

## Photoinduced Reduction of Aryl Methyl Sulfoxes on Titanium Dioxide

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Titanium dioxide has been shown to act as an effective photocatalyst in the reduction of aryl methyl sulfoxes to give the corresponding sulfoxides and sulfides, the former being the major product.

One of the most active areas of research in recent years has been the study of redox reactions employing semiconductors as photocatalysts.<sup>1,2</sup> The use of TiO<sub>2</sub> as a photocatalyst and oxidations of various types of organic compounds such as alcohols,<sup>1</sup> alkenes,<sup>1</sup> alkylaromatics<sup>1,2</sup> and sulfides<sup>3</sup> mediated by TiO<sub>2</sub> have been well documented. During oxidation, the organic substrate may donate an electron to the hole generated h<sup>+</sup> on illuminated TiO<sub>2</sub>. The electron promoted from the valence band to the conduction band also reacts with oxygen to form a superoxide radical ion which can also oxidise the substrate. However, when oxygen is removed, organic reagents can accept the photogenerated conduction band electron and this will result in the reduction of the reagent. Only a very few such reductions have been reported<sup>1,4</sup> and there is a relative paucity of information on photoinduced reductions on semiconductor surfaces.

Sulfoxes are generally reduced by metal hydrides such as LiAlH<sub>4</sub> and (*iso*-Bu)<sub>2</sub>AlH to their sulfides.<sup>5,6</sup> The difficult reduction of the S–O bond of the sulfone group to the sulfide may also be achieved by treatment with SmI<sub>2</sub>–THF–hexamethylphosphoramide.<sup>7</sup> Since the sulfonyl group is strongly electron withdrawing, electron transfer from the conduction band of TiO<sub>2</sub> will be favoured by the electron-attracting sulfonyl group. This prompted us to study the reduction of aryl methyl sulfoxes on irradiated titanium dioxide surfaces in the absence of oxygen. Here, we present our preliminary results on the photoinduced reduction of aryl methyl sulfoxes on titanium dioxide to yield sulfoxides and sulfides, the former being the major product.

Irradiation of a suspension of TiO<sub>2</sub> (1 g, Aldrich 99.9%) in an organic solvent (100 ml) containing aryl methyl sulfone (1 mmol dm<sup>-3</sup>) with 366 nm lamp (64 W) purged with nitrogen reduced the substrate to sulfoxide and sulfide. After removal of the solvent under reduced pressure, the products were

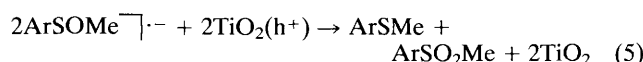
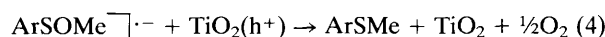
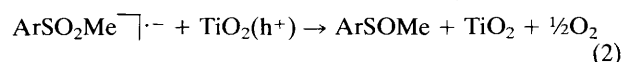
**Table 1** Reduction<sup>a</sup> of aryl methyl sulfoxes (*p*-RC<sub>6</sub>H<sub>4</sub>SO<sub>2</sub>Me) and dialkyl sulfoxes (RSO<sub>2</sub>R) on irradiated TiO<sub>2</sub> (1%) under nitrogen atmosphere

R	Solvent	Product ( <i>p</i> -RC <sub>6</sub> H <sub>4</sub> XMe or RXR) mixture (%)			<i>b</i>
		X = S	X = SO	X = SO <sub>2</sub>	
Alkyl aryl sulfoxes					
H	MeCN	9	89	2	—
H	EtOH	18	54	18	10
H	MeOH	13	86	1	—
H	Pr <sup>i</sup> OH	18	65	2	15
OMe	MeCN	18	39	39	4
OMe	EtOH	23	43	34	—
Cl	MeCN	27	51	17	5
Cl	EtOH	28	63	9	—
Et	MeCN	8	89	2	1
Br	MeCN	35	48	15	2
Dialkyl sulfoxes					
Me	EtOH	80	2	7	11
Et	EtOH	48	5	21	26

<sup>a</sup> Irradiation time: 8 h. <sup>b</sup> Disulfide and other products to be characterised.

characterised by GC. In Table 1 the yields of the reduced products based on GC are presented. The reduction of phenyl methyl sulfone in three alcohols and *p*-chloro- and *p*-methoxyphenyl methyl sulfone in ethanol demonstrates the absence of any appreciable solvent effect (Table 1) in the photo-reduction.

We propose the following tentative mechanism [eqns. (1)–(5)] for the photoinduced reduction of sulfoxes.



The proposed mechanism is substantiated by the following observations:

(i) We have also been able to obtain aryl methyl sulfides from aryl methyl sulfoxides on irradiated titanium dioxide in a nitrogen atmosphere. In a typical experiment, the reduction of an aryl methyl sulfoxide (under the same experimental conditions as for aryl methyl sulfoxes) gave the corresponding sulfide.

(ii) When a strongly electron-donating group is present in the substrate, step (1) will be less favoured. Indeed we recovered more unreacted sulfone in the case of *p*-methoxyphenyl methyl sulfone.

(iii) Attempts to increase the yield of reduced product by increasing the irradiation time have not been successful. The amount of unreacted phenyl methyl sulfone was more (80%) after 12 h of irradiation. This supports the disproportionation step (5) on titanium dioxide surface.

Under similar conditions the photoinduced reduction of dialkyl sulfoxes on TiO<sub>2</sub> yield more of sulfides (*cf.* Table 1).

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