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Oxidation of aryl methyl sulfides and sulfoxides on irradiated TiO_2

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Abstract

TiO_2 photocatalyzed oxidation of aryl methyl sulfides results in the formation of sulfoxides as the major product with small amounts of sulfones and C–S bond cleaved products. Increase in the irradiation time leads to disproportionation reaction (irradiation time determines the composition of the product). However, TiO_2 acts as an effective photocatalyst for the oxidation of aryl methyl sulfoxides to give exclusively sulfones. Photoelectrochemical studies provide support for electron transfer to occur from sulfide to the hole.

Keywords: TiO_2 photocatalysis; Oxidation of sulfides; Sulfoxides

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1. Introduction

The recognition that the surface of semiconductors in the form of colloids, powders, porous granules, thin films or bulk solids become effective redox catalysts with light has captured the attention of a wide range of scientists interested in solar energy conversion in recent years [1]. Photoinduced redox exchange can occur effectively at the surface of an irradiated semiconductor powder and this heterogeneous photocatalysis is a promising method to new chemical transformations which are inaccessible with conventional reagents or to an improved selectivity in multifunctional molecules or in mixtures of reagents. Among the various available semiconductor photocatalysts, TiO_2 is extensively employed in organic redox transformations [2–8] due to its ready availability, non-toxic nature, photochemical inertness and effective catalytic activity.

Our recent findings of photo-oxidation of triphenyl phosphine, arsine, stibine and bismuthine and deoxygenation of their oxides [9], selective oxidation of arylthioacetic acids and reduction of arylsulfonylacetic acids [10], aryl methyl and dialkyl sulfones [11] on TiO_2 surface demonstrate the usefulness and potential application of the semiconductor photocatalyst in organic synthesis.

As organic sulfides play important role in many materials such as organic polymers and biological macromolecules and are capable of yielding sulfur containing radical ion, photochemical oxidation of these substrates will be of immense interest. The photochemical oxidation of organic sulfur compounds such as sulfenamides [12,13], hydroxyalkyl aryl sulfides [14], dithiane [15], dialkyl sulfides [16] in homogeneous media either in the presence or absence of a photosensitizer and pentamethylene sulfide [17] photooxidation reaction by singlet oxygen have resulted in the formation of a mixture of products viz., sulfoxides, sulfones and C–S bond cleaved products. TiO_2 mediated photocatalytic oxidation of dialkyl sulfides [18] and diaryl sulfides [19] led to yield sulfoxides and sulfones in addition to products derived from C–S bond cleavage. Though we have recently reported that in the oxidation of arylthioacetic acids (a multifunctional organic molecule) on TiO_2 surface only the sulfur is oxidised to produce more of the arylsulfinylacetic acids without decarboxylation [10], in the case of 4-thiophenyl-1-butanol, Fox and Abdel-Wahab [20] observed that it is converted to a mixture of aldehydes and ketones without affecting the sulfur atom. However, the same authors report that butyl phenyl sulfide (the non-alcoholic analog of 4-thiophenyl-1-butanol) was converted to the corresponding sulfoxide ($35 \pm 5\%$) in a lower yield process, C–S cleavage product ($60 \pm 8\%$) representing the major competing route. Our interest in the rates of oxidation of organic sulfur compounds by several oxidants [21–32] in general and organic redox reactions of these substrates on irradiated TiO_2 in particular [10,11] prompted us to study the TiO_2 photocatalyzed oxidation of aryl methyl sulfides and sulfoxides. Though TiO_2 sensitized photo-oxidation of dialkyl sulfides [18] and diaryl sulfides [19] have been reported, the oxidation of aryl methyl sulfides and sulfoxides has not been so far investigated. Fur-

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ther, as the methyl group is affected in the oxidation of toluene [2–4], it will be of interest to know whether in aryl methyl sulfides and sulfoxides the sulfur atom is oxidised or the methyl group undergoes any reaction.

2. Experimental details

Aryl methyl sulfides, sulfoxides and sulfones were prepared as reported elsewhere [21–27,29–32]. TiO_2 (Aldrich, 99.9%) was used as received. The solvents used were HPLC or AR grade. A 1 mM solution of aryl methyl sulfide or sulfoxide in 15 ml of acetonitrile or methanol containing suspended TiO_2 (0.075 g) was saturated with oxygen and irradiated with a 400 W medium pressure mercury vapour lamp ($\lambda > 350$ nm) in an annular reactor (SAIC, India) with water filter. After centrifugation, the catalyst was separated and the solvent was removed under reduced pressure. The products were characterised by gas chromatograph (NETEL, India) fitted with flame ionization detector and SE-30 (10%) column.

Photoelectrochemical measurements were carried out using TiO_2 coated glassy carbon as working electrode, Pt as counter electrode and Ag as reference electrode in an acetonitrile solution (20 ml) containing 1 mM aryl methyl sulfide or sulfoxide and 0.1 M $LiClO_4$ as supporting electrolyte in a glass cell. The solution was irradiated using 8 W medium pressure mercury vapour lamp having maximal emission at $\lambda > 350$ nm.

3. Results and discussion

3.1. Photocatalyzed oxidation of aryl methyl sulfides

Band gap excitation of TiO_2 promotes an electron from the valence band to the conduction band thus creating a surface-bound electron–hole pair. The electron in the conduction band is readily available for transference (-0.1 V vs. SCE) while the hole in the valence band is open for oxidation (3.1 vs. SCE) [33]. In the presence of oxygen, the electron in the conduction band is trapped by it forming superoxide while leaving the hole for a single-electron oxidation of an oxidizable substrate, an electron donor. The potential level of the donor needs to be above (more negative than) the valence band position of the vacant hole. The oxidation potentials of all the aryl methyl sulfides as well as sulfoxides satisfy this condition (Tables 1 and 2) and therefore they may effectively function as electron donors to the hole.

Photocatalyzed oxidation of aryl methyl sulfides results in the formation of aryl methyl sulfoxides as the major product along with aryl methyl sulfones and products formed due to C–S bond cleavage (Table 1). Analysis of the products reveals the absence of products due to the oxidation of methyl group by the photocatalyst. In order to improve the two step

Table 1
Titanium dioxide photoinduced oxidation[a] of aryl methyl sulfides (p-R-$C_6H_4SCH_3$)

S No.	Substrate R	Irradiation time (h)	Solvent	Product mixture (%)[b]				
				S	SO	SO_2	SH	D[c]
1	H (1.53 V)	**1**	MeCN	35	53	5	2	5
	H	2	MeCN	5	71	6	4	14
	H	4	MeCN	29	51	13	2	7
	H	8	MeCN	43	18	30	1	8
	H	1	MeOH	33	30	13	3	21
	H	2	MeOH	11	67	8	3	11
	H	4	MeOH	5	70	5	4	16
	H[d]	8	MeCN	53	24	3	3	17
	H[d]	8	MeOH	51	22	2	5	20
2	OCH_3 (1.26 V)	1	MeCN	15	81	1	1	2
	OCH_3	2	MeCN	23	64	8	3	2
3	CH_3 (1.41 V)	1	MeCN	20	76	1	1	2
	CH_3	2	MeCN	18	63	9	2	8
4	C_2H_5 (1.40 V)	1	MeCN	20	76	3	0	1
	C_2H_5	2	MeCN	26	60	5	2	7
5	F (1.54 V)	1	MeCN	33	61	0	4	2
	F	2	MeCN	20	69	6	3	2
6	Cl (1.55 V)	1	MeCN	36	62	0	0	2
	Cl	2	MeCN	14	70	7	1	8
	Cl	2	MeOH	36	46	9	0	9

[a] Substrate concentration: 1 mM; Solvent: 15 ml; TiO_2: 0.075 g; Annular Reactor/350 nm/400 W.
[b] GC analysis results. Error limit: ±5%.
[c] Other products include disulfides and biphenyl.
[d] Without catalyst.
Values in parentheses are the oxidation potentials (vs. SCE) of sulfides taken from Ref. [34].

Table 2
Photo-oxidation of aryl methyl sulfoxides[a] (p-R-$C_6H_4SOCH_3$) on TiO_2

S No.	Substrate R	Product Mixture (%)[b]		
		SO	SO_2	X
7	H[c] (2.50 V)	69	13	18
	H	1	99	0
8	OCH_3 (2.35 V)	2	98	0
9	CH_3 (2.40 V)	3	97	0
10	C_2H_5 (2.30 V)	3	97	0
11	F (2.60 V)	1	99	0
12	Cl (2.45 V)	2	98	0

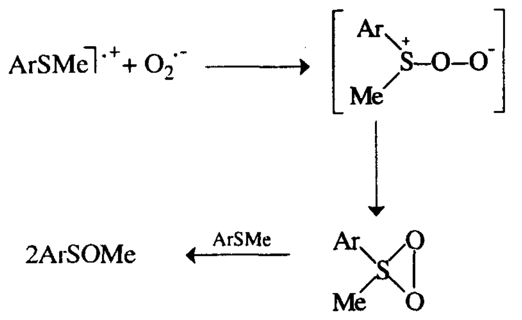
[a] Substrate concentration: 1 mM; Solvent: Acetonitrile; 15 ml; TiO_2: 0.075 g; Irradiation time: 2 h; Annular Reactor/350 nm/400 W.
[b] GC analysis results. Error limit: ±5%.
[c] Without catalyst.
X: Other products include disulfides.
Values in parentheses are the measured oxidation potentials (vs. SCE) of sulfoxides.

oxidation product, sulfone, the irradiation time has been gradually increased to 8 h. Though this leads to the formation of slightly increased amount of sulfone, the products contain more of the starting material and this has been attributed to disproportionation reaction (Eq. (7)). We propose the mechanism in Eqs. (8)–(11) wherein the photogenerated hole (h^+) readily accepts an electron from the sulfide adsorbed on the surface of the photocatalyst to give the sulfide radical cation $ArSMe]^{\bullet +}$. There are instances of formation of such a radical cation. In the 9,10-dicyanoanthracene sensitized photo-oxidation of sulfides [35], Ericksen et al. have postulated the formation of sulfide radical cation. The cations of aryl methyl sulfides were also produced by pulse radiolysis in aqueous solutions, using $SO_4^{\bullet -}$ and Tl^{+2} as the oxidizing species and the radical cations are present as monomers [36]. We presumed that sulfide radical cation produced on irradiated TiO_2 reacts with the superoxide to yield the sulfoxide as the major product via persulfoxide.

$$TiO_2 \xrightarrow{h\nu} TiO_2(h^+) + e^- \quad (1)$$

$$O_2 + e^- \rightarrow O_2^{\bullet -} \quad (2)$$

$$ArSMe + TiO_2(h^+) \rightarrow ArSMe]^{\bullet +} + TiO_2 \quad (3)$$



(4)

(5)

Disproportionation:

$$ArSOMe + TiO_2(h^+) \rightarrow ArSOMe]^{\bullet +} + TiO_2 \quad (6)$$

$$2ArSOMe]^{\bullet +} + 2e^- \rightarrow ArSMe + ArSO_2Me \quad (7)$$

C–S bond cleavage:

$$ArSMe]^{\bullet +} \rightarrow ArS^{\bullet} + Me^+ \quad (8)$$

$$ArSMe]^{\bullet +} \rightarrow Ar^{\bullet} + MeS^+ \quad (9)$$

$$2ArS^{\bullet} \rightarrow ArS{-}SAr \quad (10)$$

$$2Ar^{\bullet} \rightarrow Ar{-}Ar \quad (11)$$

It has also been shown that sulfur cations of dialkyl sulfides produced by one-electron photo-oxidation through triplet 4-carboxybenzophenone can react with superoxide to yield two equivalents of sulfoxide per equivalent of one-electron oxidized sulfur [37] as we have postulated in Eqs. (8)–(11).

One important finding is that the irradiation time plays an important role in determining the products. Lower irradiation time invariably leads to the formation of sulfoxides as the major product (see the yield of sulfoxide for all aryl methyl sulfides on irradiation for 1 h). Larger irradiation time leads to disproportionation with the result that the starting material is present more.

Photoelectrochemical measurements also provide evidence for the electron transfer from sulfide. At a constant applied potential (+1.8 V), on illumination of the TiO_2 electrode in the presence of O_2, aryl methyl sulfides exhibited photocurrent which increased with decreasing oxidation potential of the sulfide (Fig. 1). No photocurrent was observed in the absence of ArSMe even after irradiation for 6 h. The product analysis after the separation of the product mixture showed about 10% formation of sulfoxide. This would have been formed from the reaction of the sulfide cation radical and the small amount of superoxide formed from the interaction between conduction band electron and oxygen.

If the above proposed mechanism is correct, the electron transfer from sulfide to the hole, step (3) will be favoured by the presence of electron-donating group in the aryl moiety

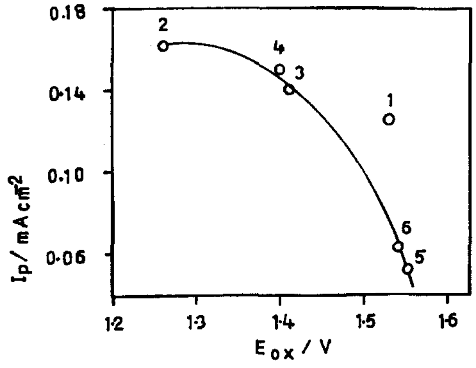


Fig. 1. Correlation of photocurrent with oxidation potential of aryl methyl sulfides. The points in the figure are referred to by the same numbers as represented in Table 1.

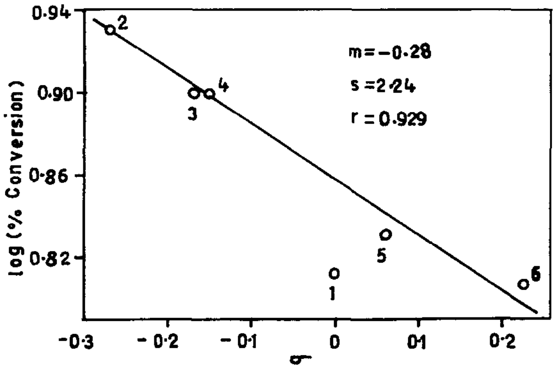


Fig. 2. Hammett plot-relationship between percentage of conversion of sulfides after 1 h of irradiation and substituent constants. Numbers in the figure refer to those in Table 1.

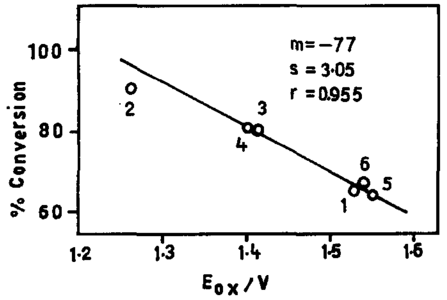


Fig. 3. Relationship between percentage of conversion after 1 h irradiation and oxidation potential of aryl methyl sulfides. Numbers in the figure refer to those in Table 1.

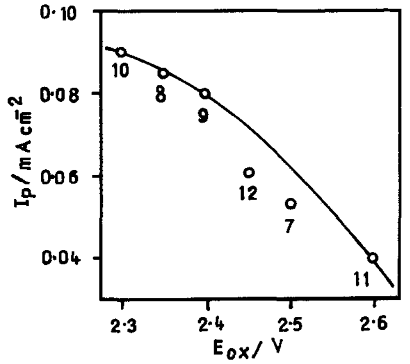


Fig. 4. Correlation of photocurrent with oxidation potential of aryl methyl sulfoxides. Numbers in the figure refer to those in Table 2.

and that should result in greater yield of the oxidized product. Indeed we observe more of oxidation products at lower irradiation time with substrates having lower oxidation potentials. A fairly good Hammett plot (Fig. 2) between percentage of conversion vs. σ with a negative slope (-0.28) also supports this. The plot of percentage of conversion with oxidation potential is also linear (Fig. 3). As disproportionation starts earlier with some aryl methyl sulfides, the results after irradiation of 1 h has been considered. The formation of thiols, disulfides, etc., may be accounted for by the dissociation of sulfide radical cation as shown in Eqs. (8)–(11).

Though the mechanism proposed is very similar to that for dialkyl sulfides, we have provided support to the mechanism and also established that irradiation time is very crucial in achieving the desired oxidation product.

3.2. *TiO_2 sensitized photo-oxidation of sulfoxides*

In an entirely different set of experiments, we find that TiO_2 is an effective catalyst to oxidize aryl methyl sulfoxides to the corresponding sulfones almost quantitatively ($>95\%$). Eqs. (12) and (13) accounts for the formation of sulfones.

Photoelectrochemical studies reveal that the photocurrent increases with decrease in oxidation potential of aryl methyl sulfoxides as observed for sulfides (Fig. 4).

$$ArSOMe + TiO_2(h+) \rightarrow ArSOMe]^{\cdot +} + TiO_2 \tag{12}$$

$$2ArSOMe]^{\cdot +} + O_2^{\cdot -} \rightarrow 2ArSO_2Me \tag{13}$$

It is difficult to produce $ArSO_2Me]^{\cdot +}$ because SO_2 group is strongly electron-withdrawing and therefore we do not find any disproportionation products during the oxidation of sulfoxides.

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