Oxidation of Aromatic Sulfides Photosensitized by TiO_2 in CH_3CN in the Presence of Ag_2SO_4. The Role of TiO_2 in the Chemistry of Sulfide Radical Cations

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A product study of the photooxidation of the aromatic sulfides **1**−**5** sensitized by TiO_2 in MeCN, in the presence of Ag_2SO_4, has been carried out. With benzyl phenyl sulfide (**1**), 4-methoxybenzyl phenyl sulfide (**2**), and phenethyl phenyl sulfide (**4**), the photooxidation led mainly to aldehydic products, benzaldehyde, 4-methoxybenzaldehyde, and phenylacetaldehyde, respectively. With benzyl 4-methoxyphenyl sulfide (**3**), the major product was the corresponding sulfoxide. Diphenyl sulfoxide was the only product observed in the oxidation of diphenyl sulfide (**5**). These results suggest α-C−H deprotonation as the major reaction path for the radical cations of **1**, **2**, and **4**, and an active role in this respect of the oxygenated basic sites present on the TiO_2 surface is envisaged. An interaction of these oxygenated centers with the sulfur atom of the adsorbed radical cation is also suggested to explain the remarkable finding that substantial amounts of sulfoxide are observed with **3** and **5**, in spite of the fact that the photooxidations were carried under nitrogen. Different than with the sulfides, the photooxidation of 4-methoxybenzyl phenyl sulfoxide leads exclusively to products of C−S bond cleavage, which is attributed to the much greater stability of sulfinyl than thiyl radicals.

Introduction

The heterogeneous photochemical oxidations of organic compounds sensitized by TiO_2, as a powder suspended in MeCN, involve the transfer of one electron from the substrate to the hole photogenerated into the semiconductor; a radical cation forms, and at the same time the electron in the conduction band is captured by a suitable acceptor, generally molecular oxygen.[1]

Recently, we found that oxygen can conveniently be replaced by Ag^+ as electron trap in the photooxidation of alkylaromatic compounds.[2,3] Under these conditions, the nature of the products could be unambiguously related to the various decomposition paths followed by the radical cations, which is not possible when working in the presence of oxygen.[1,4]

It has been considered of interest to extend this approach to aromatic sulfides, in order to get insight on the 3-fold reactivity of aromatic sulfide radical cations (C_α−H deprotonation, C−S bond cleavage, and attack at sulfur) under the heterogeneous reaction conditions of this photochemical process. Thus, we now report on the photooxidation of benzyl phenyl sulfide (**1**), 4-methoxybenzyl phenyl sulfide (**2**), benzyl 4-methoxyphenyl sulfide (**3**), phenethyl phenyl sulfide (**4**), and diphenyl sulfide (**5**), catalyzed by TiO_2 in the presence of Ag_2SO_4 in deaerated MeCN. The photooxidation of a sulfoxide, namely 4-methoxybenzyl phenyl sulfoxide (**6**), was also investigated. The photochemical oxidation of sulfides induced by TiO_2 has been previously studied, but always with oxygen as the electron trap.[5−8] Under these conditions, sulfoxides are often the exclusive products owing to the efficient triplet oxygen trapping of sulfur centered radical cation.[9] Moreover, $O_2^{\bullet-}$ is also formed, which can react with the radical cation.

Results and Discussion

In a typical experiment, a deaerated solution of the substrate in MeCN was subjected to external irradiation by a 500 W high-pressure mercury lamp, with a Pyrex filter, in the presence of TiO_2 and Ag_2SO_4, under gentle bubbling of N_2. During the irradiation, Ag was formed (presumably deposited on TiO_2) but without any consequence for the photochemical process.[3] The quantitative analysis of the reaction products and unreacted substrates was performed by ^{1}H-NMR and/or by GC. In all cases, in order to avoid overoxidation, the conversion into products was kept below 40%. The material balance is satisfactory, ranging from 85 to 95% with respect to the substrate.

The product distributions observed in the reaction of **1**−**6** are displayed in Table 1. Even though the efficiency of the process is generally quite modest, the results provide us with interesting information about the properties of sulfides radical cations when generated under

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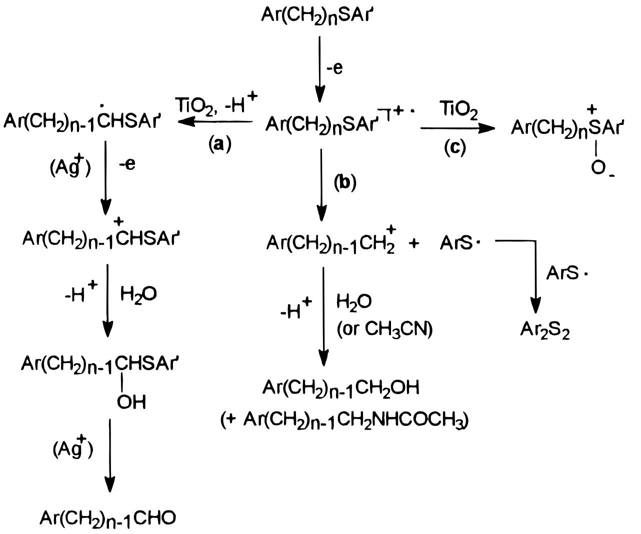
Table 1. Product Yields in TiO_2-Photosensitized Oxidation of Aromatic Sulfides and 4-$MeOPhCH_2SOPh$ in Deaerated MeCN in the Presence of Ag_2SO_4[a]

entry	substrate	unreacted substrate,[b] %	time, h	products (yields,[b] %)	
1	$PhCH_2SPh$ (**1**)	61	4	PhCHO (27)	$PhCH_2SOPh$ (3)
2		74	4	(19)	(2)[c]
3	4-$MeOPhCH_2SPh$ (**2**)	85	0.5	4-MeOPhCHO (8)	4-$MeOPhCH_2OH$ (2)[d]
4		84	1	(12)	(3)[d]
5		70	2	(17)	(4)[d]
6	4-$MeOPhSCH_2Ph$ (**3**)	67	4	PhCHO (5)	4-$MeOPhSOCH_2Ph$ (17)[e]
7	$PhCH_2CH_2SPh$ (**4**)	72	8	$PhCH_2CHO$ (13)	$PhCH_2CH_2SOPh$ (8)
8	PhSPh (**5**)	85	4	PhSOPh (10)[f]	
9	4-$MeOPhCH_2SOPh$ (**6**)	68	0.5	4-$MeOPhCH_2X$ (X = OH, 19; X = NHCOMe,[g] 8)[h]	

[a] No reaction takes place in the absence of TiO_2. [b] With respect to starting material. The average error is ±1. [c] In the presence of 2% H_2O. [d] PhSSPh is also present, but it was not quantitatively determined. [e] When MeCN was deoxygenated by the freeze-thaw technique, PhCHO (4%) and 4-$MeOPhSOCH_2Ph$ (16%) were obtained. [f] In MeCN deoxygenated as in footnote *e* PhSOPh (10%) was produced. [g] Acetamide comes from reaction of the carbocation (4-$MeOPhCH_2^+$) with the solvent followed by addition of adventitious water to the nitrilium ion.[3] [h] $PhSSO_2Ph$ is present in an equivalent amount.[16]

Scheme 1



these conditions. In the photolysis of benzyl phenyl sulfide (**1**), benzaldehyde is the major reaction product accompanied by very small amounts of benzyl phenyl sulfoxide. Reasonably, the formation of benzaldehyde can be ascribed to the C_α−H deprotonation of the sulfide radical cation[10] (path **a** in Scheme 1, $n = 1$, Ar = Ar′ = Ph). Accordingly, in this process a benzyl radical is formed that can be converted into an α-hydroxy sulfide by oxidation to carbocation and reaction of the latter with adventitious water present in the medium. A facile conversion of the α-hydroxy sulfide into benzaldehyde in the presence of Ag^+ is expected.[11] No formation of benzyl alcohol (or acetamide) is observed, which leads us to exclude the occurrence of path b (C−S bond cleavage).[12] In line with this conclusion, no diphenyl disulfide, which should also form in path **b**, was found among the reaction products.

Deprotonation is also the predominant path for the intermediate radical cation formed in the photooxidation of **2**. Accordingly, 4-methoxybenzaldehyde is the main reaction product, accompanied by small amounts of 4-methoxybenzyl alcohol and diphenyl disulfide. The latter compounds should derive, as suggested above, from C−S bond cleavage in the radical cation (path **b** in Scheme 1, $n = 1$, Ar = 4-MeOPh, Ar′ = Ph). The hypothesis that some oxidation of the alcohol to aldehyde takes place can be ruled out since the ratio between the two products is independent of the reaction time (entries 3−5 in Table 1). In the photooxidation of phenethyl phenyl sulfide (**4**), phenylacetaldehyde is the major product accompanied by phenethyl phenyl sulfoxide, thus indicating that, in this case too, path **a** in Scheme 1 ($n = 2$, Ar = Ar′ = Ph) is the main reaction route of the radical cation.

Sulfoxidation is the main reaction of **3**, and of course, the only product in that of **5**. The fact that deprotonation is only a minor reaction path of $\mathbf{3}^{\bullet+}$ has already been observed in anodic oxidation studies, even under basic conditions.[10] A plausible explanation is that in $\mathbf{3}^{\bullet+}$ there can be a substantial delocalization of the positive charge in the methoxy group. This lowers the charge density at the sulfur atom and consequently decreases the C_α−H bond acidity.

The above results indicate that, contrary to previous conclusions,[5−7] deprotonation is a much more important reaction route than C−S bond cleavage for sulfide radical cations, when these species are generated by sensitized photolysis in the presence of TiO_2. This finding is very surprising since, when generated electrochemically in the same solvent, $\mathbf{1}^{\bullet+}$ and $\mathbf{2}^{\bullet+}$ *did not undergo any deprotonation*,[10] but C−S bond cleavage was the major pathway for $\mathbf{1}^{\bullet+}$ and the exclusive pathway for $\mathbf{2}^{\bullet+}$. This drastic difference is very interesting, as it suggests an active role of TiO_2 not only in the generation of the radical cation but also in its chemistry. The most reasonable hypothesis is that the sulfide radical cations are generated at the surface of TiO_2 where deprotonation can be promoted by the oxygenated basic sites (containing hydroxyl groups).[13] In other words, TiO_2 appears to exert the role of a rather strong base. Such an active role of TiO_2 is confirmed by experiments carried out in the presence of $H_2{}^{18}O$ (0.5%)[14] showing that only *ca.* 60% of ^{18}O is

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incorporated into the benzaldehyde. Clearly, TiO_2 basic sites are not only involved in the deprotonation process but also in the subsequent steps leading to the α-hydroxy sulfide.

It seems reasonable to suggest that the oxygenated sites of TiO_2 also react with the sulfur atom of the radical cation, thus explaining the remarkable finding that sulfoxides are formed in substantial amounts in the reactions of **3**−**5**, either when the irradiations were carried out *under nitrogen* or when (photooxidation of **3** and **5**) the solutions were previously deoxygenated by the still more efficient *freeze−thaw* technique, which makes very unlikely a reaction of the sulfide radical cation with adventitious oxygen. Moreover, the possibility can also be excluded that traces of H_2O present in the solvent play a significant role in the sulfoxides formation since only negligible amounts of ^{18}O were found in the produced sulfoxide when the photooxidation of **5** was carried out in MeCN to which 0.5% of $H_2{}^{18}O$ was added.[15]

Finally, we have also studied the photooxidation of 4-methoxybenzyl phenyl sulfoxide (**6**), which led to the formation of 4-methoxybenzyl alcohol, *N*-(4-methoxybenzyl)acetamide, and diphenylthiosulfonate (Table 1, entry 9). Clearly, $\mathbf{6}^{\bullet+}$ exclusively undergoes C−S bond cleavage to form a benzyl carbocation and the sulfinyl radical, $PhSO^{\bullet}$; the latter, by dimerization followed by rearrangement, is converted in $PhSSO_2Ph$.[16] A similar result has recently been observed also in the homogeneous oxidation of **6** by Co(III).[17] The predominance of the C−S bond cleavage path with respect to deprotonation in the sulfoxide radical cation, an outcome opposite to that observed with sulfides radical cations, is certainly due to the much greater stability of $PhSO^{\bullet}$ with respect to $PhS^{\bullet}$.[16]

Experimental Section

^1H-NMR spectra were obtained on a 200 MHz spectrometer in $CDCl_3$. GC−MS analyses were performed on an instrument equipped with a 20 m × 0.2 mm silica capillary column coated with 5% diphenyl- and 95% dimethylpolysiloxane from 45 to 300 °C, connected with a mass selective detector at 70 eV. GC analyses were carried on an identical capillary column from 45 to 280 °C. The water amount in MeCN was determined with a Karl Fischer coulometer.

Materials. TiO_2 (anatase, dried at 110 °C), Ag_2SO_4, MeCN (HPLC grade), $H_2{}^{18}O$ (91 atom % ^{18}O), and diphenyl sulfide were commercially available. Benzyl phenyl sulfide (**1**), 4-methoxybenzyl phenyl sulfide (**2**), and benzyl 4-methoxyphenyl sulfide (**3**) were prepared and characterized as previously described.[10] Phenethyl phenyl sulfide (**4**) was prepared from the reaction of phenethyl bromide with thiophenol as described before[9] [^1H-NMR δ 7.35−7.10 (m, 10H, ArH), 3.15 (m, 2H, CH_2), 2.90 (m, 2H, CH_2); MS *m/z* (rel intensity) 214 M^+, 123 (100), 105, 91, 77, 65, 51, 45]. 4-Methoxybenzyl phenyl sulfoxide came from a previous study.[17]

Photochemical Oxidation. Reactions have been carried out, at room temperature, by external irradiation (500 W high-pressure mercury lamp, Pyrex filter), under magnetic stirring and gentle N_2 bubbling, of an acetonitrile solution (25 mL) of substrate (0.3 mmol), in the presence of TiO_2 (130 mg) and Ag_2SO_4 (0.3 mmol); the reactor was a cylindrical flask (i.d. = 1.6 cm, h = 16 cm) equipped with a water cooling jacket and intensive condenser. The photooxidation of **3** and **5** was also performed in a water-cooled Schlenk tube, freezing, degassing in the vacuum, and thawing the reaction mixture (for three times) before the irradiation. After double paper filtration of TiO_2, the reaction mixture was poured into water and extracted with ether. The reaction product analysis was performed by ^1H-NMR in the presence of an internal standard (1,4-dimethoxybenzene or 1,2-diphenylethane). The amount of unreacted substrate was determined, when possible, by ^1H-NMR of the crude product or by GC analysis of reaction mixture before workup, in the presence of an internal standard (1,2-diphenylethane). Material balance was always *ca.* 85−95% *vs* the amount of starting substrate.

Reaction Products. The crude reaction product was chromatographed on silica gel eluting with *n*-hexane, *n*-hexane:ethyl ether (from 9:1 to 1:1 v/v), ethyl ether, and chloroform. The structure of isolated products (benzaldehyde, 4-methoxybenzaldehyde, phenylacetaldehyde, benzyl phenyl sulfoxide, benzil 4-methoxyphenyl sulfoxide, 4-methoxybenzyl phenyl sulfoxide, diphenyl sulfoxide, phenethyl phenyl sulfoxide, benzyl alcohol, 4-methoxybenzyl alcohol, *N*-(4-methoxybenzyl)acetamide, diphenyl disulfide, and phenyl benzenethiosulfonate) was attributed by comparison with authentic specimens, commercial or available from previous works.[10,17,18]

Photochemical Oxidation in the Presence of $H_2{}^{18}O$. The photooxidations of **1** and **5** were also carried out in MeCN:$H_2{}^{18}O$ (99.5:0.5), and the reaction mixture was analyzed by GC−MS. From the comparison of the MS spectrum of benzaldehyde obtained from **1** [MS *m/z* (rel intensity) 105 (60), 106 (58), 107 (100), 108 (87)] and that of commercial benzaldehyde [105 (100), 106 (85), 107 (7)] a molar ratio $PhCH^{18}O/PhCH^{16}O$ = 1.5 was determined. The comparison for diphenyl sulfoxide produced from **6** [MS *m/z* (rel intensity) 202 (100), 203 (14), 204 (12), 205 (2)] and that of commercial diphenyl sulfoxide [MS *m/z* (rel intensity) 202 (100), 203 (15), 204 (6), 205 (1)] showed that only 5% of the original $H_2{}^{18}O$ was incorporated in the former compound.

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[15] After this addition, *ca.* 96% of the water present in the solvent is $H_2{}^{18}O$ since our MeCN already contained 0.02% H_2O (Karl Fischer coulometric titration).

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