus with six phosphor-coated fluorescent lamps (15 W each) emitting at 355 nm ( $\Delta l_{1/2}$  = 20 nm), at running water temperature (15°C), with argon bubbling through the solution. Before analysis of products, the semiconductor powder was left to decant for ca. 20 min. For the homogeneous MeOP<sup>+</sup>PF<sub>6</sub><sup>-</sup> sensitized photooxidation, the substrate  $(1.0\times 10^{-2}\,\text{M})$  and the sensitizer  $(5.0\times 10^{-3}\,\text{M})$  were dissolved in 10 ml of CH<sub>3</sub>CN and the resulting solution was irradiated with the same equipment used in heterogeneous conditions. Blank experiments, carried out by irradiating the solutions in the absence of the sensitizer (TiO<sub>2</sub> or MeOP<sup>+</sup>PF<sub>6</sub><sup>-</sup>), did not show product formation in any cases.

#### 2.3. Competitive experiments

For the heterogeneous TiO<sub>2</sub> sensitized photooxidation, the kinetic experiments were performed at 15 °C by irradiating (as above) the mixtures in 10 ml of CH<sub>3</sub>CN containing TiO<sub>2</sub> and the scavenger (in the same amounts used before) and the two substrates (sulfides or thiols) both  $5.0 \times 10^{-3}$  M. For the homogeneous MeOP<sup>+</sup>PF<sub>6</sub><sup>-</sup> sensitized photooxidation, the two substrates ( $5.0 \times 10^{-3}$  M each) and the sensitizer ( $5.0 \times 10^{-3}$  M) were dissolved in 10 ml of CH<sub>3</sub>CN. The resulting solution was irradiated as above. The  $k_{\rm rel}$  values, determined by a suitable kinetic equation [20] were the average of at least three determinations. The average error was estimated to be ca. 10%.

#### 2.4. Reaction product analysis

In both homogeneous and heterogeneous experiments the reaction mixture was analyzed after irradiation by GC, GC–MS, and <sup>1</sup>H NMR, adding an internal standard (bibenzyl) in the case of quantitative analysis. All products formed were identified by comparison with authentic specimens. Benzaldehydes **1a–3a** (Scheme 1) were commercially available. Dibenzyldisulfides **4a–6a** (Scheme 3) and 4,4'-dimethoxydibenzyl sulfide were synthetized and characterized as already reported in the literature [21,22].

# 2.5. Cyclic voltammetry

 $E_{\rm p}$  values were obtained by cyclic voltammetry experiments in CH<sub>3</sub>CN–LiClO<sub>4</sub> (0.1 M), conducted with a potentiostat controlled by a programmable function generator (cyclic voltammetry at 100 mV s<sup>-1</sup>, 1 mm diameter platinum disc anode and SCE as reference).

# 2.6. Computational methodology

Quantum mechanical calculations were carried out by using the Gaussian 09 package [23]. Charge and spin density distribution of the radical cations were obtained by using the B3LYP functional, after geometrical optimization performed with the same DFT model. All calculations were performed with a 6-311G(d,p) basis set [24].

## 3. Results and discussion

## 3.1. Photooxidation of benzyl methyl sulfides

The TiO<sub>2</sub> photosensitized oxidation of benzyl methyl sulfides **1–3** in argon deaerated CH<sub>3</sub>CN, in the presence of  $Ag_2SO_4$  as an electron acceptor, produced the corresponding benzaldehydes (**1a–3a**) as the only products coming from the benzyl moiety (Scheme 1). The percentage yields of the remaining reactants and products formed after 1 h of irradiation, referred to the initial amount of substrate, are reported in Table 1.

The material recovery was in the range 83-87%. The sulfurcontaining product, supposedly CH<sub>3</sub>SH (see below), was not detected in the reaction mixture because of its high volatility.



Scheme 1. Products formed in the photooxidation of sulfides 1-3 by TiO<sub>2</sub>.

#### Table 1

Chemical yields, relative rates  $(k_X/k_H)$  and substrates oxidation potentials  $(E_p)$  in the TiO<sub>2</sub> sensitized photooxidation reaction of benzyl methyl sulfides **1–3** in Ar-saturated CH<sub>3</sub>CN.

Sulfide	Unreacted sulfide <sup>a</sup> (%)	4X-C <sub>6</sub> H <sub>4</sub> CHO <sup>a</sup> (%)	$k_{\rm X}/k_{\rm H}$ <sup>b</sup>	$E_{\rm P}^{\rm c} \rm V$
<b>1</b> (X = OCH <sub>3</sub> )	53	30	3.6	1.55
2(X = H)	63	25	1.0	1.63
$3(X = CF_3)$	66	21	0.41	1.73

<sup>a</sup> With respect to the initial amount of substrate, after 1 h of irradiation; [sulfide] =  $1.0 \times 10^{-2}$  M, [anatase TiO<sub>2</sub>] = 7.5 g/l, [Ag<sub>2</sub>SO<sub>4</sub>] =  $1.0 \times 10^{-2}$  M.

<sup>b</sup> Determined by kinetic competitive experiments (GC analysis of unreacted substrate); [sulfide] =  $5.0 \times 10^{-3}$  M; the average error is ca. 10%.

<sup>c</sup> Oxidation peak potential vs SCE in air-equilibrated CH<sub>3</sub>CN [16].

The ratio of the photooxidation rate constant of 4-X-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SCH<sub>3</sub> ( $k_X$ ) on that of the unsubstituted sulfide ( $k_H$ ) was determined by the kinetic competitive method (data in Table 1). As shown in Fig. 1, log( $k_X/k_H$ ) values decrease linearly as the sulfide oxidation potential ( $E_p$ , Table 1) increases with good correlation coefficient (R = 0.986). In other words, the reaction rate depends on the nature of the ring substituent, being increased by an electron withdrawing substituent.

This behavior and the significantly high value of the slope  $(-5.2 V^{-1})$  are in line with a single electron transfer (SET) from the substrate to the positive hole,  $(TiO_2)_h^+$ , as rate determining step, to give the corresponding radical cation (Scheme 2). This reaction is thermodynamically feasible as the reduction potential of  $(TiO_2)_h^+$  (2.4 V vs SCE in CH<sub>3</sub>CN [25]) is much higher than that of **1–3** (1.55–1.73 V, Table 1). Actually,  $5.2 V^{-1}$  is a value higher than that observed for other functional groups (being in the range -2 to  $-3 V^{-1}$  [4,5]) for which the slope values had been related to a substrate like transition state as expected for a slightly exergonic electron transfer step [26]. Therefore, in the case of benzylic thioethers, an electron transfer with a more radical cation –like transition state should even more hold.

As reported in Scheme 2, it is reasonable that the radical cation undergoes a deprotonation at the benzylic carbon, as observed for other benzylic cation radicals (produced from alcohols, ethers, silanes and diols [1,2,4–6,8]). The formed benzylic radical is oxidized to carbocation by a second positive hole, as showed in the photoelectrochemical oxidation of benzylic alcohols and ethers at TiO<sub>2</sub> photoanodes [27,28], which yields benzaldehyde.

Our recent mechanistic study on the homogeneous electron transfer oxidation of the same benzyl thioethers photosensitized by N-methoxyphenanthridinium hexafluorophosphate (MeOP<sup>+</sup>PF<sub>6</sub><sup>-</sup>) in deaerated CH<sub>3</sub>CN showed that the benzaldehyde,



**Fig. 1.** Plot of  $\log(k_X/k_H)$  vs.  $E_p$  for TiO<sub>2</sub> photosensitized oxidation of benzyl methyl sulfides **1-3** in CH<sub>3</sub>CN.



Scheme 2. Mechanism of the photooxidation of sulfides 1-3 by TiO2.

formed by deprotonation of the intermediate radical cation, is the only observed product [16]; this was endorsed by competitive kinetic and flash photolysis experiments. Also in that case the plot  $\log(k_X/k_H)$  vs.  $E_p$  was linear, with slope of  $-3.8 \text{ V}^{-1}$ , a value close to that obtained in heterogeneous phase. Therefore, such similar results support the electron transfer as primary step in the photooxidation of benzyl thioethers with TiO<sub>2</sub>.

On the basis of the similar pattern observed in both heterogeneous and homogeneous environment the adsorption phenomena does not seem to play a significant role on the reactivity of benzyl methyl sulfides, contrary to what reported for the TiO<sub>2</sub> photosensitized oxidation of various benzyl alcohols and ethers [4,5]. Indeed, with both classes of compounds not all the substituted derivatives were linearly correlated in the plot log  $k_{\rm x}/k_{\rm H}$  vs.  $E_{\rm p}$ ; interestingly, all the substrates with strong electronwithdrawing substituents showed a similar reactivity, higher than that expected. This phenomenon was ascribed to the involvement of a single electron transfer from the lone pair orbital of the OR group (the preferential site of adsorption on TiO<sub>2</sub> surface), a process kinetically little affected by the substituent effect, rather than from the aromatic ring, whose oxidizability is depressed by strong electron-withdrawing substituents. Taking into account that the adsorption of the OR group occurs through the interaction between the oxygen lone pair and the hydroxyl group on TiO<sub>2</sub> via hydrogen bonding [5], it is obvious that such interaction is minimized with sulfides. This is in line with the known poor ability of dialkylthioethers (C-S - C) as acceptor of hydrogen bonds, given the considerable polarizability of S and the negligible electronegativity difference between C and S atoms [29].



**Scheme 3.** Products in the photooxidation of thiols **4–6** by TiO<sub>2</sub>.

# 3.2. Photooxidation of benzyl thiols

Upon irradiation of an Ar-saturated CH<sub>3</sub>CN mixture of TiO<sub>2</sub> in the presence of benzyl thiols (**4–6**) and Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as electron scavenger, the corresponding X-substituted dibenzyldisulfides **4a–6a** were produced (Scheme 3). Because of the low reactivity observed for thiols with anatase TiO<sub>2</sub>, these substrates were oxidized by using the more efficient P25 TiO<sub>2</sub>. The data obtained by quantitative analysis after 1 h of irradiation are shown in Table 2. The material recovery, considering the moles of unreacted substrate plus those of disulfide (after doubling), was in the range 91–96% (Table 2).

The redox reaction of persulfate as electron scavenger [30] is the following (Eq. (1)).

$$(TiO_2)e^- + 1/2S_2O_8^{2-} \to TiO_2 + SO_4^{2-}$$
(1)

The electron scavenger  $Ag_2SO_4$  was not used as in the case of  $TiO_2$ photooxidation of benzyl methyl sulfides, because in the presence of  $Ag^+$  a scarce recovery of material was detected, probably due to the adsorption of thiol on the particles of the silver salt. It has to be noted that the same photoproducts were obtained by use of both electron scavengers.

The kinetics of TiO<sub>2</sub> photooxidation of thiols was also investigated. In particular, competitive experiments gave the relative rate constants, expressed as ratio of  $k_{\rm X}$  (rate constant of X-C<sub>6</sub>H<sub>4</sub>CH<sub>2</sub>SH) to  $k_{\rm H}$  (rate constant of C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>SH). An interesting observation is that, as pointed out for thioethers, the reaction rate is affected by the nature of the ring substituent; in fact, it increases with the electron donating efficiency of the group. A good linear correlation between  $\log k_X/k_H$  and  $E_p$ , the peak oxidation potentials measured in this work (Table 2, see Section 2), was observed (Fig. 2, red line), with a slope of  $-3.3 \text{ V}^{-1}$ , close to values obtained for TiO<sub>2</sub>sensitized oxidation of other organic substrates [4,5] and similar to that obtained with thioethers 1-3 (-5.2, see above). Therefore, taking into account of the favorable thermodynamics of the SET process, also for the oxidation of benzyl thiols photocatalyzed by TiO<sub>2</sub> is plausible to assume the formation of a thiol radical cation as first step of the process (Scheme 4). The final products (disulfides 4a-6a) come from the dimerization of benzyl thiyl radicals  $(X-C_6H_4CH_2S^{\bullet})$  [14], formed by the deprotonation of the SH group of the thiol radical cation, being supposedly the hydrogen bound to the sulfur more acid than the benzylic one. Actually, it is reported that the hydrogen sulfide radical cation, the intermediate identified by ESR spectroscopy starting from hydrogen sulfide, is a strongly acid species, being  $pK_a(H_2S^{+\bullet})$  equal to -23 (calculated at 25 °C on the basis of a thermochemical cycle [15]) much smaller than that of deprotonation of benzylic derivatives (for example, pK<sub>a</sub> of 4-methoxytoluene radical cation is 0.45 [31]).

The adsorption phenomena were also evaluated for thiols by comparing the results in heterogeneous phase with those obtained, by product analysis and kinetic competitive experiments, for the homogeneous oxidation of **4–6** photosensitized by

### Table 2

Chemical yields, relative rates  $(k_X/k_H)$  and peak oxidation potentials  $(E_p)$  in the TiO<sub>2</sub> sensitized photooxidation reaction of benzyl thiols **4–6** in Ar-saturated CH<sub>3</sub>CN.

Thiol	Unreacted thiol <sup>a</sup> (%)	$(X-C_6H_4CH_2S)_2^a$ (%)	$k_{\rm X}/k_{\rm H}{}^{\rm b}$	$E_{\rm P}^{\rm c} \rm V$
<b>4</b> (X = $4$ -OCH <sub>3</sub> )	80	12	1.7	1.55
<b>5</b> (X = H)	83	8	1.0	1.61
6 (X=3-NO <sub>2</sub> )	90	6	0.69	1.67

<sup>a</sup> With respect to the initial amount of substrate after 1 h of irradiation; the disulfide yields were doubled; [thiol] =  $1.0 \times 10^{-2}$  M, [P25 TiO<sub>2</sub>] = 1.7 g/l, [Na<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] =  $1.0 \times 10^{-2}$  M.

<sup>b</sup> Determined by kinetic competitive experiments (GC analysis of unreacted substrate); [thiol]= $5.0 \times 10^{-3}$  M; the average error is ca. 10%.

<sup>c</sup> Oxidation peak potential vs SCE in air-equilibrated CH<sub>3</sub>CN.



**Fig. 2.** Plot of  $log(k_X/k_H)$  vs.  $E_p$  for TiO<sub>2</sub> ( $\bullet$ ) and MeOP<sup>+</sup> PF<sub>6</sub><sup>-</sup> ( $\blacksquare$ ) photosensitized oxidation of benzylic thiols **4–6** in CH<sub>3</sub>CN.

 $MeOP^+PF_6^-$  in deaerated  $CH_3CN$ . After 30 min of irradiation, disulfides were formed with all thiols in high yields (35–50%, see Table 3), considering that the oxidant moles are half of those of the thiol. Only in the case of **4** a significant amount of 4,4'- dimethoxydibenzyl sulfide (9%) was also detected in the reaction mixture. Other detected products were those derived from the N—O fragmentation of MeOP<sup>+</sup> (phenanthridine, P, and methanol) The material recovery was nearly quantitative (92–99%).

The relative reaction rates  $(k_X/k_H)$  are reported in Table 3. The good linear correlation in the plot log  $k_X/k_H$  vs.  $E_p$  shows a slope of  $-3.9 V^{-1}$  similar to that observed in heterogeneous phase (Fig. 2, black line). This evidence endorses that divalent sulfur of thiols is not a good hydrogen-bond acceptor [29], contrary to what is observed with the corresponding ring substituted benzyl alcohols which showed a clear implication of the adsorption in the TiO<sub>2</sub> photooxidation through the hydrogen-bond formation between the oxygen lone pair and the hydroxyl group on TiO<sub>2</sub> [4]. In the light of these results, the operative mechanism for the disulfide formation from thiols **4–6** in homogeneous phase can be assumed to be the one shown in Scheme 4. Unfortunately, as reported for thioethers [16], the intermediate radical cation was not detected by flash photolytic experiments because unstable, due to the high acidity, under the reported experimental conditions.

The formation of 4,4'-dimethoxydibenzyl sulfide observed only in the MeOP<sup>+</sup> photooxidation of **4** implicates a competitive reaction



Scheme 4. Mechanism of the photooxidation of sulfides 4–6 by TiO<sub>2</sub>.

#### Table 3

Chemical yields, relative rates  $(k_X/k_H)$  and substrates oxidation s  $(E_p)$  in the MeOP<sup>\*</sup>PF<sub>6</sub><sup>-</sup> photoinduced photooxidation reaction of benzyl thiols **4–6** in Ar-saturated CH<sub>3</sub>CN.

Thiol	Unreacted thiol <sup>a</sup> (%)	$(X-C_6H_4CH_2S)_2^a$ (%)	$(X-C_6H_4CH_2)_2S^a$ (%)	$k_{\rm X}/k_{\rm H}^{\rm b}$
<b>4</b> (X = $4$ -OCH <sub>3</sub> )	35	53	9	1.5
<b>5</b> (X=H)	51	48	_	1.0
<b>6</b> $(X = 3 - NO_3)$	44	48	-	0.51

<sup>a</sup> With respect to the initial amount of substrate after 30 min of irradiation; the disulfide and sulfide yields were doubled; [thiol] =  $1.0 \times 10^{-2}$  M, [MeOP<sup>+</sup>PF<sub>6</sub><sup>-</sup>] =  $5.0 \times 10^{-3}$  M. <sup>b</sup> Determined by kinetic competitive experiments (GC analysis of unreacted substrate); [thiol] =  $5.0 \times 10^{-3}$  M; the average error is ca. 10%.

path with the dimerization of the thiyl radical. Likely, a reaction mechanism could be that shown in Scheme 5, where  $4-CH_3O-C_6H_4CH_2S$  is firstly oxidized to cation by phenanthridine radical cation P<sup>+</sup>, which is the effective oxidant ( $E_{red} = 2.0 \text{ V}$  vs SCE in CH<sub>3</sub>CN, produced by dissociation of MeOP<sup>+</sup> singlet excited state [18]). Afterwards the thiyl cation loses sulfur giving a benzyl cation stabilized by the electron donating effect of 4-methoxy substituent, which attacks the nucleophilic sulfur of another thiol molecule giving the final product 4,4'-dimethoxydibenzylsulfide [15].

Likely, this product is not formed by **4** in the  $TiO_2$  sensitized oxidation because of the more favorable dimerization of benzyl thiyl radicals due to the relatively higher concentration of these intermediates close to the  $TiO_2$  surface [1].

An interesting observation regards the smaller difference of the oxidation potentials between **6** and **4** (corresponding to 0.12 V, see Table 2) with respect to that between the corresponding benzyl alcohols ( $3-NO_2-C_6H_4CH_2OH$  and  $4-MeO-C_6H_4CH_2O$ ) of 1.25 V, calculated by oxidation potentials of 2.80 V [32] and 1.55 V [5] vs SCE in CH<sub>3</sub>CN, respectively. This weaker substituent effect is in agreement with the presence of two possible electron extraction sites in the thiol structure: the aromatic ring, as for benzyl alcohols, and the sulfur atom. In order to deepen this aspect, DFT calculations were performed; the geometrical features, such as dihedral angles and bond lengths (defined in Fig. 3) of radical cations **4**<sup>+•</sup>-**6**<sup>+•</sup> are reported in Table 4.

From these data, it can be observed that the conformations of the radical cations have very similar geometries. In all optimized conformations, the CH<sub>2</sub>—S bond is almost perpendicular to the phenyl ring (the dihedral angle  $\Phi$  is ca. 95°). The atomic charges were obtained by natural population analysis (NPA) [23], while the unpaired electron spin densities were calculated using the Mulliken population analysis. From the NPA charges and spin density data obtained for the thiol radical cations (Table 5), it can be noted that the charge and spin density of **4**<sup>+•</sup>, **5**<sup>+•</sup> and **6**<sup>+•</sup> are mainly delocalized between the ring and sulfur, ie. the two electron extraction sites of the thiol. In other words, such distribution in the radical cation involves a through-space interaction between the aromatic ring and the sulfur p orbital, favored from the conformational geometry, as already observed for thioethers of analogous structure  $(X-C_6H_4CH_2SCH_3)$  [16]. In particular, the positive charge and spin density increase



**Fig. 3.** Definition of geometrical features of radical cations **4**<sup>+•</sup> and **5**<sup>+•</sup> (left) and **6**<sup>+•</sup> (right) reported in Table 4.

## Table 4

Most significant dihedral angle (deg) and bond lengths (Å) of radical cations  $4^{+\bullet}-6^{+\bullet}$  in CH<sub>3</sub>CN (CPCM model) optimised by B3LYP/6-311G(d,p).

	Φ	d1	d2	d3	d4	d5	d6	d7
4*•	95.1	1.349	1.857	1.488	1.422	1.370	1.424	1.313
5*•	95.3	1.351	1.847	1.492	1.419	1.377	1.409	1.083
6*•	94.8	1.352	1.841	1.498	1.414	1.377	1.399	1.482

Table 5

NPA Charges (qNPA) and Mulliken Spin Densities for the Most Stable Conformers of Radical Cations  $4^{\bullet\bullet} - 6^{\bullet\bullet}$ .

		Х	$C_6H_4$	CH <sub>2</sub>	S	Н
4**	q <sub>NPA</sub>	0.080	0.629	0.073	0.098	0.124
	spin	0.175	0.625	-0.021	0.226	-0.005
5**	q <sub>NPA</sub> spin		0.420 0.521	0.130 -0.014	0.300 0.507	0.150 -0.014
6**	q <sub>NPA</sub>	-0.353	0.644	0.149	0.395	0.163
	spin	0.000	0.400	0.014	0.632	-0.018

significantly on the sulfur atom (from 0.098 to 0.395 and from 0.226 to 0.632, respectively) at the expense of the substituted ring  $X-C_6H_4$  (from 0.709 to 0.291 and from 0.800 to 0.400, respectively) on going from electron donor to electron withdrawing ring



Scheme 5. Oxidation mechanism of 4-methoxybenzyl thiyl radical by P<sup>+•</sup>.

substituent. The charge and spin almost exclusively on the X-C<sub>6</sub>H<sub>4</sub> group for  $4^{+*}$  is in line with the identical oxidation potential value (1.55 V) of 4-methoxythiol and 4-methoxybenzyl alcohol. In this case the electron donating group makes the ring the sole extraction site, as well as expected on the basis of the higher oxidation potential of the hydrogen sulfide H<sub>2</sub>S [15], equal to 1.6 V vs SCE in CH<sub>3</sub>CN.

## 4. Conclusion

Benzyl methyl sulfides (1-3) and thiols (4-6) produced benzaldehyde and disulfides as main products, respectively, both in TiO<sub>2</sub>- and MeOP<sup>+</sup>- photosensitized oxidation. The formation of such products has been rationalized by an electron transfer mechanism yielding a sulfur radical cation as intermediate in the rate- determining step. The similar kinetic behavior observed in both heterogeneous and homogeneous phase suggested that the adsorption of sulfur on the semiconductor surface is so weak that, contrary to what was observed in the photooxidation of the corresponding benzyl methyl ethers and benzyl alcohols, plays no role in the reactivity of substrates **1–6**.

The charge and spin distribution in radical cations  $4^{+\circ}$ ,  $5^{+\circ}$  and  $6^{+\circ}$ , determined by DFT calculation, indicates a significant delocalization involving both the phenyl ring and the sulfur atom. This result allowed to rationalize the small effect of the ring substituent on the oxidation potential values of the investigated benzyl thiols, as already underlined for the corresponding benzyl methyl sulfides.

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