TiO2-photocatalytic oxidation of selected heterocyclic sulfur compounds [1]

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Abstract

Polynuclear-heterocyclic sulfides (**I–IV**) were oxidized dominantly to the corresponding sulfoxides and sulfones via TiO_2-mediated photocatalytic oxidation in aerated acetonitrile. Also, methylene group in **IV** and **V** and active methene groups in **VI** have been readily oxidized to carbonyl one in a high yield under the same prevailing conditions. A plausible electron transfer mechanism, in which an electron-hole pair is generated on the surface of TiO_2 by illumination, is suggested for the semiconductor-mediated photocatalysis.   © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

The discoveries of Fujishima and Honda [1] in the early seventies motivated numerous research efforts in the thorough understanding of the photo-electrochemistry of semiconductors [2–7] especially semiconducting metal oxides such as TiO_2, $SrTiO_3$ Fe_2O_3 and Pt. TiO_2 were much used [6–8].

The strong oxidizing power of the photogenerated holes (large band gap material), the chemical inertness and resistance to both photocorrosion and decomposition reactions which plague other band gap materials (e.g., Si, GaAs, GaP, InP, CdS, etc.), low cost and wide availability in addition to the nontoxicity of TiO_2 have made it a superior photocatalyst [6]. Several articles and reviews have been written on the use of TiO_2 as a photocatalyst [4,6,9–11].

The possibility of using the semiconductor/liquid junction as a site for light-stimulated redox reactions has provided a simple conceptual framework for extensive progress toward efficient hydrogen generation by water splitting [5]. Furthermore, applications of the principles of photoelectrochemistry to sensitized organic transformations has found some interest but still deserve more investigations because of its potential as a new technique for functional group modification as well as its relationship to general problems involving heterogeneous photocatalysis pollution abatement and radical ion intermediates.

Our continual interest in photoelectrocatalytic oxidation at irradiated semiconductors [12–15] inspired us to report here a recent investigation on irradiated TiO_2 (anatase) mediated photocatalytic oxidation of sulfur-containing polynuclear heterocycles and related homologues for mechanistic and synthetic purposes.

2. Experimental details

2.1. Materials

Titanium dioxide (Aldrich, Anatase powder) was dried at 120°C in the oven for 12 h and stored under nitrogen before use. Oxygen was dried by passage through a calcium chloride drying tube. Acetonitrile (Aldrich, HPLC grade) was distilled before use. Dibenzothiophene (Aldrich), Thioxanthone (Merck), and Anthracene (Merck) were commercially available and were recrystallized before use. Thioxanthene [16,17], thianthrene [18] and 9,10-dihydroanthracene [19] were prepared as reported and crystallized before use.

2.2. Apparatus

A 450-W medium pressure Hg lamp (ACE Glass, Immersion type) with a pyrex well was used as the light source. The system was covered with aluminum foil which served as light reflector and the whole apparatus was set up in a metallic

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cabinet. ^{1}H NMR were carried out using 90 MHz Varian 390 in CDCl$_3$ using TMS as an internal standard. UV spectra were performed using Shimadzu UV 2101 Pc UV–Vis scanning spectrophotometer. IR spectra were done on Shimadzu-470 spectrophotometer using KBr-Wafer technique. HPLC analyses were performed using either Merck Hitachi L-6000 UV–Vis detector or Cecil series 1000 with two pumps CE 1100 with variable wavelength monitor CE 100 and gradient programmer CE 1300 and the solvent used was methanol–water mixture (7:3). GC/MS analyses were carried out on a gas chromatograph Varian Finnigan MAT/SSQ 7000 using DB-17 (50% phenylmethylenepolysiloxane) capillary column (30 m×0.25 mm). Elemental analyses were determined using Perkin-Elmer elemental analyzer 240°C. Melting points were measured on a Mel-Temp-II melting point apparatus.

A 70×1.0 cm column chromatogram packed with silica gel was used for separation of the mixtures. TLC analyses were carried out using (40×80 mm) precoated plastic sheets covered with a thin film of silica gel with fluorescent indicator.

2.3. Measurements of oxidation potentials of I–VI

Anodic peak potentials were measured by cyclic voltammetry using glassy carbon electrode (GCE) as a working electrode in 0.1 M KNO$_3$ as a supporting electrolyte [20]. Results are found in Table 1.

2.4. General procedure

A 0.01 M solution (400 ml) of the substrate (I–VI) was prepared in dry acetonitrile and transferred to the pyrex reaction vessel. 100 mg of TiO$_2$ (anatase) was added to the solution and the mixture was sonicated in an ultrasonic bath for 15 min and irradiated for the measured period. The suspension composition was maintained by stirring with magnetic stirrer and by a slow stream of oxygen.

The irradiation process was monitored by TLC. After a measured irradiation period, titanium dioxide photocatalyst was filtered using a medium porosity frit. The filtrate was concentrated by evaporation of the volatile solvent using rotatory evaporator and the resultant product mixture was analyzed using TLC, CC, HPLC and/or GC/MS techniques.

Chemical yields of all products were determined by HPLC and or GC/MS analyses.

The major products were identified by isolation, comparison of spectral properties with authentic samples and/or GC/MS analyses. Minor products were identified by GC/MS analysis via comparison of mass spectral fragmentation pattern with library standards or authentic samples. Results are presented in Table 2.

3. Results

The present work embraces band gap irradiation of titanium dioxide (anatase) suspension in anhydrous acetonitrile and compounds I–VI while purging with oxygen.

Table 1
UV spectra and oxidation potential of I–VI

| Compound | | UV spectra | | Oxide potential (V) |
No.	Name	λ_{max} (nm)	Absorbance	
I	Dibenzothiophene	233	0.760	+ 0.70
II	Thioxanthone	255	0.723	+ 0.97
III	Thianthrene	207.4	0.482	+ 0.95
		242.2	0.423	
		256.8	0.878	
IV	Thioxanthene	206.5	0.900	+ 1.00
		246.5	0.325	
V	9,10-Dihydroanthracene	212.2	0.836	+ 1.00
		251.4	0.806	
VI	Anthracene	217.00	0.340	+ 0.99
		243.00	0.857	
		356.00	0.226	
		375.00	0.213	

The results shown in Table 2 indicate that photocatalytic oxidation of I, II, III, and IV gave, except with IV, mainly the corresponding sulfoxide and sulfone in a route similar to that observed with aryl sulfides [12,21].

I, X=–; II, X=CO; III, X=S
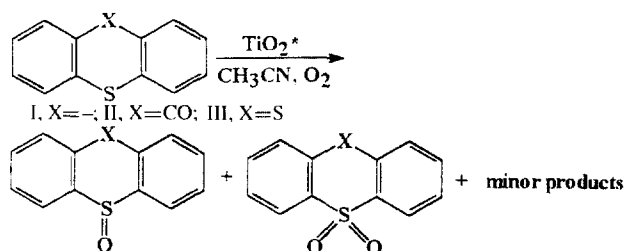
Thioxanthene (IV) produced upon photocatalylic oxidation under the same conditions a mixture of thioxanthone-9-sulfoxide (II-SO) and thioxanthone-9-sulfone (II-SO$_2$) as main products due to oxidation of the readily oxidizable methylene group along with the sulfide centre. The corresponding sulfoxide (IV-SO) and sulfone (IV-SO$_2$) were formed only in trace amounts.
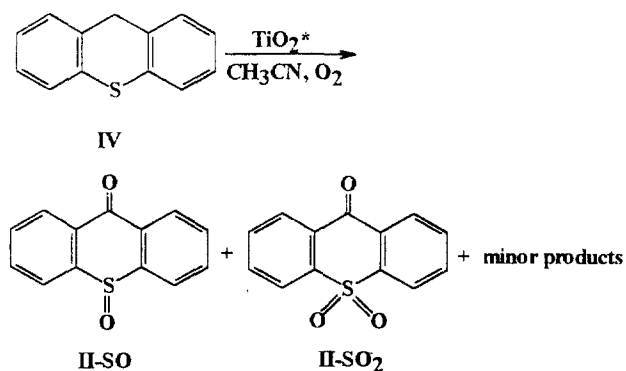

IV

II-SO   II-SO$_2$

Table 2
Photocatalytic oxidation products of I–VI:

Substrate		Time (h)	Conversion (%)	Products		
No.	Name			Sulfoxides (%)	Sulfone (%)	Other minor products (M$^+$, m/e)
I	Dibenzothiophene	10	75	I-SO (75.0)	I-SO$_2$ (21.0)	Biphenyl (m/e 154) Unknown (m/e 202)
II	Thioxanthone	8	100	II-SO (50.0)	II-SO$_2$ (47.0)	Benzoic acid (m/e 122) Dibenzothiophene (m/e 184) Dibenzothiophene-S,S-dioxide (m/e 216) Xanthone (m/e 196) Phenoxathiin-10-oxide (m/e 216) Phenoxathiin-10,10-dioxide (m/e 232) Hydroxythioxanthone-10,10-dioxide (m/e 260)
III	Thianthrene	6	90	III-S–SO (5.2) III-SO–SO (41.0)	III-S–SO$_2$ (13.9) III-SO–SO$_2$ (24.3) III-SO$_2$–SO$_2$(3.6)	Dibenzothiophene-S,S-dioxide (m/e 216) Phenoxathiin-10-oxide (m/e 216)
IV	Thioxanthene	10	100	IV-SO (trace) II-SO (54.0)	IV-SO$_2$ (trace) II-SO$_2$ (43.0)	Fluorenone (m/e 180) Dibenzothiophene (m/e 184) Dibenzothiophene-S,S-dioxide (m/e 216) Thioxanthone (m/e 212) Hydroxythioxanthone-10,10-dioxide (m/e 260)
				Major products		
V	9,10-Dihydroanthracene	1	100	9,10-Anthraquinone (94)		Phthalic acid (m/e 166) 9-Hydroxy-9-hydroanthracene-10-one (m/e 210) 9,10-Dihydroxy-9,10-dihydroanthracene (m/e 212)
VI	Anthracene	4	100	9,10-Anthraquinone (81)		Phthalic acid (m/e 166)

Similarly, illumination of titanium dioxide suspension of 9,10-dihydroanthracene (**V**) gave anthraquinone as a major product. Furthermore, the same product, anthraquinone, was formed in more than 80% upon oxidation of anthracene under the same photocatalytic oxidative conditions.
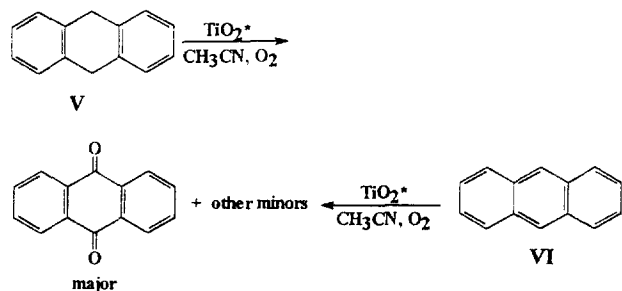
Expectedly, a mixture of five corresponding sulfoxides and sulfones (**III-S–SO; III-SO–SO; III-S–SO$_2$; III-SO–SO$_2$** and **III-SO$_2$–SO$_2$**) were formed upon treatment of **III** at the aforementioned prevailing photoelectrocatalytic oxidation conditions.
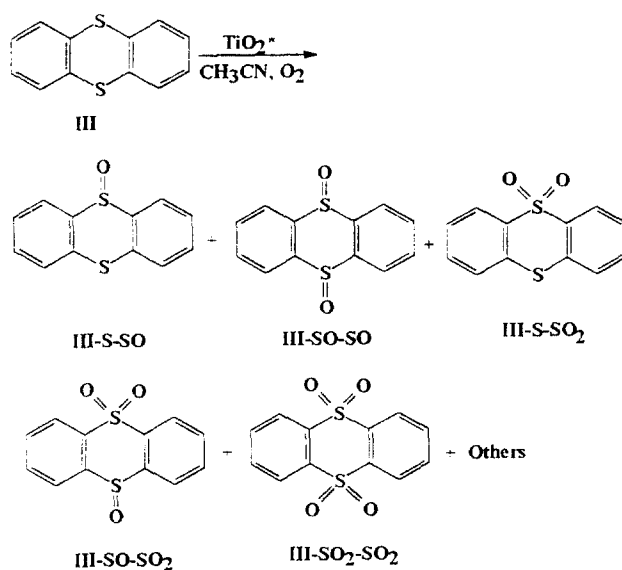
In addition to the previously reported major products, other minor compounds were identified as a result of ring oxidation, desulfurization (C–S bond cleavage), decarbonylation, oxy-

genation, hydroxylation or dimerization photocatalytic processes.

4. Discussion

Photocatalytic oxidation of the investigated compounds (I–VI) has been occurred only in the presence of light, TiO₂, and oxygen altogether as proved by preliminary experiments.

The maximum absorption of the target compounds (Table 1) ranges from 206.5 nm (IV) to 256.8 nm (III), a range that will be cut off by pyrex glass. The maximum emission of the 450-W medium pressure mercury lamps used in this study appears to be in the range of 296.7 nm to 578.0 nm (4.18 eV to 2.15 eV). Accordingly, the obtained products obviously originated through initial band gap excitation of TiO₂ rather than through the substrate.

Light absorption of energy equal to or greater than the band gap energy of TiO₂ (i.e., 3.23 eV) will result in electron ejection from the valence band to the conduction band generating a reactive electron ($E = -0.88$ V) and a positive hole ($E2.35$ V) [6,22].

In this Scheme, the primary photoelectroexcitation process effects an electron-hole pair separation at the surface of TiO₂ particle. Since the oxidation peaks of the substrates (Table 1) have a less positive potential than the valence band of TiO₂ (~2.4 V), the adsorbed substrate can capture the photogenerated hole, a thermodynamically possible process, forming a radical cation $>S^+$ [12,21]. The formation of sulfide radical cations have been postulated by Eriksson et al. [23] as a primary step in the 9,10-dicyanoanthracene, cyanoaromatic, sensitized electron transfer photo-oxidation of sulfides.

On the other side, the reported reduction potential of oxygen to the superoxide radical anion $\{O_2^{-}\}$ is -0.39 V [22,24]. Therefore, electron transfer to oxygen and the formation of the superoxide O_2^{-} is also thermodynamically possible. Thus, coadsorbed oxygen acts as an electron trap, inhibiting electron-hole recombination.

Consequently, the interaction of the photogenerated sulfur radical cations with the superoxide radical anion or with oxygen initiate a series of reactions (Scheme 1), all of which have secure precedent in known oxygenation electron transfer chemistry [25].

Formation of sulfones could be accomplished directly and/or via a secondary conversion of sulfoxides to sulfones [12,13].

It is worth mentioning that upon surveying the products in Table 2, the high chemical yield of ketones and quinones obtained in these conversions (IV, V, VI) demonstrates clearly the usefulness of TiO₂-mediated photooxidation as a synthetically variable route for manipulating oxygen functionality in multifunctional molecules. It is worth to mention that the high yields of I-SO (75%) and 9,10-anthraquinone (94%, 81%) presented in Table 2 are comparable to those reported by standard oxidation procedures (78% [26], 94%

[27]) respectively. In the case of IV and V, it is observed that photocatalytic oxidation of the methylene group competes with that of the sulfide sulfur [12], i.e., the benzylic cation radical competes with sulfide cation radical in the interfacial electron transfer step.

The C–S cleavage route is very less dominant because the thioether cation radicals of the investigated sulfides (I–IV) are particularly stabilized as ArₐS⁺ [21,23].

Photocatalytic oxidation of methylene or methene groups to carbonyl one is a result of the formation of

$$>CH_2^{+} \quad or \quad >CH^{+}$$
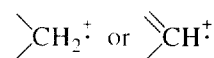
respectively, via electron-hole transfer, which in turn reacts with the anion radical O_2^{-} to form finally the corresponding ketone or quinone. The same mechanism was suggested by Liang and Liu [28] to account for photocatalytic oxidation of diphenylmethane, by Ibusuki and Takeuchi [29] for photocatalytic oxidation of toluene and by Fox et al. [30] in the case of naphthalenes. The oxidation of V, for example, to anthraquinone could be directly and/or through the formation of the hydroxy intermediates (V–OH) and (V–2OH). However, identification of (V–OH) and (V–2OH) in the photolysate of V by HPLC as well as by GC/MS analysis where two products of M⁺ at m/e 210 and M⁺ at m/e 212 were observed, substantiate the intermediacy of alcohols in the photocatalytic oxidation processes (Scheme 2). Oxidation of alcohols to the corresponding ketone accounts for their presence in the reaction mixture although in very small quantities (Scheme 2). On other hand, the presence of minor amounts of hydroxyl derivatives in the photolysates of I, IV and V could be also ascribed to the participation of unavoidable traces of water in acetonitrile in the reaction processes as a source for hydroxy radicals [15], Scheme 2. Interestingly, the supposition of endoperoxide (VI–O₂) formation as reported by Fox et al. [30], can give rise to anthraquinone or phthalic acid (Scheme 3).
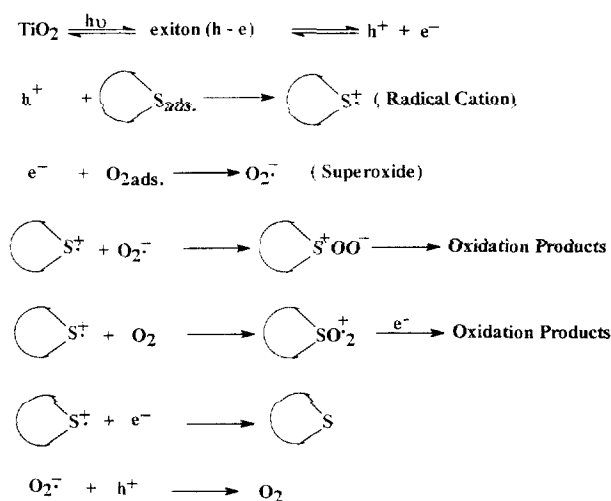
Scheme 1.
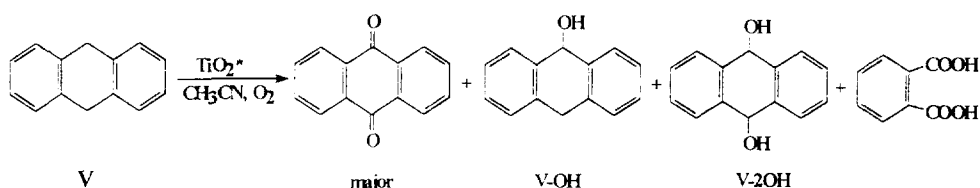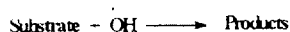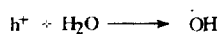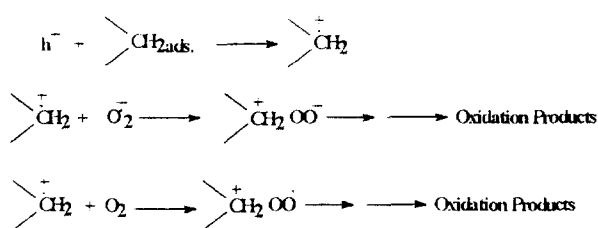
Scheme 2.
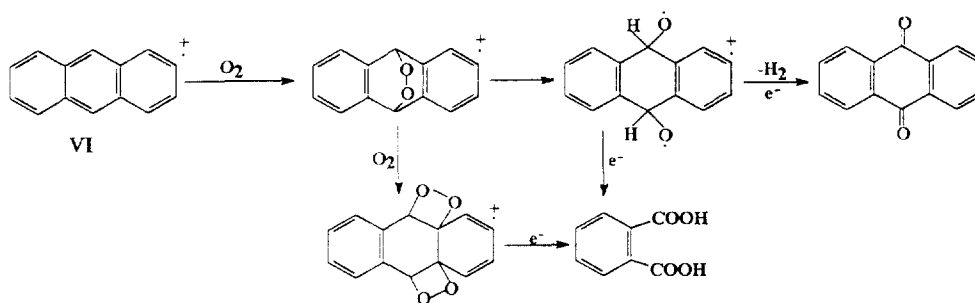
Scheme 3.

Activity of the 9 and 10 positions in anthracene is responsible for the formation of bridged anthracene-9,10-endoperoxide [31].

4.1. Mechanisms of photocatalytic oxygenation

The mechanisms of photocatalytic oxygenation are given in Schemes 1–3.

5. Conclusions

The obtained results revealed that photocatalytic oxidation of polynuclear heterocyclic sulfides to the corresponding sulfoxides and sulfones is attainable in a good yield. Furthermore, the same applied photocatalytic oxidative technique can be used for synthesis of cyclic ketones and quinones via oxidation of benzylic methylene or active methene groups in the polynuclear homo- or heterocycles. Besides the synthetic value of this reaction, the strong physiological response induced by contact of sulfur compounds with skin or lungs decreases markedly if the sulfur is oxidized [14,32].

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