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Photoredox reactions of ArXCOOH ($X = CH_2$, OCH_2, SCH_2, $SOCH_2$ or SO_2CH_2) on TiO_2

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Abstract

TiO_2 acts as a site-selective photocatalyst for sulphur compounds containing S or SO_2 and COOH groups in redox reactions. While phenylacetic and phenoxyacetic acids undergo oxidative decarboxylation on irradiated TiO_2, arylthioacetic acids are oxidized to the corresponding sulphinylacetic acids. Arylsulphonylacetic acids undergo photoinduced reduction with retention of carboxyl group.

Keywords: Photoredox; Titanium dioxide; Photocatalyst

1. Introduction

It has been well established in recent years that photoinduced redox exchange can occur efficiently at the surface of an irradiated semiconductor powder. These photoredox reactions on irradiated semiconductor surfaces are likely to provide access to hitherto inaccessible reactions or to an improved selectivity in multifunctional molecules [1-3]. TiO_2 is widely used as the semiconductor photocatalyst in many organic reactions owing to its non-toxic nature, chemical stability, ready availability and ability to be used repeatedly without substantial loss of catalytic activity [1]. Irradiation of TiO_2 promotes an electron from the valence band to the conduction band, making it available for transfer, while the positive equivalent, the hole (h^+) in the valence band is ready to accept an electron from the substrate. A substrate that receives an electron from the semiconductor would be reduced whereas that donates an electron to the semiconductor is oxidized. Although irradiated TiO_2 has been used to oxidize several organic sulphides such as dialkyl, diphenyl and dibenzyl sulphides [4] to the corresponding sulphoxides and sulphones, there are no reports on the oxidation of divalent organic sulphur compounds containing active functional groups such as -COOH. During photosensitized oxidation of organic acids in the presence of TiO_2 or dialkyl ketones, decarboxylation is the most favoured process [5]. Compared with photo-oxidation, there are only a limited number of studies of photoinduced reduction on TiO_2 surfaces and they include the reduction of aldehydes and ketones [6], nitroaromatics [7] and aryl methyl sulphones [8]. The mostly negative potential of electrons at the conduction band of the semiconductor and the ease of oxygen reduction by electrons account for the limited success of organic reductions on semiconductor surfaces. Photoinduced electron transfer reactions of arylthioacetic acids with sensitizers such as polypyridyl chromium(III) complexes [9] and benzophenone [10] have resulted in the formation of aryl methyl sulphides with concomitant decarboxylation. As it is an interesting challenge to achieve site selectivity in photocatalytic redox reactions of multifunctional organic molecules, we studied in general redox reactions of ArXCOOH ($X = CH_2$, OCH_2, SCH_2, $SOCH_2$ or SO_2CH_2) and in particular photooxidation of arylthioacetic acids and photoreduction of arylsulphonylacetic acids on the surfaces of particulate TiO_2. Our studies indicate that phenylacetic and phenoxyacetic acids in the presence of oxygen undergo decarboxylation quantitatively on irradiation in the presence of TiO_2, but photoredox reactions occur at the sulphur or sulphonyl site without any decarboxylation in sulphur-containing acids.

2. Experimental details

Arylthioacetic, arylsulphinylacetic, arylsulphonylacetic acids, aryl methyl sulphides, sulphoxides and sulphones have been prepared by known methods [11]. Commercial samples of phenylacetic and phenoxyacetic acids were recrystallized. Solvents used were either AR or HPLC grade. Aldrich TiO_2 (99.9% pure) was employed as the catalyst.

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Table 1
TiO_2-catalysed photo-oxidation of arylthioacetic acids [a] (p-$RC_6H_4SCH_2COOH$)

R	Irradiation time (h)	Solvent	oduct mixture (%) [b]		
			Sulphinyl acid	Starting material	To be characterized
H	3	MeOH	63	36	1
H	3	MeCN	56	41	3
H	4	$CHCl_3$	53	31	16
Cl	3	MeOH	75	23	2
CH_3	3	MeOH	70	27	3

[a] Substrate concentration 1 mM; solvent, 100 ml; catalyst (TiO_2), 0.5%; immersion reactor/, 125 W/, 350 nm.

[b] GC analysis results; error limit, ±5%. With a 1% concentration of catalyst and 12 h of irradiation of phenylthioacetic acid in MeCN, the percentage yields of the products sulphinyl acid, methyl phenyl sulphoxide, methyl phenyl sulphide and the other products to be characterized are 13, 28, 9 and 36 respectively. With 1% TiO_2 in MeOH or MeCN under oxygen atmosphere, phenylacetic or phenoxyacetic acids yield more than 90% toluene or anisole.

A suspension of TiO_2 (0.5%) in organic solvent (100 ml for oxidation or 15 ml for reduction) containing the substrate, ArXCOOH (1 mM), was irradiated by an immersion reactor with a 125 W medium pressure mecury vapour lamp ($\lambda > 350$ nm) for oxidation or an annular reactor with a 400 W medium pressure mecury vapour lamp ($\lambda > 350$ nm) for reduction (both of the reactors were from SAIC, India). The important details are given below in Tables 1 and 2. After centrifugation, the catalyst was separated and the solvent was removed under reduced pressure. The products were characterized by gas chromatography (GC) (Netel, India) using flame ionization detector and an SE-30 (10%) column, IR spectra and thin layer chromatography.

3. Results and discussion

3.1. Photo-oxidation of ArXCOOH (X = CH_2, OCH_2 or SCH_2)

Solutions of phenylacetic acid or phenoxyacetic acid in methanol in the presence of suspended TiO_2 and oxygen on irradiation gave toluene or anisole in better than 90% yield. This decarboxylation is analogous to the photo-oxidation of acetic acid to methane and carbon dioxide as reported by Kraeutler and Bard [12] and also to that of other aliphatic acids and benzoic acid on TiO_2 [13]. There have also been several reports of the photochemical decarboxylation of arylacetic acids in the presence of various electron acceptors [14].

Irradiation of a suspension of TiO_2 in oxygen-saturated methanol containing phenylthioacetic acid or p-substituted phenylthioacetic acids yields about 70% of arylsulphinylacetic acids (no further oxidation to sulphonylacetic acid). In chloroform and acetonitrile also the major product is arylsulphinylacetic acid (Table 1). The increase in irradiation time and catalyst concentration did not improve the yield of sulphinylacetic acid, but led to some decarboxylation. Thus photocatalytic oxidation of sulphur-containing aromatic acids occurs mainly at the sulphur atom. It is presumed that the substrate transfers the electron to the photogenerated hole, with the formation of a positive charge on the sulphur atom,

Table 2
TiO_2-photoinduced reduction [a] of arylsulphonylacetic acids (p-$RC_6H_4SO_2CH_2COOH$) in methanol

Substrate [b]	Product mixture (%) [c]						
R	1	2	3	4	5	6	7
H	36	51	5			7	1
Cl	5	75	6		3	8	3
Br	2	81	16				1
F		45	45		5	5	1
CH_3	13	72	3		5	7	
OCH_3	1	88	6			4	1
H [d]	26	33	36			5	
$C_6H_5SOCH_2COOH$	71	9		1	16	2	1

[a] Substrate Concentration 1 mM; Solvent, 15 ml; TiO_2, 0.5%; irradiation time, 2 h; annular reactor, 350 nm, 400 W.

[b] GC analysis results; error limit, ±5%.

[c] 1, p-$RC_6H_4SCH_2COOH$; 2, p-$RC_6H_4SOCH_2COOH$; 3, p-$RC_6H_4SO_2CH_2COOH$; 4, p-$RC_6H_4SCH_3$; 5, p-$RC_6H_4SOCH_3$; 6, p-$RC_6H_4SO_2CH_3$; 7, to be characterized.

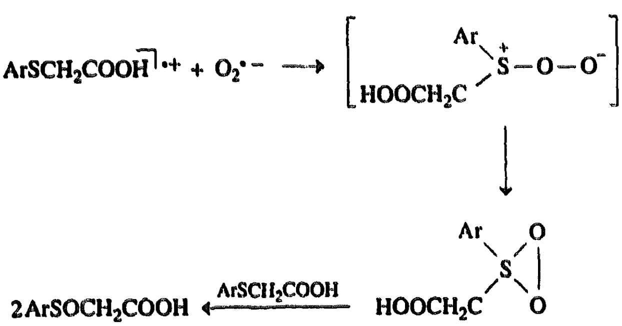
[d] Solvent, acetonitrile. With a 1% concentration of catalyst and 12 h of irradiation of phenylsulphonylacetic acid in MeOH under a nitrogen atmosphere, the percentage yields of the products methyl phenyl sulphone, methyl phenyl sulphoxide, methyl phenyl sulphide, sulphinyl acid, sulphenyl acid and the other products to be characterised are 8, 45, 10, 18, 4 and 10 respectively.

and the sulphur part of the acid is strongly adsorbed on the catalyst. This adsorbed radical cation then interacts with the superoxide giving the sulphinyl acid. The photocatalysed oxidation of arylthioacetic acids is believed to follow a mechanism similar to that proposed for the oxidation of sulphides [4] involving superoxide as shown below:

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

$$O_2 + e^- \longrightarrow O_2^{\bullet -}$$

$$ArSCH_2COOH + TiO_2(h^+) \longrightarrow ArSCH_2COOH]^{\bullet +} + TiO_2$$



At high concentration of the catalyst, decarboxylation occurs with phenylthioacetic acid (see Table 1). It is believed that the carboxyl group also is adsorbed and that may promote decarboxylation. When the irradiation time was increased under identical TiO_2 concentration (0.5%) from 3 to 6 or 8 or 12 h, we observed decarboxylation together with oxidation of decarboxylated products. Thus the influence of irradiation time is also important in determining the product and we have optimized the catalyst concentration and irradiation time as shown in Table 1 to obtain more selectivity and higher product yield.

3.2. Photoinduced reduction of ArXCOOH (X = $SOCH_2$ or SO_2CH_2)

On band gap irradiation of TiO_2 suspended in methanol in a nitrogen atmosphere, arylsulphonylacetic acids are converted to a mixture of sulphinyl and sulphenyl acids with the former as the major product (Table 2). In the absence of TiO_2, no reduction has occurred. When the irradiation time and amount of catalyst were increased, decarboxylated and deoxygenated products such as sulphones, sulphoxides and sulphides were formed. Under the condition of lower concentration of catalyst (0.5%), the strong binding of the sulphonyl group on the photocatalyst presumably results in the reduction of the sulphonyl group without concomitant decarboxylation. On the basis of the experimental results and our own findings [8] on the photoinduced reduction of sulphones on TiO_2, we propose the following probable mechanism for the reduction of sulphonyl acids to sulphinyl acids and sul phenyl acids.

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

$$ArSO_2CH_2COOH + e^- \longrightarrow ArSO_2CH_2COOH]^{\bullet -}$$

$$ArSO_2CH_2COOH]^{\bullet -} + TiO_2(h^+) \longrightarrow ArSOCH_2COOH + TiO_2 + 1/2O_2$$

$$ArSOCH_2COOH + e^- \longrightarrow ArSOCH_2COOH]^{\bullet -}$$

$$ArSOCH_2COOH]^{\bullet -} + TiO_2(h^+ \longrightarrow ArSCH_2COOH + TiO_2 + 1/2O_2$$

In an independent experiment, we have also observed that phenylsulphinylacetic acid has undergone photoinduced reduction to phenylthioacetic acid, providing evidence for the above mechanism.

For the formation of decarboxylated products under increased time of irradiation and concentration of TiO_2, a mechanism analogous to that proposed for the photosensitized decarboxylation of carboxylic acids by aromatic ketones may be visualized:

$$ArSO_2CH_2COOH + e^- \longrightarrow ArSO_2CH_2COOH]^{\bullet -}$$

$$ArSO_2CH_2COOH]^{\bullet -} + TiO_2(h^+) \longrightarrow ArSO_2CH_3 + CO_2$$

The sulphones and sulphoxides are further deoxygenated as proposed by us recently [8]:

$$ArSO_2CH_3 + e^- \longrightarrow ArSO_2CH_3]^{\bullet -}$$

$$ArSO_2CH_3]^{\bullet -} + TiO_2(h^+) \longrightarrow ArSOCH_3 + TiO_2 + 1/2O_2$$

$$ArSOCH_3 + e^- \longrightarrow ArSOCH_3]^{\bullet -}$$

$$ArSO_2CH_3]^{\bullet -} + TiO_2(h^+) \longrightarrow ArSCH_3 + TiO_2 + 1/2O_2$$

At high concentration of the catalyst, the carboxyl group is also presumably adsorbed owing to the availability of more sites on the catalyst.

In a recent report, it has been observed that photoinduced reduction of 4- and 3-nitroacetophenones and also 12-nitrodoccanoic acid on TiO_2 gave only the corresponding amino compounds without reduction of carbonyl group or decarboxylation [7].

Thus the above redox reactions clearly demonstrate the usefulness of semiconductor-mediated photoredox reactions in achieving site selectivity in multifunctional molecules.

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