

# TiO<sub>2</sub>-catalyzed photooxygenation of cinnamic acid derivatives via their radical cations

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## Abstract

Photooxygenation of cinnamic acid derivatives was investigated by using titanium dioxide as a heterogeneous photocatalyst. Benzaldehyde derivatives were efficiently produced by the photooxygenation of the cinnamic acid derivatives having methoxy groups on the phenyl ring. When titanium dioxide was added to acetonitrile solutions of methoxy-substituted cinnamic acids, the color of the suspension changed from colorless to pale yellow. The photooxygenation might proceed through photoinduced single electron transfer from cinnamic acid derivatives to titanium dioxide. Adsorption of the carboxyl group of cinnamic acid derivatives onto the surface of titanium dioxide accelerated the photoinduced electron transfer.

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**Keywords:** Titanium dioxide; Cinnamic acid derivatives; Photoinduced electron transfer; Radical cation; Adsorption

## 1. Introduction

Semiconductor-catalyzed photoreactions of organic molecules have been extensively investigated in the last few decades [1–4]. Semiconductors such as TiO<sub>2</sub>, CdS, and ZnS are utilized as redox-type heterogeneous photocatalysts for photoinduced electron transfer reactions using photoexcitation from their valence bands to conduction bands [5–20]. Hitherto various alkenes have been shown to undergo semiconductor-catalyzed photoreactions in the presence of oxygen, producing, for example, ketones, aldehydes, epoxides, and hydroperoxides [21–27]. However, the efficiency, selectivity, and chemical yields are not necessarily high in these photoreactions. The adsorption of carboxylic acids or carboxylates on the surface of TiO<sub>2</sub> plays an important role for the connection of dyes on TiO<sub>2</sub> as well as acceleration of electron-transfer as exemplified by the Grätzel cell [28,29]. With the aim of exploring the synthetic utility of TiO<sub>2</sub>-catalyzed photoreactions, we developed efficient syntheses of 3,5-diaryl-1,2-dioxolanes and 3,6-diaryl-1,2-dioxanes by using TiO<sub>2</sub>-catalyzed photooxygenation of 1,2-diarylcyclopropanes and 1,1-diarylethenes, respectively

[30,31]. Here we report the photooxygenation of cinnamic acid derivatives and related aromatic compounds with an emphasis on how adsorption of organic molecules influences TiO<sub>2</sub>-catalyzed photooxygenation. From the experimental results, we found that the efficiency of the photooxygenation and adsorption were closely correlated.

## 2. Experimental

Cinnamic acid derivatives were prepared by Knoevenagel condensation [32] as follows. A pyridine (20 mL) solution of malonic acid (12 mmol), substituted benzaldehyde (10 mmol), and piperidine (0.15 mmol) was refluxed for 15 h until evolution of CO<sub>2</sub> ceased. After cooling to room temperature, the solution was poured into ice-cooled 2N HCl aqueous solution (110 mL). Then the precipitate was collected by suction filtration and washed with water. Recrystallization of the solid from ethanol gave pure cinnamic acid derivatives.

Mg(ClO<sub>4</sub>)<sub>2</sub> was purchased and used without purification. TiO<sub>2</sub> was donated from Ishihara Sangyo, Co., Ltd. (ST-01 and ST-21) and the Catalysis Society of Japan (P-25, Degussa, Co., Ltd.). Acetonitrile was distilled over P<sub>2</sub>O<sub>5</sub>.

Photoirradiation was carried out by the following procedure. Into a Pyrex tube (12 mmφ × 10.5 cm), cinnamic acid derivative

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Table 1  
Photooxygenation of Cinnamic acid derivatives Catalyzed by TiO<sub>2</sub>

Entry	Compounds	Substrate		Catalyst and additive	Atmosphere	Irradiation time (h)	Yields of products (%) <sup>a</sup>				Recovery of <b>1</b> (%) <sup>a</sup>
		R <sup>1</sup>	R <sup>2</sup>				<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	
1	<b>1a</b>	4-MeO	COOH	TiO <sub>2</sub> (ST-01)	O <sub>2</sub>	5	23	40	10	9	13
2	<b>1a</b>	4-MeO	COOH	TiO <sub>2</sub> (ST-01) / Mg(ClO <sub>4</sub> ) <sub>2</sub>	O <sub>2</sub>	5	32	22	6	0	40
3	<b>1a</b>	4-MeO	COOH	none	O <sub>2</sub>	5	18	0	0	0	82
4	<b>1a</b>	4-MeO	COOH	TiO <sub>2</sub> (ST-01)	Ar	5	44	trace	0	0	48
5	<b>1b</b>	3-MeO	COOH	TiO <sub>2</sub> (ST-01)	O <sub>2</sub>	5	37	7	11	2	43
6	<b>1c</b>	3,4-(MeO) <sub>2</sub>	COOH	TiO <sub>2</sub> (ST-01)	O <sub>2</sub>	5	34	23	0	trace	38
7	<b>1d</b>	3-MeO, 4-OH	COOH	TiO <sub>2</sub> (ST-01)	O <sub>2</sub>	5	39	trace	0	0	49
8	<b>1e</b>	H	COOH	TiO <sub>2</sub> (ST-01)	O <sub>2</sub>	5	14	4	11	0	22
9	<b>1f</b>	4-MeO	CHO	TiO <sub>2</sub> (ST-01)	O <sub>2</sub>	5	13	3	0	0	78
10	<b>1g</b>	4-MeO	COOMe	TiO <sub>2</sub> (ST-01)	O <sub>2</sub>	5	52	2	0	0	46
11 <sup>b</sup>	<b>1h</b>	4-MeO	CH <sub>2</sub> OH	TiO <sub>2</sub> (ST-01)	O <sub>2</sub>	5	0	16	0	0	31
12	<b>1a</b>	4-MeO	COOH	TiO <sub>2</sub> (ST-01)	O <sub>2</sub>	3	34	29	12	2	23
13	<b>1a</b>	4-MeO	COOH	TiO <sub>2</sub> (ST-21)	O <sub>2</sub>	3	42	8	4	2	37
14	<b>1a</b>	4-MeO	COOH	TiO <sub>2</sub> (P-25)	O <sub>2</sub>	3	31	7	3	trace	31
15	<b>1a</b>	4-MeO	COOH	TiO <sub>2</sub> (ST-01) / H <sub>2</sub> O	O <sub>2</sub>	3	2	7	20	10	2
16	<b>1a</b>	4-MeO	COOH	TiO <sub>2</sub> (ST-21) / H <sub>2</sub> O	O <sub>2</sub>	3	23	4	4	6	30
17	<b>1a</b>	4-MeO	COOH	TiO <sub>2</sub> (P-25) / H <sub>2</sub> O	O <sub>2</sub>	3	26	3	3	15	34
18	<b>1c</b>	3,4-(MeO) <sub>2</sub>	COOH	TiO <sub>2</sub> (ST-01) / H <sub>2</sub> O	O <sub>2</sub>	5	7	34	7	30	10

Conditions: Substrate (0.1 mmol), TiO<sub>2</sub> (20 mg), Mg(ClO<sub>4</sub>)<sub>2</sub> (0.05 mmol, entry 2), CH<sub>3</sub>CN (8 mL) or CH<sub>3</sub>CN (6 mL) + H<sub>2</sub>O (4 mL), 300 W high-pressure mercury lamp, Pyrex, stirred by a magnetic stirrer, RT. Particle sizes are 7 nm (ST-01), 20 nm (ST-21), and 30 nm (P-25).

<sup>a</sup> Yields of products were determined by <sup>1</sup>H NMR.

<sup>b</sup> **1f** (18%) and **2f** (3%) were also obtained.

(0.1 mmol), TiO<sub>2</sub> (20 mg), acetonitrile (8 mL), and a stirrer bar were placed and sealed with a rubber septum. After bubbling of dioxygen injected through a needle for 20 min, the suspension was irradiated by a 300 W high-pressure mercury lamp with continuous stirring and continued bubbling of dioxygen for 3–5 h (See Table 1). After this time, TiO<sub>2</sub> was removed by centrifugal separation (3000 rpm, 30 min) and subsequent decantation. The TiO<sub>2</sub> was washed with methanol and precipitated by centrifugal separation again. The combined filtrate was evaporated. Yields of products were determined by <sup>1</sup>H NMR spectra of the crude mixture, obtained using a Varian Mercury 300 spectrometer (300 MHz), comparing with the reported data of **1a** [33–35], **1b** [36], **1c** [33,37], **1d** [38], **1e** [39], **1f** [40–42], **1g** [43–46], **1h** [42,44,47], **2a** [48], **2f** [49], **2g** [50,51], **5a** [52,53], **5b** [53], and **5c** [54].

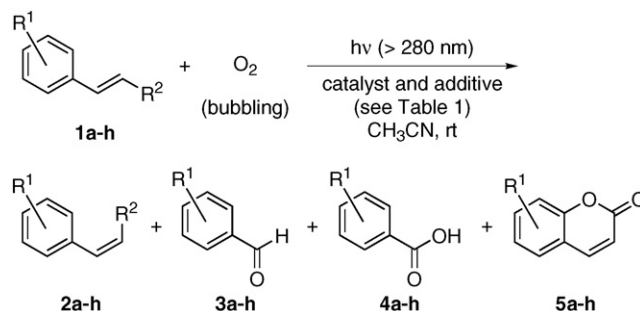
Adsorption of cinnamic acid derivatives was estimated by the following procedure. TiO<sub>2</sub> (3, 6, 9, 12 mg) was added to acetonitrile solutions of **1a–h** (5.0 × 10<sup>-4</sup> M), and then the suspensions were stirred by a magnetic stirrer for 30 min. After adsorption complexes were removed by centrifugal separation (3000 rpm, 30 min), the supernatant solution was diluted 20-fold. UV absorption spectra of the diluted supernatant solutions were measured using a Jasco V-530 spectrophotometer (Fig. 1). Diffuse reflectance spectra of adsorption complexes were recorded on a Shimadzu UV-2200A spectrometer, and absorbance was determined using the Kubelka–Munk equation.

Desorption of **1a–e** from adsorption complexes was estimated by the following procedure. The adsorption complex (12 mg) of **1a** on TiO<sub>2</sub> was added to acetic acid (10 mL), methanol (10 mL), or acetonitrile (10 mL), and stirred by a magnetic stirrer for 30 min. After centrifugal separation (3000 rpm, 30 min), UV absorption of the supernatant solutions was measured. The

amount of desorption was evaluated by the increase in the absorbance.

### 3. Results and discussion

Irradiation of an acetonitrile solution containing *p*-methoxycinnamic acid (**1a**) in the presence of suspended TiO<sub>2</sub> (ST-01) under a constant stream of dioxygen with a 300 W high-pressure mercury lamp through a Pyrex filter (>280 nm light) gave a *cis*-isomer (**2a**), *p*-methoxybenzaldehyde (**3a**), *p*-methoxybenzoic acid (**4a**), and a coumarin derivative (**5a**) in 23, 40, 10, and 9% yields, respectively (Scheme 1, Table 1, entry 1). In the presence of Mg(ClO<sub>4</sub>)<sub>2</sub>, yields of **3a–5a** decreased (entry 2). In the absence of TiO<sub>2</sub> or under Ar atmosphere, only *cis–trans* photoisomerization took place (entries 3, 4). Similar irradiation of 3,4-dimethoxycinnamic acid (**1c**) afforded aldehyde **3c** in 23% yield, whereas 3-methoxycinnamic acid (**1b**), ferulic acid (**1d**), and unsubstituted cinnamic acid (**1e**) gave poor yields of **3–5** (entries 5–8). In the photoreaction of aldehyde **1f**



Scheme 1.

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