

TiO₂-catalyzed photooxygenation of cinnamic acid derivatives via their radical cations

Hajime Maeda*, Hideyuki Nakagawa, Kazuhiko Mizuno*

*Department of Applied Chemistry, Graduate School of Engineering, Osaka Prefecture University,
1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan*

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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 TiO₂, 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 TiO₂ plays an important role for the connection of dyes on TiO₂ as well as acceleration of electron-transfer as exemplified by the Grätzel cell [28,29]. With the aim of exploring the synthetic utility of TiO₂-catalyzed photoreactions, we developed efficient syntheses of 3,5-diaryl-1,2-dioxolanes and 3,6-diaryl-1,2-dioxanes by using TiO₂-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 TiO₂-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 CO₂ 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(ClO₄)₂ was purchased and used without purification. TiO₂ 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 P₂O₅.

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

* Corresponding authors. Tel.: +81 72 254 9294; fax: +81 72 254 9289.
E-mail address: maeda-h@chem.osakafu-u.ac.jp (H. Maeda).

Table 1
Photooxygenation of Cinnamic acid derivatives Catalyzed by TiO₂

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

Conditions: Substrate (0.1 mmol), TiO₂ (20 mg), Mg(ClO₄)₂ (0.05 mmol, entry 2), CH₃CN (8 mL) or CH₃CN (6 mL) + H₂O (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).

^a Yields of products were determined by ¹H NMR.

^b **1f** (18%) and **2f** (3%) were also obtained.

(0.1 mmol), TiO₂ (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, TiO₂ was removed by centrifugal separation (3000 rpm, 30 min) and subsequent decantation. The TiO₂ was washed with methanol and precipitated by centrifugal separation again. The combined filtrate was evaporated. Yields of products were determined by ¹H 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].

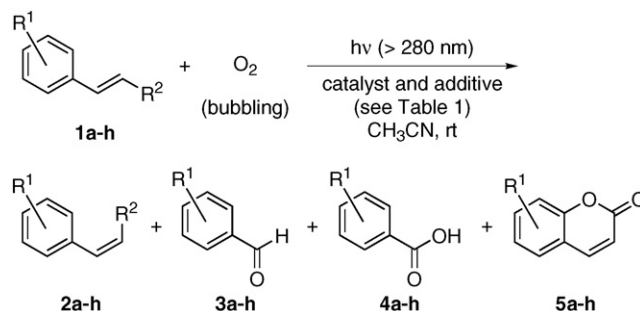
Adsorption of cinnamic acid derivatives was estimated by the following procedure. TiO₂ (3, 6, 9, 12 mg) was added to acetonitrile solutions of **1a–h** (5.0 × 10⁻⁴ M), and then the suspensions were stirred by a magnetic stirrer for 30 min. After adsorption complexes were removed by centrifugal separation (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 TiO₂ 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 TiO₂ (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(ClO₄)₂, yields of **3a–5a** decreased (entry 2). In the absence of TiO₂ 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.

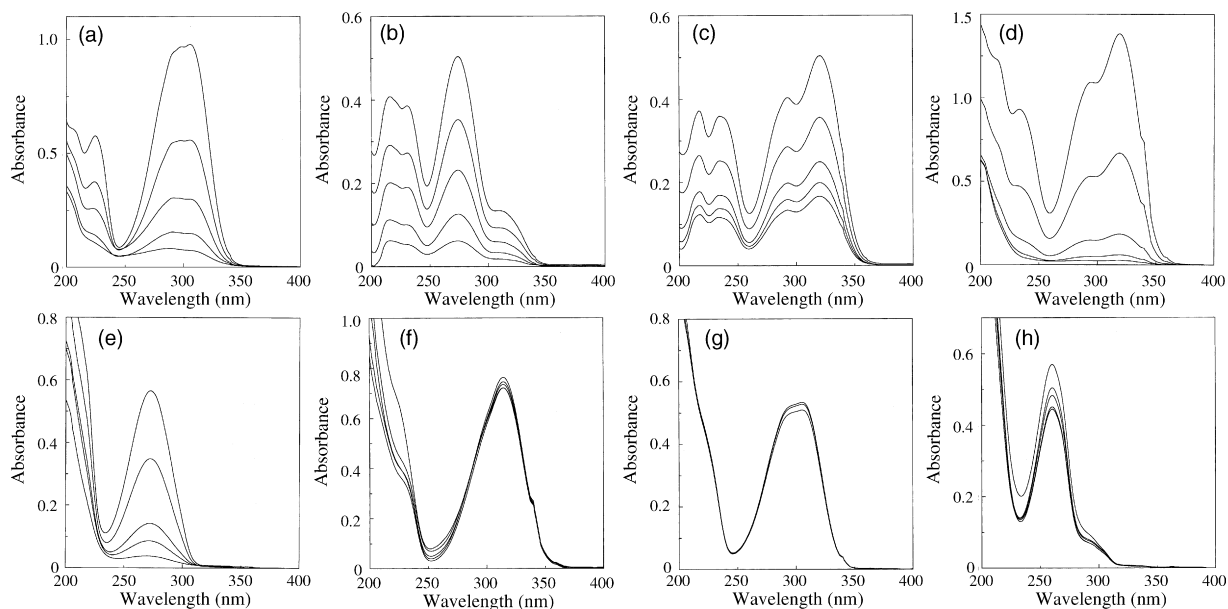


Fig. 1. UV absorption spectra of CH_3CN solutions (5.0×10^{-4} M) containing (a) **1a**, (b) **1b**, (c) **1c**, (d) **1d**, (e) **1e**, (f) **1f**, (g) **1g**, and (h) **1h** by adding TiO_2 (0, 3, 6, 9, 12 mg). Each suspension was filtrated by centrifuge and diluted 20-fold before measurement of UV absorption.

and ester **1g** which do not have carboxyl groups, **3f–g** were hardly produced (entries 9, 10). Photooxygenation of alcohol **1h** gave **3h**, **1f**, and **2f** in 16, 18, and 3% yields, respectively (entry 11).

Particle sizes of TiO_2 are critical for the product distribution because the surface area should be changed depending on the particle size. The yields of photooxygenated products **3a** and **4a** decreased with increasing the particle sizes of TiO_2 in the order of ST-01 (7 nm) > ST-21 (20 nm) > P-25 (30 nm) (entries 12–14). Photoirradiation in the presence of a large excess of water increased the yield of 7-methoxycoumarin **5a** (entries 15–17). When 3,4-dimethoxy derivative **1c** was allowed to react in the presence of water, 6,7-dimethoxycoumarin **5c** was obtained in 30% yield (entry 18).

We estimated the adsorption ability of these molecules on the TiO_2 surface [55–58]. TiO_2 (3, 6, 9, 12 mg) was added to 5.0×10^{-4} M acetonitrile solutions of **1a–h**, and then the suspensions were stirred for 30 min. After adsorption complexes were removed by centrifugal separation, the UV absorption spectra of 20-fold diluted supernatant solutions were measured (Fig. 1). The reduced absorbance indicated the adsorption amounts of **1a–h** onto the TiO_2 surface. From these spectra, it was demonstrated that the carboxylic acids **1a,d,e** were adsorbed on TiO_2 in **1**: TiO_2 = ca. 1:12 ratio by weight. Adsorption abilities of **1b** and **1c** were lower than those of **1a,d,e**. Alcohol **1h** slightly adsorbed to TiO_2 , but aldehyde **1f** and ester **1g** hardly adsorbed.

Desorption of adsorbates **1a–e** from adsorption complexes was also estimated by the relative comparison of the supernatant solutions. When an adsorption complex (12 mg) of **1a** on TiO_2 was stirred for 30 min in acetic acid, methanol, or acetonitrile, 80, 30, and <1% of **1a** were desorbed, respectively.

The color of the adsorption complexes depended on the substituents. When TiO_2 was added to acetonitrile solutions of methoxy-substituted cinnamic acid derivatives **1a,c,d**, the color-

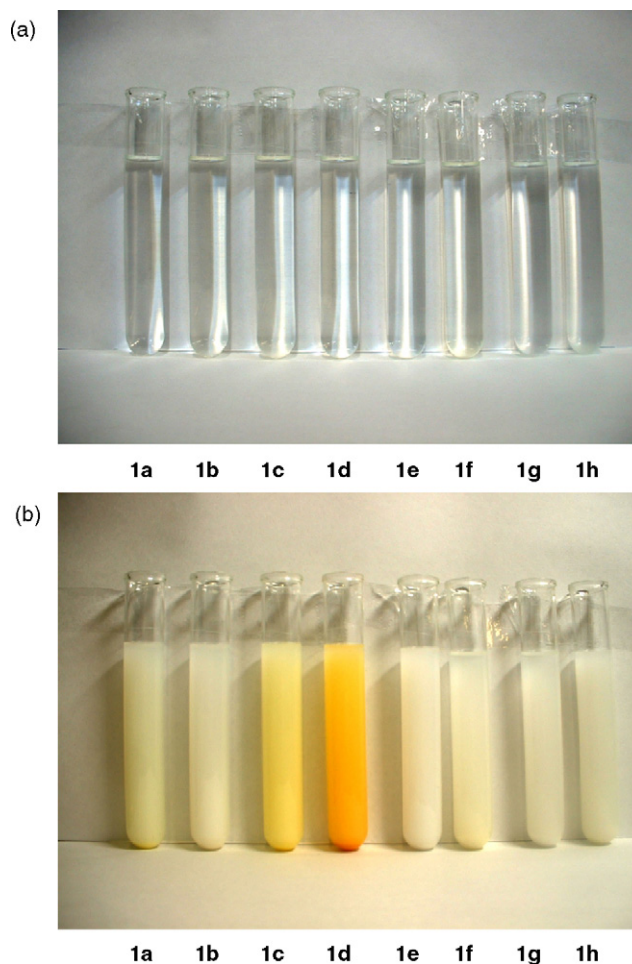
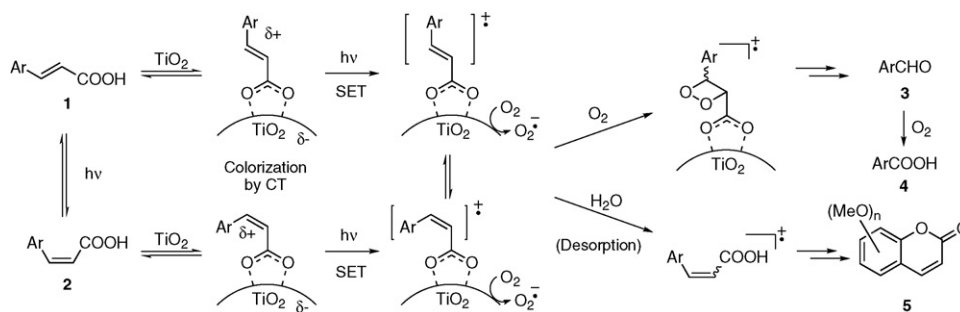


Fig. 2. Colorization of CH_3CN solutions containing **1a–h** (a) before and (b) after the addition of TiO_2 (ST-01).



Scheme 2.

less solutions immediately turned into pale yellow suspensions (Fig. 2). Among them, the suspension of ferulic acid **1d** was the most intensely colorized. The colorization of adsorption complexes was evidently supported by diffuse reflectance spectra of the adsorption complexes of **1a** and **1e** on TiO₂ (Fig. 3). Absorbance of the adsorption complex of **1a** on TiO₂ spread to the visible region, but that of **1e** terminated within the ultraviolet region.

From these results, we propose an electron-transfer mechanism for the TiO₂-catalyzed photooxygenation of cinnamic acid derivatives as shown in Scheme 2. Carboxylic acids **1a–e** adsorb on the TiO₂ surface by their carboxyl groups. The colorization in the cases of *para*-methoxy-substituted derivatives **1a,d,e** in particular suggested that charge transfer from adsorbates to adsorbent is involved. Photoirradiation of TiO₂ in acetonitrile causes the promotion of an electron into the conduction band (−0.8 V versus SCE) to generate a hole in the valence band (+2.4 V versus SCE) [1–6,13,19,22,27,59,60]. One-electron transfer from **1a–e** to the valence band should take place as an exothermic process to produce the radical cations of these substrates, because their oxidation potentials are sufficiently low [61–65]. In addition, electron transfer from the conduction band to O₂ ($E_{\text{red}}^0 = -0.86$ V versus SCE in CH₃CN) [66–68] to produce O₂^{•−} is a thermodynamically permissible process [1–6,19,22,27]. *Cis–trans* photoisomerization proceeds upon photoirradiation with or without TiO₂ as well as via the radical cations. Then the radical cation reacts with dioxygen to give a dioxetane radical cation. The dioxetane radical cation

undergoes bond cleavage and subsequent back electron transfer to produce benzaldehyde derivative **3**, which suffers further oxygenation to form **4**. A good correlation appears to exist between adsorption and the efficiency of the photooxygenation [69].

One-electron transfer from compound **1a** to 1,4-dicyanonaphthalene in homogeneous CH₃CN/H₂O solution upon photoirradiation is known to produce the radical cation of **1a**, which cyclizes to give 7-methoxycoumarin (**5a**) [70,71]. We propose that the addition of water accelerates the desorption of adsorbates, thus increasing the yields of **5a** and **5c**.

We have previously reported that TiO₂-catalyzed photooxygenation of methoxy-substituted 1,2-diarylethenes and 1,2-diarylcyclopropanes was accelerated by the addition of Mg(ClO₄)₂ [30,31]. The enhancement effect was explained by the suppression of back electron transfer from TiO₂[−] to radical cations due to the interaction between Mg²⁺ and ionic species such as TiO₂[−] and O₂^{•−} or the interaction between ClO₄[−] and radical cations [30,31,72–81]. Another possibility for the effect of Mg(ClO₄)₂ is that the magnesium salt may accelerate the desorption of radical cations of 1,2-diarylethenes and 1,2-diarylcyclopropanes from the TiO₂ surface due to the enhanced cationic charge on the surface [82]. In the present study, addition of Mg(ClO₄)₂ slightly reduced the efficiency of the photooxygenation. Since the adsorption of substrates on the TiO₂ surface and the resultant neighboring effect [58] are the main contributing factors to the electron transfer and subsequent oxygenation process, Mg(ClO₄)₂ may disturb these processes by the effects described above.

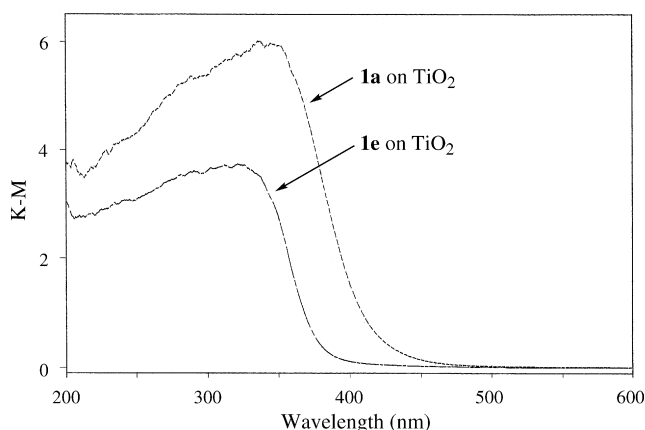


Fig. 3. Diffuse reflectance spectra of adsorption complexes of **1a** and **1e** on TiO₂ (ST-01).

4. Conclusion

TiO₂-catalyzed photooxygenation of cinnamic acid derivatives proceeded to give benzaldehyde derivatives and benzoic acid derivatives via their radical cations. The efficiency of the photooxygenation strongly correlates with adsorption ability on TiO₂ surface and oxidation potentials of substrates. Adsorption complexes of methoxy-substituted cinnamic acids were colorized by a charge transfer interaction between adsorbates and adsorbent. Addition of water accelerated the desorption of adsorbates to make the yield of coumarin derivatives increase.

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