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Effect of Substituents on TiO_2 Photocatalytic Oxidation of *trans*-Stilbenes

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Suguru Higashida was born in Hyogo, Japan. He received B.Sc. from Kwansei Gakuin Univ. in 1986 and M.Ed. from Osaka Kyoiku Univ. in 1988, and D.Eng in 1999 from Osaka University. In 1988, he became Research Associate at Osaka Prefectural College of Technology, Japan, and to Associate Professor in 1998, and to Professor in 2010. His research interests include photocatalytic oxidation of organic compounds and TiO_2 photocatalyst.

Abstract

Photocatalytic reaction of *trans*-stilbene on TiO_2 particles produces benzaldehyde with high selectivity in acetonitrile-water mixed solvent. Introduction of electron-donating substituents to the benzene rings accelerated the reaction. On the other hand, the rate was decelerated by electron-withdrawing substituents. These results suggest that the reaction proceeds by hydroperoxo or hydroperoxy, which were formed on TiO_2 surface by UV irradiation, rather than free OH radicals.

Keywords: TiO_2, Photocatalyst, Epoxidation

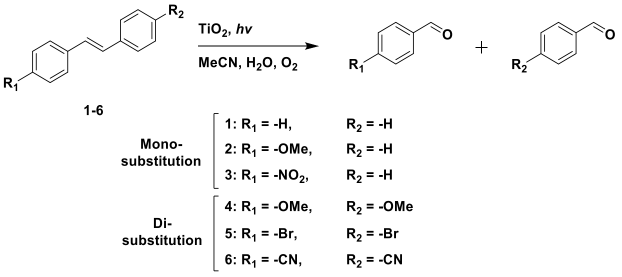
1. Introduction

Utilization of light energy to drive chemical processes has been one of the most active research areas in chemistry. The photocatalytic process using a TiO_2 photocatalyst has widely been studied and utilized to decompose pollutants in a mild condition.[1] Most organic compounds included in air or water can be completely mineralized to CO_2 and H_2O.[2] The reactions on TiO_2 photocatalyst are considered to be caused by reactive oxygen species such as free hydroxy radical ($^{\bullet}OH$) and super oxide radical anion ($O_2^{\bullet -}$), which are generated by photogenerated electron and hole pairs generated under ultraviolet light irradiation.[3-6] Although the photochemical reaction on TiO_2 photocatalyst is generally believed to proceed by these oxidative species, detailed mechanisms still remain unsettled and they seem to be strongly dependent on experimental conditions.[7] Many efforts are now directed toward clarification of the mechanisms of TiO_2 photocatalytic reactions under different conditions.[7-8]

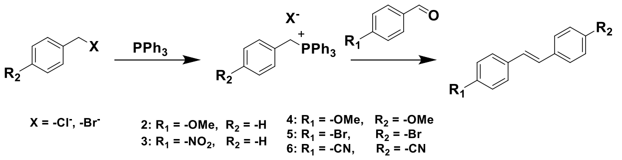
Of photocatalytic reactions, those of aromatic compounds have been extensively studied using TiO_2 photocatalyst.[9-12] During the course of their reactions, intermediates having hydrophilic functional groups such as hydroxy (-OH) and carboxy (-COOH) groups were produced before the complete oxidation of the aromatic compounds into CO_2 and H_2O.[11-12] Production of these variety of oxidation products have motivated us to develop new organic synthetic methods using TiO_2 photocatalyst.[13-14] We have reported that phenanthrene is converted to a lactone derivative by the TiO_2 photocatalytic reaction albeit with a moderate yield.[15] We recently found that an aromatic diacid compound is photocatalytically converted to lactone as a result of decarboxylation on UV-irradiated TiO_2.[16] This result suggested that the conversion of phenanthrene to a lactone compound proceeds via a diacid compound, which is produced photocatalytically by the cleavage of the double bond of phenanthrene. This idea urged us to study the photocatalytic reactivity of the double bonds of stilbene and related compounds and to compare the reactivities with that of phenanthrene. Although stilbenes, especially *cis*-stilbenes, have structural similarity to phenanthrene, their reactivities are very different because the double bond connecting the two aromatic rings of stilbene has little contribution to their aromaticity. Oxidative cleavage of the alkene double bond of *trans*-stilbene leading to benzaldehyde has been one of the well-known reactions of TiO_2 photocatalytic oxidation of aromatic compounds.[9] In the case of non-aromatic alkenes, however, we found that 1-decene was selectively converted to 1,2-epoxydecane using a TiO_2 photocatalyst under oxygen atmosphere.[17] This result suggests that epoxide is formed as an intermediate in oxidation of *trans*-stilbene. Confirmation of the process and the mechanism will be helpful to get more understanding of the reaction.

Examination of the effect of electron density at the reactive position on the reactivity is a useful method to clarify the reaction mechanisms. Stradiotto and co-workers recently studied the TiO_2 photocatalytic oxidation of aromatic rings having different substituents, and found that electron-donating groups such as methoxy group accelerate the reaction, while electron-withdrawing groups such as trifluoro methyl group decelerate the reaction.[18] We thought that it should be interesting to study the effect of the substituents on the reaction of stilbenes by using stilbene derivatives having different electron-donating and electron-withdrawing substituents, as shown in Scheme 1.

2. Experimental



Scheme 1. Photocatalytic reactions studied; *trans*-stilbene (**1**), mono-substituted *trans*-stilbenes (**2**, **3**), and di-substituted *trans*-stilbenes (**4-6**) were used as the substrates.



Scheme 2. Synthesis scheme of mono- or di-substituted *trans*-stilbenes

In the experiments, reagent-grade stilbene **1** was purchased from Tokyo Chemical Industry Co. Ltd. and used without further purification. The substituted stilbenes **2-6**, as shown in Scheme 1, were synthesized by Wittig reaction from the corresponding substituted aromatic aldehydes and substituted or non-substituted benzyl bromides (Scheme 2).[19] Nuclear Magnetic Resonance (NMR) spectra were obtained on a Jeol Delta V 5.0 JNM-ECS spectrometer. The chemical shift values were referenced against for tetramethylsilane for ^{1}H-NMR (0.0 ppm) and against $CDCl_3$ (77.0 ppm) for ^{13}C-NMR.

Preparation of mono-substituted *trans*-stilbenes (2 and 3)

Benzylbromide (12.3 g, 72 mmol) and triphenylphosphine (18.8 g, 72 mmol) were added to 50 mL of toluene in a 200 mL eggplant flask, and the mixture was heated at 70 °C for 3 h. The resulting precipitate was collected by filtration and washed with hexane, and benzyltriphenylphosphoniumbromide was obtained (30.1 g, isolated yield 97%). Benzyl triphenylphosphoniumbromide (0.95 g, 2.2 mmol) thus obtained was added, together with *p*-anisaldehyde (3.0 mmol) and 3 mL of 1 M aqueous sodium hydroxide solution, to 6 mL of methanol in a 50 mL eggplant flask and the mixture was stirred for 6 h at room temperature to obtain 4-methoxy-*trans*-stilbene **2**. Similarly, 4-nitro-*trans*-stilbene **3** was obtained using *p*-nitrobenzaldehyde as the aldehyde. The resulting precipitate were collected by filtration and washed with cooled methanol. For their purification, the products were dissolved with ethyl acetate and neutralized with 10 mL of 1% aqueous hydrochloric acid solution. The organic layer was sequentially washed with saturated sodium hydrogen carbonate solution and saturated sodium chloride solution. Then, the organic layer was dried over anhydrous sodium sulfate and the solvent was removed in vacuo with a rotary evaporator. The products (**2** and **3**) were further purified by silica-gel column chromatography. Their NMR data were as follows.

4-methoxy-*trans*-stilbene 2 (isolated yield 35%)

^{1}H-NMR (400 MHz, $CDCl_3$) : δ 3.84 (3H, s), 6.89 (2H, d, J = 8.6 Hz), 6.96 (1H, d, J = 16.0 Hz), 7.04 (1H, d, J = 16.0 Hz), 7.20 (1H, td, J = 7.6 Hz and 1.0 Hz), 7.36 (2H, td, J = 7.6 Hz and 1.0 Hz), 7.44 (2H, d, J = 8.6 Hz), 7.49 (2H, dd, J = 7.6 Hz and 1.0 Hz)

^{13}C-NMR (100 MHz, $CDCl_3$) : δ 55.43, 114.10, 126.25, 126.70, 127.26, 128.83, 128.75, 128.91, 130.21, 137.74, 159.38

4-nitro-*trans*-stilbene 3 (isolated yield 51%)

^{1}H-NMR (400 MHz, $CDCl_3$) : δ 7.14 (1H, d, J = 16.0 Hz), 7.28 (1H, d, J = 16.0 Hz), 7.33 (1H, td, J = 7.2 Hz and 1.0 Hz), 7.40 (2H, td, J = 7.2 Hz and 1.0 Hz), 7.56 (2H, dd, J = 7.2 Hz and 1.0 Hz), 7.65 (2H, d, J = 8.4 Hz), 8.23 (2H, d, J = 8.4 Hz)

^{13}C-NMR (100 MHz, $CDCl_3$) : δ 124.10, 126.25, 126.84, 127.01, 128.83, 128.88, 133.28, 136.14, 143.37, 146.26

Preparation of di-substituted *trans*-stilbenes (4, 5 and 6)

Preparation of 4, 4'-dimethoxy-*trans*-stilbene 4

4-Methoxybenzylchloride (2.82 g, 18 mmol) and triphenylphosphine (4.72 g, 18 mmol) were added to 10 mL of toluene in a 100 mL eggplant flask, and the mixture was heated at 100 °C for 3 h. The resulting precipitate was collected by filtration and washed with hexane, and 4-methoxybenzyltriphenylphosphoniumchloride was obtained (3.79 g, 50%). 4-Methoxybenzyltriphenylphosphoniumchloride (0.92 g, 2.2 mmol) thus obtained was added, together with *p*-anisaldehyde (0.41 g, 3.0 mmol) and 3 mL of 1 M aqueous sodium hydroxide solution, to 6 mL of methanol in a 50 mL eggplant flask, and the mixture was stirred for 6 h at room temperature to obtain 4,4'-dimethoxy-*trans*-stilbene **4**. The resulting product was collected by filtration and washed with cooled methanol. The NMR data was as follows.

4, 4'-dimethoxy-*trans*-stilbene 4 (isolated yield 33%)

^{1}H-NMR (400 MHz, $CDCl_3$) : δ 3.82 (6H, s), 6.89 (4H, d, J = 8.8 Hz), 6.93 (2H, s), 7.43 (4H, d, J = 8.8 Hz)

^{13}C-NMR (100 MHz, $CDCl_3$) : δ 55.31, 114.05, 126.11, 127.38, 130.41, 158.94

Preparation of 4, 4'-dibromo-*trans*-stilbene 5

4-Bromobenzylbromide (4.50 g, 18 mmol) and triphenylphosphine (4.72 g, 18 mmol) were added to 10 mL of toluene in a 100 mL eggplant flask, and the mixture was heated at 100 °C for 3 h. The resulting precipitate was collected by filtration and washed with hexane, and 4-bromobenzyl triphenylphosphoniumbromide was obtained (8.18 g, 88%). 4-Bromobenzyltriphenylphosphoniumbromide (0.51 g, 1.0 mmol) thus obtained was added, together with 4-bromobenzaldehyde (0.37 g, 2.0 mmol) and potassium *tert*-butoxide (0.11 g, 1.0 mmol), to 9 mL of chloroform in a 100 mL eggplant flask, and the mixture was stirred for 44 h at room temperature to obtain 4,4'-dibromo-*trans*-stilbene **5**. The resulting precipitate was collected by filtration and washed with cooled methanol. The NMR data was as follows.

4, 4'-dibromo-*trans*-stilbene 5 (isolated yield 38%)

^{1}H-NMR (400 MHz, $CDCl_3$) : δ 7.02 (2H, s), 7.37 (4H, d, J = 8.8 Hz), 7.48 (4H, d, J = 8.8 Hz)

^{13}C-NMR (100 MHz, $CDCl_3$) : δ 121.62, 127.99, 128.07, 131.84, 135.84

Preparation of 4, 4'-dicyano-*trans*-stilbene 6

4-Cyanobenzylbromide (1.76 g, 9.0 mmol) and triphenylphosphine (2.36 g, 9.0 mmol) were added to 10 mL of toluene in a 100 mL eggplant flask, and the mixture was heated at 110 °C for 7 h. The resulting precipitate was collected by filtration and washed with hexane, and 4-cyanobenzyltriphenyl phosphoniumbromide was obtained (3.90 g, 94%). 4-Cyanobenzyltriphenylphosphoniumbromide (0.50 g, 1.1 mmol) thus obtained was added, together with 4-cyanobenzaldehyde (0.14 g, 1.0 mmol) and potassium *tert*-butoxide (0.12 g, 1.1 mmol), to 10 mL of chloroform in a 100 mL eggplant flask, and the mixture was stirred for 17 h at room temperature to obtain 4,4'-dicyano-*trans*-stilbene **6**. The resulting precipitate was collected by filtration and washed with cooled methanol. The NMR data was as follows.

4, 4'-dicyano-*trans*-stilbene 6 (isolated yield 64%)

^{1}H-NMR (400 MHz, $CDCl_3$) : δ 7.58 (2H, s), 7.85 (4H, d, J = 8.0 Hz), 7.87 (4H, d, J = 8.0 Hz)

^{13}C-NMR (100 MHz, $CDCl_3$) : δ 106.26, 114.94, 123.66, 126.50, 128.74, 137.15

Photocatalytic Reactions

The photocatalytic reactions of **1-3** were carried out in a Pyrex-glass test tube (φ = 18 mm), which contained each of **1-3** (0.5 mmol), acetonitrile-4% (w/w) water mixture (10 mL), and TiO_2 powder (40 mg, 0.5 mmol, 1 eq.); the concentration of **1-3** was 50 mmol/L. For the photocatalytic reactions of **4-6**, since their solubility of the symmetric stilbenes was so low, their reactions were carried out in highly diluted solution (3.57 mmol/L) using 0.1 mmol of the compound; the volume of the solution was 28 mL. P25 (Nippon Aerosil Co., Ltd.) was used as the TiO_2 photocatalyst for all the reactions, because we had

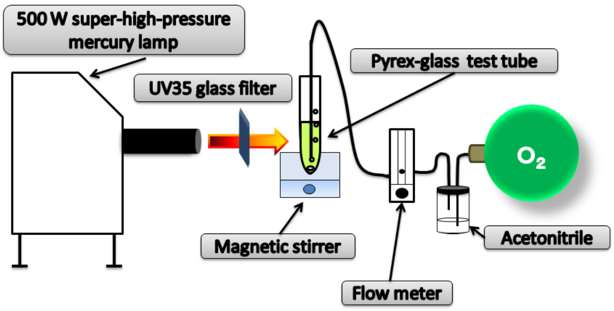


Figure 1. Schematic of set-up for TiO_2 photocatalytic reactions.

found that this powder showed the highest activity for the oxidation of *trans*-stilbene. The high photocatalytic activity of this power for the oxidation of various organic compounds has been attributed to the synergy effect between rutile and anatase particles included in it.[20]

During the reaction, the solution was magnetically stirred to suspend the TiO_2 particles and bubbled with oxygen gas at a rate of 2.0 mL/min. In the absence of oxygen, the photocatalytic reaction hardly proceeded. A 500 W super-high-pressure mercury lamp was used as the light source, and deep UV component ($\lambda < 350$ nm) was filtered out with a UV35 glass filter (Hoya Corporation) to prevent photoexcitation of the substrates (Figure 1).

All of the reactions were carried out at room temperature. As the reactions proceeded, a small portion of the solution was periodically sampled and analyzed by high performance liquid chromatography (HPLC) with an instrument (HITACHI L-6000 series) equipped with an octadecyl-silica column. Mixture of acetonitrile and water (7:3) was used as an eluent.

3. Results and Discussion

Photocatalytic reaction of non-substituted *trans*-stilbene **1**, which was carried out as a control experiment, produced benzaldehyde, as shown in Figure 2a. The yield reached 85% after UV light irradiation for 30 h (Figure 3). However, benzaldehyde was not obtained when the reaction was carried out in acetonitrile containing no water. These results indicate that **1** is oxidized with high selectivity using water as the oxygen source. Probably introduction of oxygen atoms to the product proceeds via surface OH groups, which are supplied from water molecules

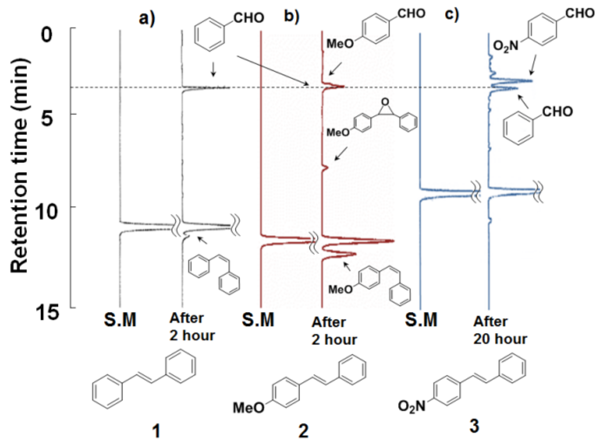


Figure 2. HPLC charts for the solutions of *trans*-stilbene and mono-substituted *trans*-stilbenes before (starting material) and after the TiO_2 photocatalytic reaction; (a) *trans*-stilbene **1**, (b) methoxy-substituted *trans*-stilbene **2**, and (c) nitro-substituted *trans*-stilbene **3**. Since the reactivity of **3** was very low, photoirradiation was continued for 20 h.

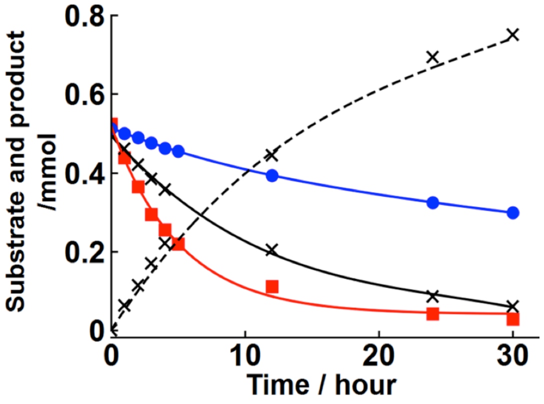


Figure 3. Time courses of photocatalytic reaction of *trans*-stilbene and its derivatives; *trans*-stilbene **1** (black line), methoxy-substituted *trans*-stilbene **2** (red line) and nitro-substituted *trans*-stilbene **3** (blue line). Black broken line stands for benzaldehyde produced from **1**. The yield reached 85% after UV light irradiation for 30 h.

If the same type of reactions takes place for the reactions of mono-substituted stilbenes, the expected products by the oxidative cleavage of the double bond are benzaldehyde and the corresponding mono-substituted benzaldehydes. They are indeed observed in the products by the HPLC analysis (Figures 2b and 2c). However, we also observed some other products. In the case of **2**, which has a methoxy-substituent, an epoxide and the *cis-trans* isomerized products were identified (Figure 2b). From **3**, which has a nitro-substituent, more different kinds of products were produced, judging from the appearance of many small unassignable peaks in the HPLC chart (Figure 2c).

Concerning the conversion rates of the stilbenes, **2** showed the increased rate and **3** showed the decreased rate compared with the non-substituted stilbene **1**, as shown in Figure 3. The results show the tendency of the conversion rate to increase by the introduction of an electron-donating group and to decrease by the introduction of an electron-withdrawing group. However, concerning the effect of the electron donating group, the increase in the rate should partly be attributed to the production of the epoxide and *cis-trans* isomerization.

In order to further confirm the effect of the substituents, introduction of the same substituents to both benzene rings of stilbene at para-position is helpful. Using these substrates, the analysis of the products becomes much easier because the same substituted aldehydes are produced from a stilbene molecule by the cleavage of the double bond. When di-substituted stilbenes (**4**-**6**) are oxidatively cleaved at the double bond, the expected products are 4-methoxy benzaldehyde (from **4**, dimethoxy group), 4-bromo benzaldehyde (from **5**, dibromo group), and 4-cyanobenzaldehyde (from **6**, dicyano group). In addition, the effect of the substituents is expected to be enhanced because of the doubled substituents.

In these experiments, the initial concentration was fixed at 3.57 mmol/L for all the di-substituted and non-substituted stilbenes and their reactivities were compared. Interestingly, production of the *cis* forms was scarce from these symmetric stilbenes, and the selectivity of the formation of the aldehydes

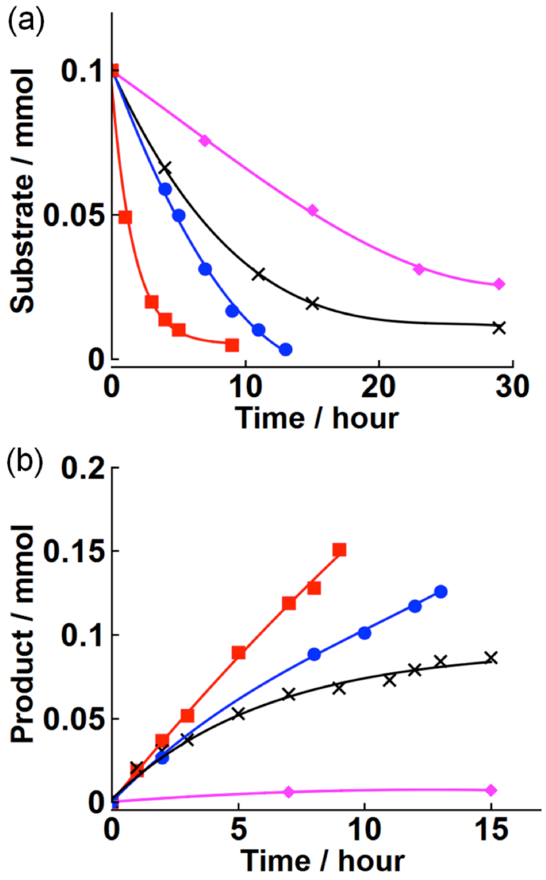


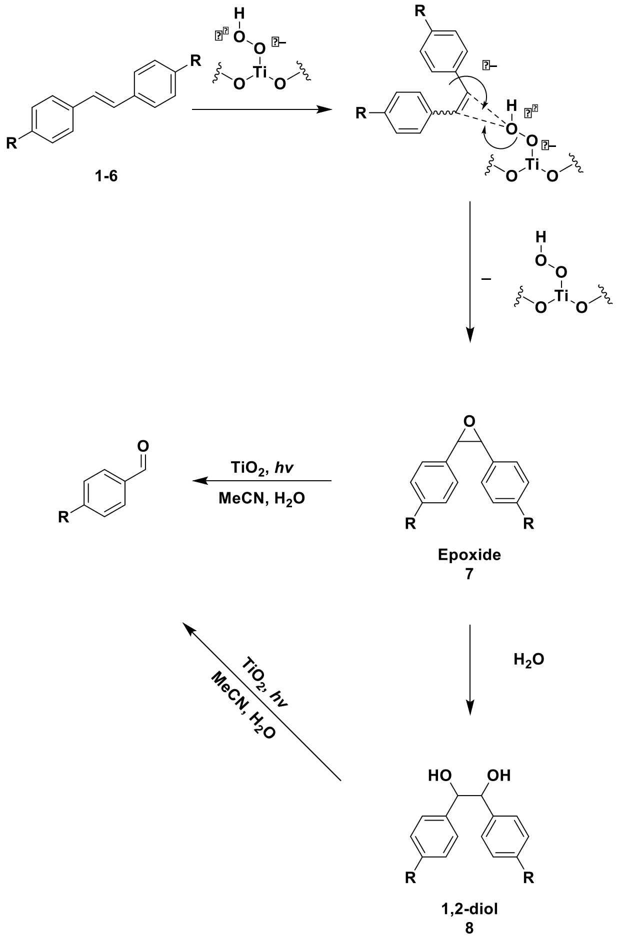
Figure 4. Time courses of photocatalytic reaction of di-substituted and non-substituted *trans*-stilbenes; (a) decay of substrates and (b) rise of products. Substrates used are dimethoxy *trans*-stilbene **4** (red line), dibromo *trans*-stilbene **5** (blue line), non-substituted *trans*-stilbene **1** (black line), and dicyano *trans*-stilbene **6** (magenta line). The products are 4-methoxy benzaldehyde (from **4**, red line), 4-bromo benzaldehyde (from **5**, blue line), benzaldehyde (from **1**, black line), and 4-cyanobenzaldehyde (from **6**, magenta line).

was generally high except **6**, which has electron-withdrawing substituents. For **4** and **5**, which have electron-donating substituents, the rate of the reaction was higher than that of non-substituted stilbene **1**, as shown in Figure 4. The decay rates for these stilbenes seem to be faster than the rise rates of the products, which seems to be due to the formation of epoxides as intermediates, as discussed later. The yields of aldehydes at the stage of 10 h-irradiation reached 80% for **4**, and about 65% for **1** and **5**.

These results clearly show the tendency of the rate of the double-bond cleavage to increase by the introduction of electron-donating substituents and to decelerate by the introduction of electron-withdrawing substituents, which is the same tendency observed using mono-substituted stilbenes.

It should be noted that benzoic acids, which are commonly produced by conventional chemical oxidation of stilbenes, were scarcely included in the products of the TiO_2 photocatalytic reactions of **1-6** as far as the reactions were continued for less than 10 h. We consider that, if the reactions had been continued for longer time, benzoic acids would have been produced from the aldehydes.

In photochemistry, production of aldehyde from stilbene has been well known.[21] In this case, stilbenes are converted to 1,2-dioxetane by singlet molecular oxygen ($^1O_2$), which is photochemically produced from molecular oxygen ($^3O_2$). Then, the 1,2-dioxetane is automatically cleaved to aldehydes. In this process, the formation of $^1O_2$ is the key, which is produced either by direct photoexcitation of $^3O_2$ in the ground state or by energy transfer from photoexcited substrates in their triplet states to $^3O_2$. Both of these processes proceed only under deep UV light. In some earlier studies on TiO_2 photocatalytic reactions of stilbenes, these processes may have been involved.[9] However, in the present study, they do not contribute to the actual reactions because we carefully removed the deep UV component using the UV cut-off filter. Another possibility of production of aldehydes from alkenes is the path via epoxide. Once epoxide is formed, aldehydes are produced by hydrolysis of the epoxide bond. In chemical epoxidation of alkenes, 3-chloroperbenzoic acid (*m*CPBA) is commonly used as the oxidant, and the reaction is known by the name of Prilezhaev epoxidation.[22] This reaction is driven by the electrophilic oxygen O (δ^+) in the OOH group of *m*CPBA and is accelerated by introduction of electron-donating groups to the alkenes.[23] This tendency is in agreement with the results of the photocatalytic reactions that stilbenes having electron donating substituents show higher reactivity and also higher yield of aldehydes, as mentioned above. In addition, we did observe the photocatalytic production of epoxide from methoxy-substituted stilbene and it was compared with the standard sample by HPLC analysis, as shown in Figure 2b.



Scheme 3. Proposed mechanism of photocatalytic Production of aldehydes from *trans*-stilbenes.

Taking into accounts these facts, we propose the mechanism of photocatalytic production of aldehydes from stilbenes, as shown in Scheme 3. First, titanium-based peroxide species are formed on the surface of TiO_2 by the holes photogenerated in TiO_2.[24] Second, epoxides are produced from stilbenes by surface hydroperoxo or hydroperoxy, rather than free OH radicals, in a manner like Prilezhaev epoxidation. Lastly, epoxide **7** is converted to aldehydes. Alternatively, this final process may proceed via 1,2-diol compound **8**, feasibility of which was confirmed using **8 (R = H)** as the starting material ; the yield of benzaldehyde was obtained 92% for 9 h by HPLC analysis. However, we couldn't determine two passes, because 1,2-diol compound **8** was not isolated due to adsorption to TiO_2 surface. As a whole, we consider that the oxygen insertion to the double bond is the critical step, and that the electron-donating groups introduced into stilbene enhance this process. So far, many authors have suggested that free hydroxy radicals ($^{\bullet}OH$) and super oxide radical anions ($O_2^{\bullet -}$), especially the former, are the active species in photocatalytic oxidation of organic compounds. However, it is difficult to explain our findings about the reaction of stilbenes on the basis on the chemistry of these species. Although further intensive studies are necessary to confirm the mechanisms, our proposed mechanism, which give importance to the TiO_2 surface in photocatalytic reactions, may be useful to deepen the understanding the mechanisms of many other photocatalytic oxidation processes of organic compounds.

4. Conclusion

In literature photocatalytic reactions have mostly been discussed in terms of mineralization of harmful or undesirable materials. In these applications, photogeneration of strong oxidation species is imperable and such species as free OH radicals have been assumed to be involved in the efficient photocatalytic reactions. However, it is also known that different kinds of intermediates are produced, sometimes with high selectivity, before their complete mineralization. Our results showed that electron-donating and electron-withdrawing substituents introduced to *trans*-stilbenes gave specific effects on their TiO_2-photocatalyzed reactions. The results suggested that the reactions proceeded by hydroperoxo or hydroperoxy, which were formed on TiO_2 surface by UV irradiation, rather than OH radicals. We consider that discussion of photocatalytic reactions on the basis of organic chemistry will be important to deepen their understanding, which may also contribute to open new methods in organic synthetic chemistry.

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