

Research Article

Photooxidation of Some Organic Sulfides under UV Light Irradiation Using Titanium Dioxide Photocatalyst

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The photocatalytic oxidation of three organic sulfide compounds (thioethers); methyl phenyl sulfide (MPS), benzyl phenyl sulfide (BPS), and diphenyl sulfide (dPS) using titanium dioxide (TiO_2) photocatalyst suspension under UV light irradiation in aqueous-acetonitrilic (5/95), was studied. Three types of experiments were carried out: (a) the solution was eliminated from atmospheric oxygen by a flow of argon before irradiation, (b) the solution was irradiated with continuous bubbling of oxygen, and (c) the irradiation was carried out at neutral atmospheric oxygen conditions. Results showed that the process will proceed in the presence of pure oxygen much better than atmospheric oxygen or in the absence of oxygen. In fact, no detectable products were observed in the presence of atmospheric oxygen or argon flux. Besides the main products such as methyl phenyl sulfoxide, benzyl phenyl sulfoxide, diphenyl sulfoxide, diphenyl disulfide, benzaldehyde, phenyl propyl sulfide, and n-butyl phenyl sulfide, trace concentrations of dibenzyl, biphenyl, thiophenol, benzyl alcohol, benzene, benzyl phenyl sulfone, diphenyl sulfone, and methyl phenyl sulfone were detected. Thus in summary, this study provides an example of specific, controlled oxidative chemistry in organic substrates adsorbed on photoactivated TiO_2 surface.

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1. INTRODUCTION

Reduced sulfur compounds such as sulfides, disulfides, and mercaptans are the by-products of industrial processes and are known as waste, natural waters, and the earth's atmosphere pollutants [1, 2]. The spontaneous oxidation of these sulfides leads to formation of tropospheric SO_2 , which is eventually converted into H_2SO_4 , one of the main components in acidic rains through the reaction with atmosphere humidity [3]. Since the smells of these organic sulfides are often unpleasant for human life, their odor treatment is important.

The photooxidation of sulfur containing compounds in the presence of singlet oxygen has been investigated in the last decades and several of mechanisms have been identified, depending on the reaction conditions.

Titanium dioxide (TiO_2) has been vigorously used as the photocatalyst for environmental clean up [4–11] and it has been utilized for technological applications [12, 13], because of distinguished characteristics [14, 15]: (a) it is inexpensive, nontoxic, and very stable with high photocatalytic efficiency, (b) it promotes ambient temperature oxidation

of the major classes of indoor air pollutants, (c) complete degradation of a broad range of pollutants can be achieved under certain operating conditions, and (d) no chemical additives are required. It is well known that electron-hole pairs are generated when TiO_2 is irradiated by UV photons with energy higher than the TiO_2 band gap energy (3.2 eV) and these charge carriers can migrate to the TiO_2 surface to initiate redox reactions with adsorbed substrates. However, the mechanism of photooxidation of sulfides on the TiO_2 surface is still under discussion [16–23], it is proposed that the surface hydroxyl groups react with the holes to form the surface-bound OH radicals, which then oxidize the surface adsorbed substrates. The chemical identification of the hydroxylated oxidation intermediate, EPR detection of surface hydroxyl radicals in aqueous TiO_2 sols, the scavenging hydroxyl radicals, and the kinetic isotope effects support this mechanism [24–32]. Several researchers also have reported that the surface bound OH radicals are key species for oxidation reaction because the diffusion of surface-bound OH radicals from the TiO_2 surface into the bulk solution is minimal [32, 33]. The effectiveness of large particles in these reactions is understandable from the properties of

TiO₂ particles, which indicate that band bending is necessary to oxidize sulfide compounds. To develop the band bending in particles, their size and donor density are important. Usually, rutile powders have larger particle sizes than the anatase powders, because they are produced at higher temperature, and thus are advantageous for band bending [34].

Recently, Majima et al. have reported the one-electron oxidation of several aromatic compounds adsorbed on the surface of the TiO₂ powder suspension in CH₃CN by nanosecond time-resolved diffuse reflectance (TDR) spectroscopy and they have concluded that the OH groups play an important role in the adsorption on the surface of TiO₂ and the efficiency of the one-electron oxidation of the substrates [23, 35–37].

In a nonaqueous medium or in the atmosphere especially, it is expected that the TiO₂ particle surfaces are the main reaction fields for the direct oxidation of adsorbed substrate. However, only a few quantitative studies have been reported on the oxidation processes of organic compounds on the TiO₂ particle surfaces and the interaction between the substrate and TiO₂ surface. Fox and Coworkers notified that many oxidation reactions appear to occur due to direct electron transfer from several substrates to the photoexcited TiO₂ particles in a nonaqueous solution such as acetonitrile [20, 38, 39].

Vorontsov et al. have researched the photocatalytic gas-phase oxidation of diethyl sulfide over several types of TiO₂ photocatalysts. Several organic products were detected in the gas phase and on the catalytic surface corresponding to C-S bond cleavage and direct oxidation of sulfur or carbon atoms. Carbonate and sulfate species, detected on the TiO₂ surface after complete photooxidation of diethyl sulfide, are suggested as being responsible for TiO₂ deactivation. Organic radical cations are one of the most important intermediates in the photochemical electron-transfer reactions [40, 41].

Recently, we have reported the heterogeneous photocatalytic mineralization of some thiols on the Degussa P25 TiO₂ [42, 43], some cyclic saturated amines on the ZnO photocatalyst [44] and some organic sulfides using aqueous suspension of titanium dioxide suspension [34]. But to the best of our knowledge from literature, less attention has been paid to the quantitative studies on the photocatalytic oxidation processes of the organic sulfides and their mechanism in a nonaqueous medium. Therefore, in the present paper we have investigated the one-electron oxidation processes of methyl phenyl sulfide (MPS), benzyl phenyl sulfide (BPS) and diphenyl sulfide (dPS) adsorbed on the surface of TiO₂ powder in organic suspension. We observed a wide range of oxidation products using gas chromatography-mass spectroscopy (GC-MS) analytical procedures, during photocatalytic oxidation of the TiO₂ powder suspended in organic medium. We chose acetonitrile as the solvent for the photocatalytic reactions since this solvent is relatively stable and gives results for comparison. Furthermore, addition of oxygen was examined in order to increase the rate of oxidation reaction and variety of products. The results obtained here

can be used as the reference for evaluating reactions in hydrocarbons, which aim at the development of the photooxidative desulfurization process.

2. EXPERIMENTS

2.1. Materials

Titanium dioxide powder (TiO₂) used as photocatalyst was commercially available and supplied from Aldrich. These particles were composed mostly of rutile and had a BET surface area of 22 m²g⁻¹. Methyl phenyl sulfide (MPS), benzyl phenyl sulfide (BPS), diphenyl sulfide (dPS), and acetonitrile (analytical grade) were prepared from Merck and used without further purification. The structure of the initial organic sulfides is summarized in Scheme 1.

2.2. Photooxidation equipment

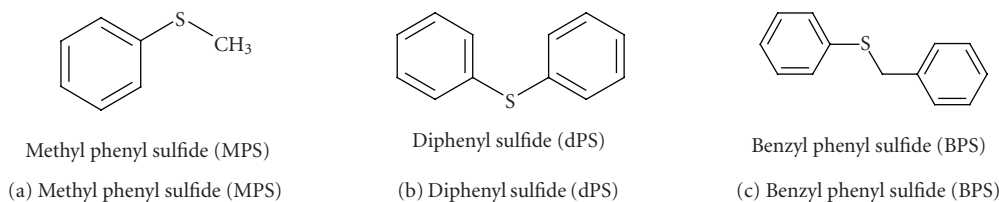
The oxidation processes were carried out in the Pyrex tubular photoreactor using a 400 W high pressure mercury lamp as a light source. The suspension inside the photoreactor was continuously agitated by a magnetic stirrer. A constant temperature water bath was connected to the reactor and thermostat (Hake model F-122) was set to 25–30°C. Oxygen or argon was introduced to the solution from gas cylinders at a flow rate of 5 mL min⁻¹ through a needle valve. The set up used in this study has been described previously [34].

2.3. Photoirradiation procedure and analyses

In each experiment 20 mL of MPS, MBS or dPS aqueous-acetonitrile (5/95) solution (5 × 10⁻² M) was placed in a photoreactor and 50 mg of TiO₂ photocatalyst was added to the solution.

Three types of experiments were carried out: (a) the solution was eliminated from atmospheric oxygen by a flow of argon before irradiation, (b) the solution was irradiated with continuous bubbling of oxygen, and (c) the irradiation was carried out at neutral atmospheric oxygen conditions.

After illumination time at constant temperature (25–30°C), photocatalysts were completely removed by a Hettich EBA 85 centrifuge. Then solutions were filtered through a Millipore filter (pore size 0.22 μm). The organic products were separated and determined by an analytical gas chromatographic instrument using a Fisons 8060 series gas chromatograph equipped with a flame ionization detector and OV-1 15 m × 0.32 mm column. The GC-MS analysis was carried out utilizing a Fisons 8060 GC and a Trio 1000 mass selective detector. Some of the products were separated by a thin-layer chromatography (TLC) using CCl₄ : CH₃OH, 15 : 1 as solvent and were recrystallized using methanol. The ¹H NMR spectra of these compounds were obtained mostly from acetone-d₆ solutions with a Bruker Advance RDX 500 MHz spectrometer. IR spectroscopy (Philips, PU 9716) was employed as an additional tool for characterization of some final reaction products.



SCHEME 1: Molecular structure of the initial organic sulfides and their symbols.

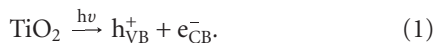
3. RESULTS AND DISCUSSION

3.1. Photooxidation products and their chemical yields

The heterogeneous photooxidation of MPS, BPS, and dPS has been examined. The list of all products detected after photocatalytic oxidation is given in Table 1. Besides of the main products such as methyl phenyl sulfoxide, benzyl phenyl sulfoxide, diphenyl sulfoxide, diphenyl disulfide, benzaldehyde, phenyl propyl sulfide, and n-butyl phenyl sulfide, trace concentrations of dibenzyl, biphenyl, thiophenol, benzyl alcohol, benzene, benzyl phenyl sulfone, diphenyl sulfone, and methyl phenyl sulfone were detected. Experiments with a controlled flux of oxygen and argon were monitored. The obtained results were compared with the results of photocatalytic oxidation in the neutral atmosphere. We observed that the process will proceed in the presence of pure oxygen much better than atmospheric oxygen or in the absence of oxygen. In fact, no detectable products were observed in the presence of atmospheric oxygen or argon flux. In addition, the effect of TiO_2 photocatalyst on the yield of products was investigated. As a result, to obtain an efficient photooxidation reaction, presence of TiO_2 was necessary and lack of photocatalyst leads to the sharp reduction of photooxidation products. In fact, no products were detected during photooxidation processes in the absence of TiO_2 photocatalyst.

3.2. Mechanism of products formation over TiO_2

One may speculate on possible mechanisms lying behind the formation of detected products. Generally, the following sequence of events is thought to be responsible for photocatalytic activity of TiO_2 particles. It is well known that TiO_2 particles generate free charge carriers, electrons and holes, under the bounding gap excitation (1),



After their generation within the short light pulse, both electron and hole are extremely rapidly trapped in surface states of the semiconductor particle within subpicoseconds or a few picoseconds after excitation [5] (2):



According to previous research activities, these photogenerated carriers then react with variously dissolved or absorbed

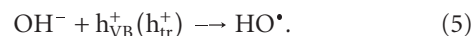
component. The captured positive hole oxidizes organic molecules by surface hydroxyl radicals. The fast recombination kinetics of the untrapped or trapped charge carriers have been studied in detail by several groups [45–49]. Although most trapped charge carriers recombine quickly, that is, within less than 30 ps (3):



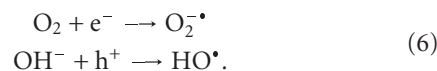
The sequence of the processes can include water dissociation on the TiO_2 surface due to formation of surface hydroxyl group:



Followed by oxidation of hydroxide group by the hole:

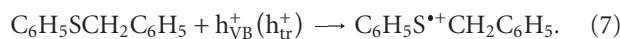


In the oxidation of organic compounds, the hydroxyl radical (HO^\bullet), which comes from the oxidation of adsorbed water or OH^- , is the primary oxidant. The captured electrons reduce added dioxygen to the superoxide radical anions, where the presences of oxygen can prevent the recombination of hole-electron pairs,

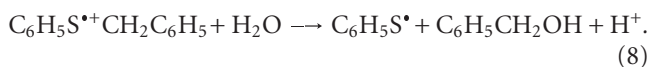


On the basis of various photooxidation products of the consideration thioethers, several pathways are possible to discuss the mechanism of these reactions.

The adsorbed thioethers on the TiO_2 surface can oxidize by trapped positive holes to produce sulfide radical cations. The formation of sulfur radical cation as intermediate in the photosensitized oxidation of sulfides in reality is accepted and proved. The redox potential of sulfides is about +1.8 V with respect to the normal hydrogen electrode that is lower than redox potential of holes in TiO_2 (+3 V) [40] so that the formation of sulfide radical cation by hole is clear:



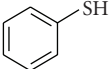
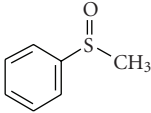
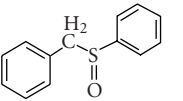
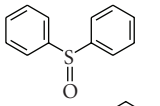
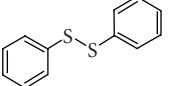
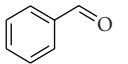
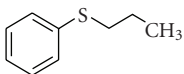
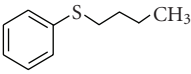
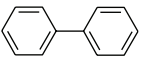
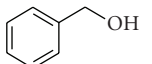

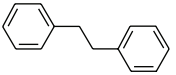
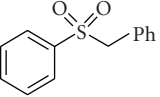
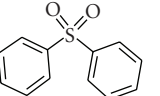
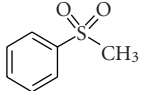
The hydrolysis of this radical cation must take place:



Further oxidation of the $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ intermediate on the TiO_2 surface led to the formation of benzaldehyde:



TABLE 1: List of the observed oxidation products and their percentages during photocatalytic oxidation of 20 mL aqueous-acetonitrilic (5/95) solution of MPS, BPS or dPS (5×10^{-2} M) over TiO_2 using 400 W high pressure mercury lamp at 25–30°C after 24 h irradiation time; and flux of O_2 (5 mL min^{-1}).

No	Chemical name	Structural formula	Identification based on	^a Yields base on initial sulfides		
				MPS	BPS	dPS
1	Thiophenol		^b MS		Trace	Trace
2	Methyl phenyl sulfoxide		MS, ¹ H NMR, ^c IR	54		
3	Bezyl phenyl sulfoxide		MS, ¹ H NMR, IR		50	
4	Diphenyl sulfoxide		MS, ¹ H NMR, IR			72
5	Diphenyl disulfide		MS	~ 4	~ 4	~ 5
6	Benzaldehyde		MS		5	
7	Phenyl propyl sulfide		MS	Trace	5	3
8	n-butyl phenyl sulfide		MS	Trace	5	8
9	Biphenyl		MS		Trace	
10	Benzyl alcohol		MS		Trace	
11	Benzene		MS	Trace	Trace	Trace
12	Dibenzyl		MS		Trace	
13	Benzyl phenyl sulfone		MS			Trace
14	Diphenyl sulfone		MS		Trace	
15	Methyl phenyl sulfone		MS	Trace		

^aOnly yield of each product is given under initial sulfides

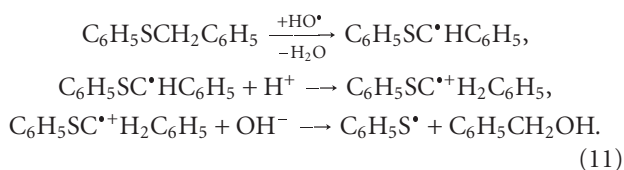
^bMass spectrum;

^cInfrared spectrum

Dimerization of two thiyl radicals caused the formation of disulfides (diphenyl disulfide), which was observed in the experiment in trace value,

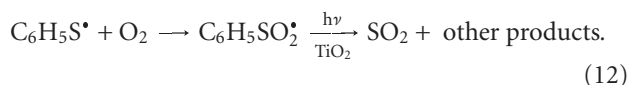


It is possible to describe the formation of thiyl radicals and benzaldehyde in another way. As was observed by pulse radiolysis, hydroxyl radical react with thioether and adduct ($\text{RR}'\text{S}^\bullet - \text{OH}$) can be formed, which at low concentration of thioether leaving out of H_2O lead to formation the $\text{RSR}'(-\text{H})^\bullet$ radical. The next possible steps can include protonation followed by attack by a surface hydroxide group due to formation of thioether α -carbon radical:



As it was mentioned above, further oxidation of $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ leads to the formation of benzaldehyde and dimerization of thiyl radicals which can produce diphenyl disulfide.

A possible alternative to recombination of thiyl radicals is their interaction [50] with oxygen, which should eventually lead to sulfur dioxide formation:

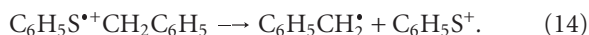


Further oxidation of SO_2 results in the formation of sulfate ions residing on the surface of TiO_2 .

Recombination of the thiyl radical and a radical generated from benzaldehyde can be considered as a possible route to phenyl thiobenzoate [51]:



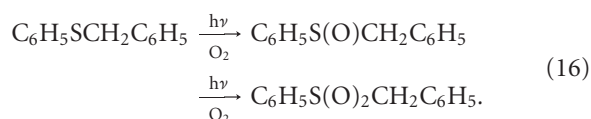
Also, an alternative process of decomposition of the thiyl radical cation leads to the formation of benzyl radicals [52]:



Dimerization of two benzyl radicals causes the formation of dibenzyl, which was observed in the products in trace value,



Another possible path can be the direct reaction of sulfides with oxygen in the presence of UV photons [53]:



Other processes may be operational during the photocatalytic oxidation of BPS, MPS, and dPS on the TiO_2 surface and could yield diphenyl sulfoxide, thiophenol, methyl phenyl sulfoxide, phenyl propyl sulfide, n-butyl phenyl sulfide, biphenyl, benzene, diphenyl sulfone, and methyl phenyl sulfone. Some of these products were detected in trace amounts by GC-MS method. As said previously, the concentrations of all products were determined by GC method.

4. CONCLUSION

This study revealed that TiO_2 photocatalytic one-electron oxidation reactions of MPS, BPS, and dPS adsorbed on the surface of TiO_2 powder suspension in acetonitrile were observed. High varieties of products were detected by GC-MS analysis, ^1H NMR, and IR spectroscopy. The percentages of these products were determined by GC chromatography. These results suggest that these photocatalytic reactions were initiated by the formation of a surface bound cation radical generated by an interfacial electron transfer. The photogenerated hole localized at the surface of the irradiated semiconductor is trapped by an adsorbed organosulfur compound, which generated an adsorbed cation radical. In other words, the chemical bonding between substrates and the TiO_2 surface play an important role in the oxidation mechanism as well as adsorption on the surface of TiO_2 particles.

Results obtained in the presence of pure oxygen, atmospheric oxygen, and in the absence of oxygen showed that the process will proceed in the presence of pure oxygen much better than atmospheric oxygen or in the absence of oxygen. In fact, no detectable products were observed in the presence of atmospheric oxygen or argon flux. These results extensively verified that the rate of photooxidation processes and yield of products in the absence of TiO_2 photocatalyst vigorously decreased. Thus in summary, this study provides an example of specific, controlled oxidative chemistry in organic substrates adsorbed on photoactivated TiO_2 surface.

ACKNOWLEDGMENT

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