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Formation of dimer radical cation of 1,1-dianisylethylene through two-step hole transfer processes during TiO_2 photocatalytic reactions

Takashi Tachikawa, Sachiko Tojo, Mamoru Fujitsuka and Tetsuro Majima*

The Institute of Scientific and Industrial Research (SANKEN), Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan

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Abstract—The formation of the 1,1-dianisylethylene dimer radical cation ($(DAE)_2^{\cdot+}$) during TiO_2 photocatalytic reactions was successfully investigated by the transient absorption measurement with time-resolved diffuse reflectance spectroscopy. This reaction was explained in terms of the cascade hole transfer processes from the photo-generated holes in the TiO_2 particles to free DAE (DAE_{free}) in the bulk solution mediated by the radical cation of *p*-phenylbenzoic acid adsorbed on the TiO_2 surface ($PBA^{\cdot+}_{ads}$).

The TiO_2 photocatalytic degradation of organic compounds for the purpose of purifying water or wastewater from industries and households has gained a lot of attention.[1] The primary step in the photocatalytic reaction is the generation of pairs of electrons and holes in the TiO_2 particles by UV irradiation with an energy higher than the TiO_2 band gap energy, and these charges can migrate to the TiO_2 surface to initiate redox reactions with the adsorbates.[2–6] The overall efficiency of these redox reactions is determined by several factors, for example, the accessible difference between the potentials of the band edges of the TiO_2 and the substrates, the adsorption of the substrates on the TiO_2 surface, and the recombination dynamics between charge carriers. As is well known, organic radical cations are important intermediates in photochemical electron-transfer reactions[7,8] and have received much attention regarding their reactivities on/in the heterogeneous materials such as zeolite and silica.[8] It is also important for the development of synthetic organic photochemistry to clarify the reaction dynamics of radical cations at the TiO_2 surface by time-resolved spectroscopic methods. Recently, we studied the one-electron oxidation reactions of several aromatic compounds adsorbed on the surface of a TiO_2 powder by time-resolved diffuse reflectance (TDR) spectroscopy and concluded that the –OH group plays an important role in the adsorption on the surface of TiO_2 and the efficiency of the one-electron oxidation of the substrates producing the radical cations.[6] Therefore, a high one-electron oxidation efficiency is hardly expected for the nonadsorbed molecules.

In this study, we have investigated the one-electron oxidation process of 4-phenylbenzoic acid (PBA) adsorbed on the TiO_2 surface and the subsequent reactions of the radical cation of PBA adsorbed on the TiO_2 surface ($PBA^{\cdot+}_{ads}$) with 1,1-dianisylethylene (DAE) ($Ar_2C{=}CH_2$: Ar = 4-methoxyphenyl) in CH_3CN by TDR spectroscopy. The TDR method is a powerful tool for the investigations of the photochemical reactions on/in the heterogeneous materials.[5,6,9] The aim of this work is focused on the one-electron oxidation processes of adsorbates by the photo-excited TiO_2 particles and the reactivity of the radical cation adsorbed on the TiO_2 surface.

First, we examined the adsorption and desorption dynamics of the substrates on the surface of a TiO_2 powder (P25, Japan Aerosil) slurried in CH_3CN at room temperature. The adduct formation constants (K_{ad}) of $3.8 \pm 0.3 \times 10^4$ and $2 \pm 1\ M^{-1}$ were determined from the Langmuir adsorption isotherms for PBA and DAE, respectively, using steady-state UV absorption spectroscopy.[6] The large K_{ad} value obtained for PBA, which is about 4 orders of magnitude greater than that

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Keywords: TiO_2; Time-resolved diffuse reflectance spectroscopy; One-electron oxidation reaction; Radical cation.

* Corresponding author. Tel.: +81-6-6879-8495; fax: +81-6-6879-8499; e-mail: majima@sanken.osaka-u.ac.jp

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obtained for DAE, clearly indicates that PBA can preferentially adsorb on the $\mathrm{TiO_2}$ surface, while DAE is not adsorbed and exists as a free molecule in solution.

TDR spectra were observed during the 355 nm laser photolysis (5 ns FWHM, 1.5 mJ pulse^{-1}) of the $\mathrm{TiO_2}$ powder in the presence of PBA and DAE in $\mathrm{CH_3CN}$ at room temperature.[6] Figure 1 shows the TDR spectra obtained at 60, 150, and 500 ns after the laser flash during the laser photolysis of $\mathrm{TiO_2}$ with 355 nm light in the presence of PBA (2 mM) an DAE (5 mM) in Ar-saturated $\mathrm{CH_3CN}$ at room temperature. The absorption values attributed to the substrates adsorbed on the $\mathrm{TiO_2}$ surface (%abs.) were obtained by subtracting the absorption value observed in the absence of the substrates from that observed in the presence of the substrates.[5,6,9] The transient absorption band with a peak at about 700 nm appeared immediately after the laser flash as shown in Figure 1. This absorption band is similar to that obtained during the 355 nm laser flash photolysis of the 10-methylacridinium ion ($\mathrm{AcrH^+}$) in the presence of PBA in the bulk $\mathrm{CH_3CN}$ solution, although a slight red shift was observed. Therefore, we assigned this transient absorption band at 600–780 nm to $\mathrm{PBA}_{\mathrm{ads}}^{\cdot+}$, which was generated from the one-electron oxidation reaction with the photo-generated oxidizing species such as h_{vb}^{+} or the trapped holes (h_{tr}^{+}) at the $\mathrm{TiO_2}$ surface as given by Eqs. 1 and 2

$$\mathrm{TiO_2} + hv \rightarrow h_{\mathrm{vb}}^{+}(h_{\mathrm{tr}}^{+}) + e_{\mathrm{cb}}^{-}(e_{\mathrm{tr}}^{-}), \tag{1}$$

$$h_{\mathrm{vb}}^{+}(h_{\mathrm{tr}}^{+}) + \mathrm{PBA}_{\mathrm{ads}} \rightarrow \mathrm{PBA}_{\mathrm{ads}}^{\cdot+}. \tag{2}$$

As shown in Figure 1, this absorption band decreased in the time scale of 500 ns with a concomitant rise in a new absorption band with a peak at 490 nm. The new absorption band is quite similar to that of the dimer radical cation of DAE ($(\mathrm{DAE})_2^{\cdot+}$).[10,11] This absorption band was hardly observed during the laser flash photolysis of the $\mathrm{TiO_2}$ powder in the absence of PBA as shown in the inset of Figure 1. It should be noted that the %abs. at 500 nm increased about 5 times by the addition of PBA. These results clearly suggest that the formation of $\mathrm{DAE}^{\cdot+}$ resulted from the hole transfer reaction from $\mathrm{PBA}_{\mathrm{ads}}^{\cdot+}$ to the free DAE ($\mathrm{DAE_{free}}$), and then diffused into the bulk $\mathrm{CH_3CN}$ solution and reacted with $\mathrm{DAE_{free}}$ to generate $(\mathrm{DAE})_2^{\cdot+}$ as given by Eqs. 3 and 4

$$\mathrm{PBA}_{\mathrm{ads}}^{\cdot+} + \mathrm{DAE_{free}} \rightarrow \mathrm{PBA_{ads}} + \mathrm{DAE}_{\mathrm{free}}^{\cdot+}, \tag{3}$$

$$\mathrm{DAE}_{\mathrm{free}}^{\cdot+} + \mathrm{DAE_{free}} \rightarrow (\mathrm{DAE})_2^{\cdot+}. \tag{4}$$

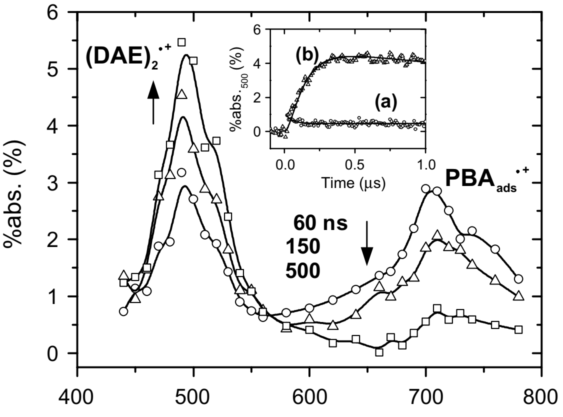


Figure 1. TDR spectra obtained at 60, 150, and 500 ns after the laser flash during the 355 nm laser photolysis of $\mathrm{TiO_2}$ powder in the presence of PBA (2 mM) and DAE (5 mM) in an Ar-saturated $\mathrm{CH_3CN}$ solution. Inset: time profiles of % absorption observed at 500 nm during the laser photolysis of $\mathrm{TiO_2}$ with 355 nm light in the presence of DAE (5 mM) without (a) and with (b) PBA (2 mM) in Ar-saturated $\mathrm{CH_3CN}$ solutions. The solid lines represent a nonlinear least squares curve using k_{HT} of $1.9 \pm 0.3 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$ and k_{D} of $5 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$ and a bi-exponential curve fitted to the kinetic traces obtained for (a) and (b), respectively.

Unfortunately, we cannot observe the TDR spectra for the 1,1-diarylethylenes[10,11] such as 1,1-diphenylethylene and 1,1-ditolylethylene because of the strong laser scattering, low signal-to-noise ratio, and the photoexcitation of the $\mathrm{TiO_2}$ powder at a wavelength below 430 nm.

In order to clarify the hole transfer kinetics between $\mathrm{DAE_{free}}$ and $\mathrm{PBA}_{\mathrm{ads}}^{\cdot+}$, we estimated the formation rates of $(\mathrm{DAE})_2^{\cdot+}$ at the various DAE concentrations. The nonlinear least squares curve fits were then performed by numerically solving a system of coupled linear first-order differential equations for the concentrations of $\mathrm{PBA}_{\mathrm{ads}}^{\cdot+}$, $\mathrm{DAE}_{\mathrm{free}}^{\cdot+}$, and $(\mathrm{DAE})_2^{\cdot+}$ based on Eqs. 3 and 4 by the Runge–Kutta method. The kinetic parameters are listed in Table 1. We used the reported rate constant for the formation of $(\mathrm{DAE})_2^{\cdot+}$ ($k_{\mathrm{D}} = 5 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$).[11] The time profiles observed for the different DAE concentrations are well reproduced by using the same data set within experimental error, strongly supporting the fact that the obtained fitting parameters are reasonable, although perfect fits do not occur in the time range shorter than ~80 ns because of the laser scattering as shown in the inset of Figure 1. The HT rate constant (k_{HT}) from $\mathrm{PBA}_{\mathrm{ads}}^{\cdot+}$ to $\mathrm{DAE_{free}}$ of $(1.9 \pm 0.3) \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$ was determined from the nonlinear least squares curve fits. The obtained k_{HT} value, however, was remarkably small compared with that ($12 \times 10^9\ \mathrm{M^{-1}\,s^{-1}}$) reported for the electron transfer reaction from DAE to $\mathrm{AcrH^+}$ in the excited singlet state ($^1\mathrm{AcrH^{+*}}$) in $\mathrm{CH_3CN}$.[11] It is considered that the significant decrease in the k_{HT} value is mainly due to the steric hindrance at the reaction sites on the $\mathrm{TiO_2}$ surface.

Table 1. Hole transfer rate constant (k_{HT}) from $\mathrm{PBA}_{\mathrm{ads}}^{\cdot+}$ to $\mathrm{DAE_{free}}$, formation rate constant (k_{D}) of $(\mathrm{DAE})_2^{\cdot+}$, and driving force ($\Delta G_{\mathrm{el}}$) values for the electron transfer from DAE in the present system and in the bulk $\mathrm{CH_3CN}$ solution

Hole donor	k_{HT} ($10^9\ \mathrm{M^{-1}\,s^{-1}}$)	k_{D} ($10^9\ \mathrm{M^{-1}\,s^{-1}}$)	$-\Delta G_{\mathrm{el}}$ (eV)
$\mathrm{PBA}_{\mathrm{ads}}^{\cdot+}$ on $\mathrm{TiO_2}$	1.9 ± 0.3	5	0.76[b]
$^1\mathrm{AcrH^{+*}}$ in $\mathrm{CH_3CN}$	12[a]	5[a]	1.0[c]

[a] Ref. 11.

[b] Ref. 12.

[c] The oxidation potential of DAE is reported in Ref. 13.

We also observed the TDR spectra during the laser photolysis of the TiO_2 with 355 nm light in the presence of PBA (2 mM) and DAE (5 mM) in O_2-saturated CH_3CN as shown in Figure 2. The absorption band with a peak at 500 nm observed at 500 ns was very similar to that of the oxygenated 1,6-radical cation of DAE (ox-$(DAE)_2^{\bullet+}$).[11] This result also suggests that $(DAE)_2^{\bullet+}$, which is generated by the HT reaction from $PBA_{ads}^{\bullet+}$ to DAE_{free} at the TiO_2 surface, diffuses into the bulk solution.

The cascade HT reaction processes are shown in Scheme 1. First, $PBA_{ads}^{\bullet+}$ was generated from the one-electron oxidation reaction with h_{vb}^+ or h_{tr}^+ at the TiO_2 surface within the laser pulse duration of 5 ns. The HT from $PBA_{ads}^{\bullet+}$ to DAE_{free} then occurs at the TiO_2 surface. The generated $DAE_{free}^{\bullet+}$ diffuses into the bulk CH_3CN solution and dimerizes with DAE_{free}. In the presence of O_2, as shown in Figure 2, the ox-$(DAE)_2^{\bullet+}$ is generated via the bimolecular reaction process with the O_2 molecule in the bulk CH_3CN solution ($k_{O2} = 1 \times 10^9\,M^{-1}\,s^{-1}$)[11]. This intermediate would be reduced to the 1,2-dioxane as a predominant product together with a small amount of ketone as reported elsewhere.[10,11]

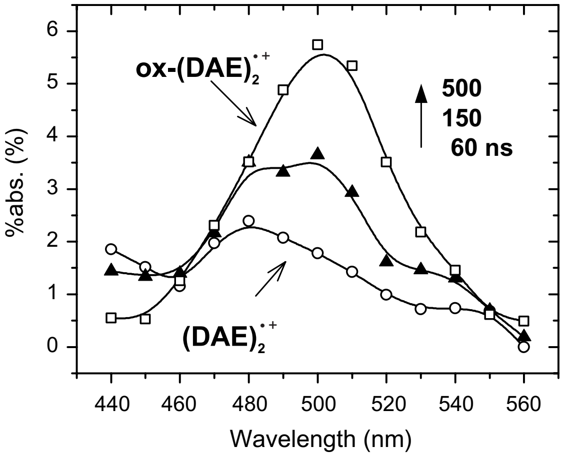
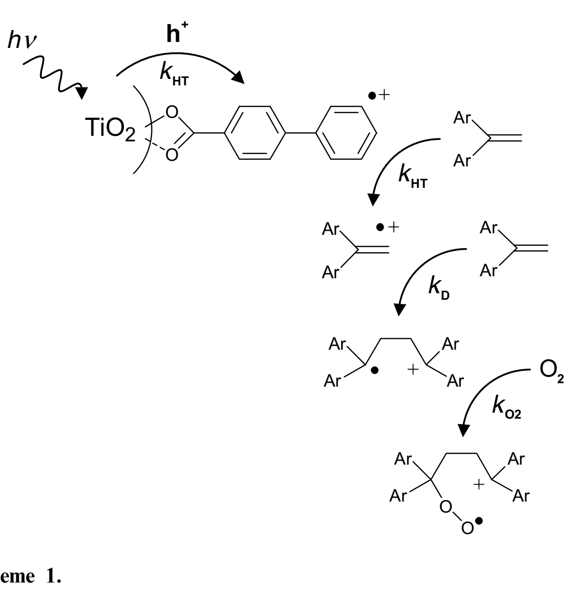


Figure 2. TDR spectra obtained at 60, 150, and 500 ns after the laser flash during the 355 nm laser photolysis of TiO_2 powder in the presence of PBA (2 mM) and DAE (5 mM) in an O_2-saturated CH_3CN solution.



Scheme 1.

In summary, we have investigated the one-electron oxidation reaction of PBA adsorbed on the TiO_2 surface and the subsequent reactions at the TiO_2 surface and in the bulk CH_3CN solution. The formation of $(DAE)_2^{\bullet+}$ by the addition of PBA is explained by the two-step HT reactions from TiO_2 (h^+) to DAE_{free} mediated by $PBA_{ads}^{\bullet+}$ at the TiO_2 surface. The present cascade HT processes will lead to new synthetic processes.

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References and notes

1. (a) Fujishima, A.; Rao, T. N.; Tryk, D. A. *J. Photochem. Photobiol. C: Photochem. Rev.* **2000**, *1*, 1–21; (b) Mills, A.; Hunte, S. L. *J. Photochem. Photobiol. A* **1997**, *108*, 1–35; (c) Hoffmann, M. R.; Martin, S. T.; Choi, W.; Bahnemannt, D. W. *Chem. Rev.* **1995**, *95*, 69–96; (d) Linsebigler, A. L.; Lu, G.; Yates, J. T., Jr. *Chem. Rev.* **1995**, *95*, 735–758.
2. (a) Rothenberger, G.; Moser, J.; Grätzel, M.; Serpone, N.; Sharma, D. K. *J. Am. Chem. Soc.* **1985**, *107*, 8054–8059; (b) Serpone, N.; Lawless, D.; Khairutdinov, R.; Pelizzetti, E. *J. Phys. Chem.* **1995**, *99*, 16655–16661.
3. (a) Howe, R. F.; Grätzel, M. *J. Phys. Chem.* **1987**, *91*, 3906–3909; (b) Nakaoka, Y.; Nosaka, Y. *J. Photochem. Photobiol. A.: Chem.* **1997**, *110*, 299–305.
4. (a) Fox, M. A.; Dulay, M. T. *Chem. Rev.* **1993**, *93*, 341–357; (b) *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: New York, 2001; Vol. 2.
5. (a) Draper, R. B.; Fox, M. A. *J. Phys. Chem.* **1990**, *94*, 4628–4634; (b) Draper, R. B.; Fox, M. A. *Langmuir* **1990**, *6*, 1396–1402.
6. (a) Tachikawa, T.; Tojo, S.; Fujitsuka, M.; Majima, T. *Chem. Phys. Lett.* **2003**, *382*, 618–625; (b) Tachikawa, T.; Tojo, S.; Fujitsuka, M.; Majima, T. *Langmuir*, **2004**, *20*, 2753–2759.
7. (a) *Photoinduced Electron Transfer*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988, Parts A–D; (b) *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: New York, 2001; Vol. 2.
8. (a) Garcia, H.; Roth, H. D. *Chem. Rev.* **2002**, *102*, 3947–4008; (b) Morkin, T. L.; Turro, N. J.; Kleinman, M. H.; Brindle, C. S.; Kramer, W. H.; Gould, I. R. *J. Am. Chem. Soc.* **2003**, *125*, 14917–14924.
9. (a) Wilkinson, F.; Willsher, C. J. *J. Photochem.* **1986**, *33*, 273–278; (b) Furube, A.; Asahi, T.; Masuhara, H.; Yamashita, H.; Anpo, M. *Res. Chem. Intermed.* **2001**, *27*, 177–187.
10. Kojima, M.; Ishida, A.; Takamuku, S. *Chem. Lett.* **1993**, 979–982.

11. Fujita, M.; Shindo, A.; Ishida, A.; Majima, T.; Takamuku, S.; Fukuzumi, S. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 743–749.
12. Cyclic voltammogram was obtained for PBA by using a conventional three-electrode system (BAS, CV-50W) in CH_3CN at room temperature. A platinum electrode was used as the working electrode and an $Ag/AgNO_3$ electrode was used as the reference electrode.
13. Gollnick, K.; Schnatterer, A.; Utschick, G. *J. Org. Chem.* **1993**, *58*, 6049–6056.