Evaluation of the Efficiency of the Photocatalytic One-Electron Oxidation Reaction of Aromatic Compounds Adsorbed on a TiO_2 Surface

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Abstract: The TiO_2 photocatalytic one-electron oxidation mechanism of aromatic sulfides with a methylene bridging group (-$(CH_2)_n$-, $n=0$–4) between the 4-(methylthio)phenyl chromophore and the carboxylate binding group on the surface of a TiO_2 powder slurried in acetonitrile (MeCN) has been investigated by time-resolved diffuse reflectance (TDR) spectroscopy. The electronic coupling element (H_{DA}) between the hole donor and acceptor, which was estimated from the spectroscopic characteristics of the charge transfer (CT) complexes of the substrates (S) and the TiO_2 surface, exhibited an exponential decline with the increasing of the methylene number of S. The determined decay factor (β) of 9 nm^{-1} also supports the fact that the 4-(methylthio)phenyl chromophore is separated from the TiO_2 surface. The efficiency of the one-electron oxidation of S adsorbed on the TiO_2 surface, which was determined from the relationship between the amount of adsorbates and the concentration of the generated radical cations, significantly depended on the H_{DA} value, but not on the oxidation potential of S determined in homogeneous solution.

Keywords: adsorption • electron transfer • photochemistry • radical ions • titanium oxide

Introduction

It is well-known that electron-hole pairs are generated when TiO_2 is irradiated by UV photons with an energy higher than the TiO_2 band-gap energy, and that these charge carriers can then migrate to the TiO_2 surface to initiate various redox reactions of the adsorbates. Such interfacial electron (hole) transfer reactions are fundamental processes in water-splitting reaction for hydrogen evolution,[1] the degradation of organic pollutants,[2–6] the surface wettability conversion,[7] and so on. The origins and reactivities of reactive species such as the photogenerated electrons and holes,[8–10] $O_2^{\cdot-}$,[11] H_2O_2,[12] and OH radicals[4,13–15] during the photocatalytic reactions have been investigated using various methods. For example, it is proposed that the surface hydroxyl groups react with the holes to form the surface-bound OH radicals, which then oxidize the surface adsorbates.[4] Recently, Nakamura and Nakato investigated the photooxidation of water adsorbed on the TiO_2 surface by in situ FT-IR absorption and photoluminescence measurements, and concluded that the oxygen photoevolution is initiated by a nucleophilic attack of a H_2O molecule on a photogenerated hole at a surface lattice O site, not by oxidation of a surface OH group by the hole.[16] Henderson and Onishi also clarified the surface sites associated with charge transfer and trapping during the photodecompostion of trimethyl acetic acid adsorbed on the rutile TiO_2 surface by using scanning tunneling microscopy and electron energy loss spectroscopy.[17] They directly estimated the extent of the electron trapping with the yields of the photodesorption fragments, which resulted from the hole transfer reactions between the photogenerated hole and trimethyl acetic acid in the absence of oxygen.

Although a great deal of research has been conducted on the photodecomposition of organic compounds during TiO_2 photocatalytic reactions, only a few quantitative studies have been reported for the one-electron oxidation processes of organic compounds adsorbed on a TiO_2 surface using time-resolved spectroscopy. A further understanding of the one-electron oxidation processes of organic compounds adsorbed on the TiO_2 surface may lead to novel developments of efficient photocatalytic systems specific to particular chemical species.

The time-resolved diffuse reflectance (TDR) method is a powerful tool for investigations of photocatalysis under various conditions.[10d–g,18–20] In a nonaqueous medium or air, it is expected that the TiO_2 particle surfaces are the main reaction fields for the direct oxidation of organic compounds. In

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fact, TDR spectroscopy has been used to study the interfacial charge transfer between adsorbate and TiO_2. Fox and co-workers studied the oxidation processes of various organic compounds and concluded that many oxidation reactions appear to occur by direct hole transfer from the photo-excited TiO_2 powder to organic compounds adsorbed on the TiO_2 surface in acetonitrile.[19]

Recently, we investigated the one-electron oxidation reactions of several aromatic compounds, such as aromatic sulfides and biphenyl derivatives, adsorbed on the TiO_2 surface in acetonitrile (MeCN) by using nano-second TDR spectroscopy.[20a–c] We successfully evaluated the efficiencies of the one-electron oxidation reactions of substrates (S) from the relationship between the amounts of S adsorbed on the TiO_2 surface and the concentrations of the generated radical cations of S. We also estimated the electronic coupling elements (H_{DA}) between S and TiO_2 by steady-state diffuse reflectance measurements and found that the efficiency of the one-electron oxidation significantly depends on H_{DA}.[20b] However, it is not always easy to determine the crucial factor in the one-electron oxidation processes of S adsorbed on the TiO_2 surface due to the difficulty in varying the fundamental parameters, the distance between the hole donor and acceptor (d_{DA}), H_{DA}, and the free energy change (ΔG_{HT}) for a hole transfer (HT) reaction in an independent and quantifiable manner. Such studies were performed for the electron-transfer (ET) reaction from methylene-bridged molecular adsorbates or tripodal sensitizers to semiconductor nanocrystalline films.[21,22] For example, Lian et al. investigated the relative rates of photoinduced interfacial ET as a function of the methylene bridge length (number of methylene groups: $n=1$–5).[21] They observed a breakdown in the exponential dependence of the rate on the bridge length for $n=1$ and 2. This breakdown provides a strong evidence for the possible change in the mechanism from the nonadiabatic limit to the adiabatic limit.

In the present study, we investigated the one-electron oxidation of aromatic sulfides with a methylene bridging group ($-(CH_2)_n-$, $n=0$–4) between the 4-(methylthio)phenyl chromophore and the carboxylate binding group (see Figure 1) during TiO_2-photocatalytic reactions by using TDR spectroscopy. The efficiencies of the one-electron oxidation reactions of S are evaluated from the relationship between the concentrations of the radical cations generated from the one-electron oxidation reactions by the photogenerated holes in the TiO_2 particles and the amount of adsorbates. The effects of the oxidation potentials of S and H_{DA} on the efficiency of the one-electron oxidation reaction are discussed along with data previously obtained for other aromatic compounds.

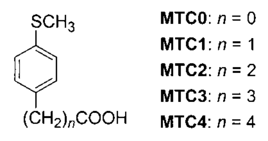

Figure 1. Molecular structures of substrates.

Results and Discussion

Langmuir adsorption isotherms: Figure 2 shows the Langmuir adsorption isotherms of S on the TiO_2 surface in MeCN at 22 °C.

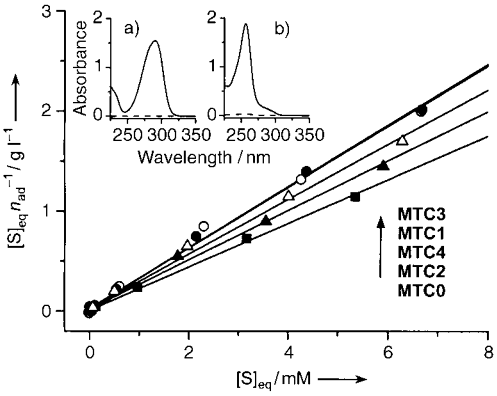

Figure 2. Langmuir adsorption isotherms of **MTC0** (■), **MTC1** (○), **MTC2** (▲), **MTC3** (●), and **MTC4** (△) on the TiO_2 powder in MeCN. Inset: steady-state UV absorption spectra of **MTC0** (0.5 mM) a) and **MTC3** (1.5 mM) b) in MeCN at room temperature. Solid lines indicate the spectra observed for substrates in bulk MeCN. Broken lines indicate those observed for substrates after reaching the adsorption equilibrium in MeCN.

According to the Langmuir adsorption models,[23–25] the amount of equilibrium adsorption, n_{ad}, can be expressed by the following Equation (1):

$$[S]_{eq}/n_{ad} = a \cdot [S]_{eq} + b \qquad (1)$$

where $[S]_{eq}$ is the equilibrium S concentration in the bulk solution, $a = L/n_s$ is the reciprocal amount of adsorbate for a monolayer coverage and $K_{ad} = a/b$ is the equilibrium constant for surface adsorption. The n_{ad} values were calculated from the difference in the absorbance with and without TiO_2 powder in MeCN solutions. The UV absorption spectra observed for **MTC0** (a) and **MTC3** (b) are shown in the inset of Figure 2 as representative examples. For example, Figure 2b shows the absorption spectra of 1.5 mM (M ≡ mol dm^{-3}) **MTC3** in bulk MeCN (solid line) and **MTC3** in MeCN after reaching the adsorption equilibrium with the surface of the TiO_2 particles (broken line). The TiO_2 particles in solution were completely removed by centrifugation (10000 rpm, 10 min). The absorption spectrum absorbance of **MTC3** in MeCN after reaching the adsorption equilibrium indicated a reduction of 98 % compared to that of **MTC3** in MeCN in the absence of TiO_2 powder. This result clearly suggests that the **MTC3** is strongly adsorbed on the TiO_2 surface in MeCN. The obtained K_{ad} and ns values for S are summarized in Table 1. The K_{ad} values of $(2.9 \pm 1.0) \times 10^4$ and $(1.1–1.2 \pm 0.6) \times 10^4\,M^{-1}$ were determined for **MTC0** and **MTC1–4**, respectively. These values are greater than those observed for 4-(methylthio)phenyl methanol and the hydroxyl-substituted biphenyls,[20a–c] suggesting that the -COOH group is strongly adsorbed on the TiO_2 surface compared

Table 1. Equilibrium constants of adsorption (K_{ad}) and the amount of saturated sites (n_s) for S obtained from Langmuir plots shown in Figure 2.

Substrate	K_{ad} [10^4 M^{-1}]	n_s [10^{-4} mol g^{-1}]
MTC0	2.9 ± 0.6	2.2 ± 0.2
MTC1	1.2 ± 0.4	1.6 ± 0.2
MTC2	1.1 ± 0.4	2.0 ± 0.2
MTC3	1.1 ± 0.4	1.6 ± 0.2
MTC4	1.1 ± 0.4	1.8 ± 0.2

with the -OH group. The relatively large K_{ad} value for **MTC0**, compared with those for **MTC1–4**, is mainly due to the strong electronic interaction between S and the TiO_2 surface. This tendency is quite consistent with that observed for the hydroxyl-substituted biphenyls adsorbed on the TiO_2 surface.[20b]

Formation of CT complexes between the substrates and TiO_2 surface: Figure 3 shows the steady-state diffuse reflectance difference spectra observed for TiO_2 samples containing **MTC0**, **MTC1**, and **MTC3** (10 mM) at room temperature. The delta absorbance value (ΔAbs.) is defined as the difference in the absorbances of the spectra observed for samples in the presence and the absence of S. As shown in the inset of Figure 3, good linear relationships between ΔAbs. and n_{ad} were observed for all the substrates, clearly indicating the formation of a charge transfer (CT) complex between S and the TiO_2 surface. These CT bands were observed for all the substrates and were very similar to that observed for catechol as reported elsewhere.[24,26]

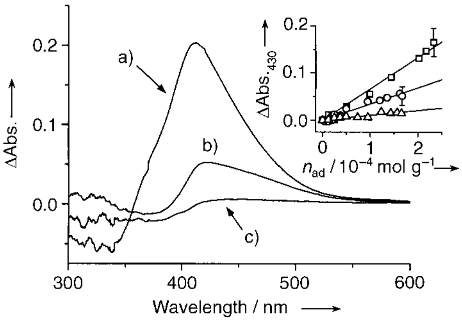

Figure 3. Steady-state diffuse reflectance difference spectra observed for the TiO_2 slurries containing a) **MTC0**, b) **MTC1**, and c) **MTC3** (10 mM) at room temperature (ΔAbsorbance = Absorbance (TiO_2 + S) − Absorbance (TiO_2)). Inset: the relationship between ΔAbsorbance (ΔAbs.) at 430 nm and the amount of adsorbates (n_{ad}) for **MTC0** (□), **MTC1** (○), and **MTC3** (△).

In a two-state model, a simple evolution of the transition moment, using Mulliken's approach of donor–acceptor systems, yields Equation (2) according to Hush,[27]

$$H_{AD} = \frac{2.06 \times 10^{-3} (\nu_{CT} \varepsilon_{CT} \Delta\nu_{1/2})^{1/2}}{d_{DA}} \tag{2}$$

where ν_{CT}, $\Delta\nu_{1/2}$, and ε_{CT} are the energy of the spectral band (in cm^{-1}), its full width at half-height (in cm^{-1}), and the molar extinction coefficient (in M^{-1}cm^{-1}), respectively. As shown in Figure 4a, the "effective" distance between TiO_2 as a hole-donor and S as a hole-acceptor (d_{DA}) can be estimated by Equation (3),[28]

$$d_{DA} = 0.5 + 0.127 \times n \text{ [nm]} \tag{3}$$

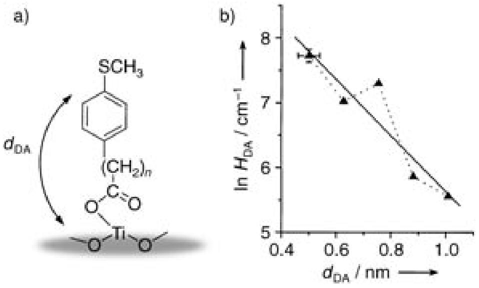

Figure 4. a) Model of substrates adsorbed on the TiO_2 and b) the relationship between H_{DA} and d_{DA}.

where n is the number of methylenes in the alkane chain and 0.5 nm is d_{DA} evaluated for the structure of **MTC0** from the PM3 molecular orbital calculation.[29]

As mentioned above, good linear relationships between ΔAbs. and n_{ad} were observed for all the substrates. These results clearly indicated that almost every S molecules yield CT complexes with the TiO_2 surface in the present S concentrations. Therefore, we estimated the ε_{CT} values from the quantitative relationship between ΔAbs. and n_{ad} by using the ε_{CT} value (5×10^4 M^{-1}cm^{-1} at 400 nm) for the catechol–TiO_2 CT band as a reference.[26] The spectroscopic parameters and H_{DA} values determined for the S–TiO_2 complexes are summarized in Table 2.

Figure 4b shows the relationship between d_{DA} and H_{DA}. The d_{DA} dependence of H_{DA} is usually given by Equation (4),[30]

$$H_{DA} \propto \exp(-\frac{\beta}{2} \cdot d_{DA}) \tag{4}$$

where β is a decay parameter which depends on the intervening atomic and molecular structure. A linear relationship between d_{DA} and $\ln H_{DA}$ was obtained, suggesting that H_{DA} depends on d_{DA} in accordance with Equation (4). We then determined the β value of 9 ± 1 nm^{-1} from Equation (4); this value indicates that the 4-methylthiophenyl chromophore is well separated from the TiO_2 surface by the methylene bridging group. The determined β value is closer to those (5–9 nm^{-1}) calculated for the electronic interaction through saturated alkane chains via the superexchange model, while larger β values (~30 nm^{-1}) are expected for a through-space pathway.[31] In the present systems, therefore, the methylene bridges play an important role in assisting the

Table 2. Spectroscopic parameters and the coupling elements (H_{DA}) of S–TiO$_2$ complexes.

Substrate	ν_{CT} [cm^{-1}]	$\Delta\nu_{1/2}$ [cm^{-1}]	ε_{CT} [10^3 M^{-1}cm^{-1}][a]	d_{DA} [nm][b]	H_{DA} [10^3 cm^{-1}]
MTC0	24300	4230	2.9 ± 0.2	0.5 ± 0.05	2.3 ± 0.2
MTC1	23700	3940	1.3 ± 0.2	0.63	1.2 ± 0.3
MTC2	23700	4060	3.0 ± 0.4	0.75	1.7 ± 0.3
MTC3	23300	3900	0.25 ± 0.1	0.88	0.4 ± 0.2
MTC4	23300	3900	0.18 ± 0.1	1.0	0.3 ± 0.1

[a] Estimated from the quantitative relationship between ΔAbs. and n_{ad} using the ε_{CT} value (5×10^4 M^{-1} cm^{-1} at 400 nm) for the catechol–TiO$_2$ CT band as a reference.[26] [b] Estimated from $d_{DA} = 0.5 + 0.127 \times n$ (nm), where n is the number of methylenes in the alkane chain and 0.5 nm is d_{DA} evaluated from the PM3 molecular orbital calculation for the structure of **MTC0**.

electronic interaction between S and the TiO$_2$ surface as suggested elsewhere.[21]

Interestingly, we also observed an unusual oscillation in the diminution of H_{DA} with the chain length. Theoretical studies predict that the dependence of H_{DA} on the number of spacers in the short alkyl chains deviates from the exponential and oscillates between odd and even n values.[32] In brief, this effect arises from taking a linear combination of powers of the positive and negative eigenvalues corresponding to the various electronic states on the bridge. In the present systems, a similar odd–even oscillation in the diminution of H_{DA} was observed, as a carbon atom of -COOH group being bound to the TiO$_2$ surface was included in the n value.[33]

One-electron oxidation reaction of adsorbates: TDR absorption spectra were observed during the laser photolysis of TiO$_2$ with 355 nm light (1.5 mJ pulse^{-1}, 1 Hz) in the absence and presence of S in MeCN at room temperature.

Figure 5 shows the TDR spectra obtained during the laser photolysis of TiO$_2$ with the 355 nm light in the presence of S in MeCN. The transient absorption band at 450–650 nm immediately appeared after the laser flash. The obtained TDR spectra were quite consistent with the transient absorption spectra attributed to the radical cations of S ($S^{\bullet+}$) observed during the 355 nm laser flash photolysis of chloranil in the presence of S in MeCN and during the pulse radiolysis of an N$_2$O-saturated aqueous solution in the presence of **MTC0**[34] or **MTC1**,[35] although the spectral shapes were broader than those obtained in the bulk MeCN. These broad spectra clearly indicate the interaction between $S^{\bullet+}$ and the TiO$_2$ surface.

As mentioned in the Introduction, TiO$_2$ particles generate the valence band hole (h^+_{VB}) and the conduction band electron (e^-_{CB}) during the band gap excitation [Eq. (5)],

$$TiO_2 \xrightarrow{h\nu} h^+_{VB} + e^-_{CB} \qquad (5)$$

After their generation, both the electrons and holes are rapidly trapped in the surface states of the TiO$_2$ particles within sub- or a few picoseconds [Eq. (6) and (7), respectively],

$$h^+_{VB} \rightarrow h^+_{tr} \qquad (6)$$

$$e^-_{CB} \rightarrow e^-_{tr} \qquad (7)$$

These photogenerated carriers then participate in the redox processes at the surface. The fast recombination kinetics of the untrapped or trapped charge carriers have been studied in detail by several groups.[8c,d,10d,10e] Although most trapped charge carriers quickly recombine, that is, within less

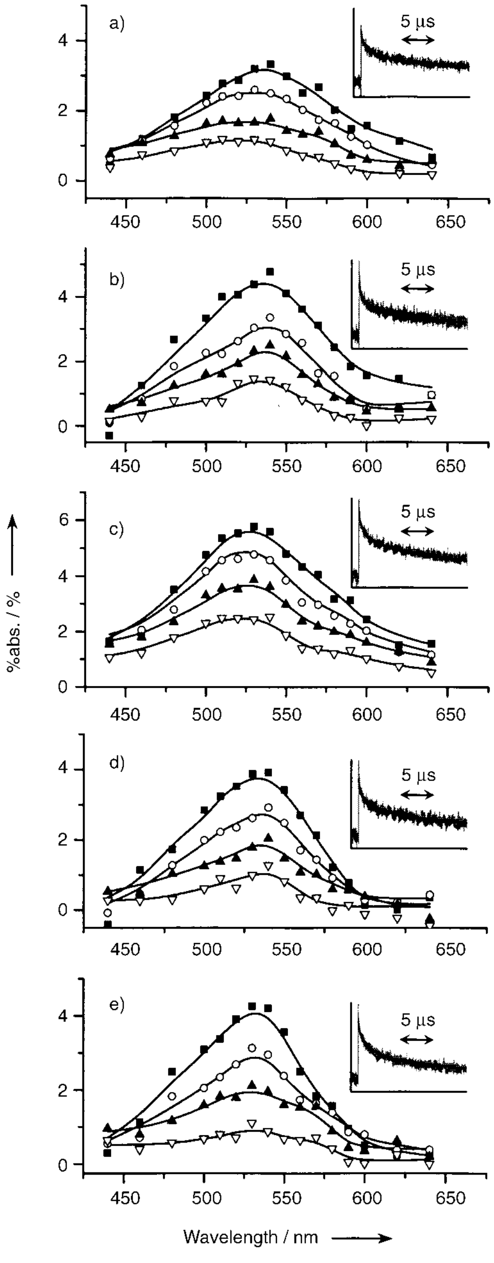

Figure 5. TDR spectra attributed to $S^{\bullet+}$ observed at 0.1 (■), 0.5 (○), 2 (▲), and 5 µs (▽) after the laser flash during the 355 nm laser photolysis of TiO$_2$ powder in the presence of a) **MTC0** (0.5 mM), b) **MTC1** (2 mM), c) **MTC2** (2 mM), d) **MTC3** (2 mM), and e) **MTC4** (2 mM) in MeCN. Inset: the %abs. at 540 nm versus time after a laser flash during the 355 nm laser flash photolysis of TiO$_2$ powder. Solid lines indicate the results fitted by the stretched exponential function.

than 30 ps [Eq. (8)],

$$e_{tr}^{+} + h_{VB}^{+}(h_{tr}^{+}) \rightarrow \text{heat} \quad (8)$$

Although most charge carriers quickly recombine, a minority that trapped at the surface of the particles will be available for reactions with adsorbates such as a surface-bound OH^- and O_2. A trapped positive hole, such as a surface-bound OH radical, typically oxidizes an organic molecule and thus induces its further oxidative degradation.

According to the Marcus theory, the free energy change for an HT (ΔG_{HT}) from holes in the TiO_2 particle to S is simply given by Equation (9),[30]

$$\Delta G_{HT} = E_S - E_{ox} \quad (9)$$

where E_S and E_{ox} are the oxidation potentials of S and the oxidizing species, respectively. The E_S values for S are summarized in Table 2. It is clear that **MTC0** can be hardly oxidized by the surface-bound OH radical which has E_{ox} value of about 1.5 V versus NHE in water.[13] Therefore, we assume that the h_{VB}^{+} or the shallow trapped positive holes (h_{tr}^{+}) are the main oxidizing species in the present systems as given by Equation (10),

$$h_{VB}^{+}(h_{tr}^{+}) + S \rightarrow S^{\cdot+} \quad (10)$$

where h_{VB}^{+} has an E_{ox} of 2.66 V versus NHE which is a potential of the valence band edge.[36]

The decay kinetics of $S^{\cdot+}$ is worth clarifying, because the efficiency of the photocatalytic reaction is significantly dependent on the interfacial charge recombination rate which competes with many others. The charge recombination reaction between the trapped electrons and $S^{\cdot+}$ was influenced by numerous factors, for example, the relaxation time from the shallow to deeply trapped states, the redox potentials of the substrates, and the distance between the electron acceptor and donor.[37] As shown in the inset of Figure 5, the observed time traces were well reproduced using a stretched exponential function ($\%\text{abs.} \propto \exp(-(t/\tau)^{\gamma})$, where τ is the average lifetime and γ is a heterogeneous parameter).[38] For example, the τ values of 3.9 and 3.7 μs and the γ values of 0.32 and 0.40 were determined for **MTC1** (2 mM) and **MTC4** (2 mM), respectively. Interestingly, the obtained τ values are almost the same in spite of the difference in d_{DA}, whereas the efficiencies of the one-electron oxidation are quite different as presented in the next section. Recent transient absorption demonstrates that e_{tr}^{-} immediately reacted with scavenger molecules, while the free e_{CB}^{-} reacted very slowly because these are distributed in the bulk.[10h] We also observed almost the same signal traces for the oxygen and argon gas-saturated samples, suggesting that $S^{\cdot+}$ mainly recombines with e_{CB}^{-} in the present time regime. Therefore, it seems that the observed insensitivity of τ to d_{DA} results from the long back ET distance between the surface-bound $S^{\cdot+}$ and e_{CB}^{-} in the bulk TiO_2 particles, where the average primary particle size is 21 nm, compared with d_{DA} between S and the TiO_2 surface (0.5–1.0 nm). In such a case, the charge recombination (CR) rate would be limited by the motion of electrons.

One-electron oxidation mechanisms: In the present experiments, it is possible to extract the relative change in the $S^{\cdot+}$ concentration from the initial signal intensity ($\%\text{abs.}^{t=0}$) due to the fact that the signal intensity was found to be approximately proportional to the transient concentrations, although we do not know the absolute concentration of $S^{\cdot+}$.[18]

Figure 6 shows the relationship between n_{ad} and $\%\text{abs.}^{t=0}/\varepsilon^{\cdot+}$, where $\varepsilon^{\cdot+}$ is the molar extinction coefficient of $S^{\cdot+}$. The $\varepsilon^{\cdot+}$ values of $S^{\cdot+}$ were evaluated from the transient absorption spectra observed during the 355 nm laser flash photolysis of chloranil in the presence of S in bulk MeCN and are summarized in Table 3.

Table 3. Spectroscopic parameters obtained by TDR measurements, molar extinction coefficients of $S^{\cdot+}$ ($\varepsilon^{\cdot+}$), and the oxidation potentials of substrates (E_S).

Substrate	λ_{max}^{TDR} [nm]	$\varepsilon^{\cdot+}$ [$10^3 M^{-1} cm^{-1}$] (λ_{max} [nm])[a]	E_S [V vs NHE]
MTC0	540	2.6 ± 0.2(545)	1.86
MTC1	540	4.4 ± 0.3(545)	1.67
MTC2	535	5.6 ± 0.3(545)	1.63
MTC3	540	5.8 ± 0.3(545)	1.60
MTC4	540	5.8 ± 0.3(545)	1.60

[a] Determined from the transient absorption spectra attributed to $S^{\cdot+}$ observed during the 355 nm laser flash photolysis of chloranil in the presence of S in MeCN.[39]

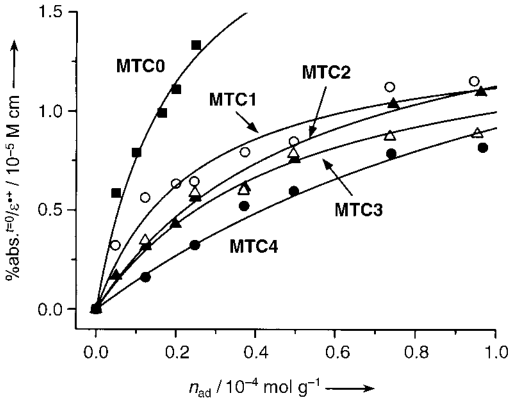

Figure 6. The relationship between the initial transient signal intensity ($\%\text{abs.}^{t=0}$) corrected by $\varepsilon^{\cdot+}$ values and n_{ad} for **MTC0** (■), **MTC1** (○), **MTC2** (▲), **MTC3** (△), and **MTC4** (●). The lines are arbitrarily.

As shown in Figure 6, the $\%\text{abs.}^{t=0}$ values increased with the increasing of n_{ad} at the present S concentration, suggesting that $S^{\cdot+}$ is generated by a bimolecular reaction with the photogenerated oxidizing species on the TiO_2 surface. A similar n_{ad} dependence of $\%\text{abs.}^{t=0}$ is observed for other systems.[20] As shown in Figure 7, because the HT reaction rate (k_{HT}) from the photogenerated holes (h^+) in the TiO_2 particles to S competes with the fast CR reaction rate (k_{CR}), the

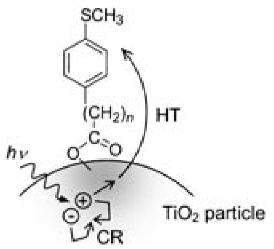

Figure 7. Schematic image of the hole transfer (HT) from the photogenerated holes (h^+) to S adsorbed on the TiO_2. CR denotes the charge recombination between the photogenerated electrons (e^-) and h^+.

quantum yield of $S^{\cdot+}$ generated by HT (ϕ_{HT}) is tentatively given by Equation (11),[6]

$$\phi_{HT} = \frac{k_{HT}\cdot n_{ad}}{k_{CR}+k_{HT}\cdot n_{ad}} \tag{11}$$

Because $k_{CR} \gg k_{HT} \times n_{ad}$, the ϕ_{HT} values are approximately proportional to the n_{ad} values. The observed relationship is quite consistent with that predicted from Equation (11).

As clearly indicated in Figure 6, the efficiency of the one-electron oxidation is in the order **MTC0** > **MTC1** > **MTC2** ≥ **MTC3** > **MTC4**. Here, we define the efficiency factor (α) for the one-electron oxidation of S adsorbed on the TiO_2 surface by Equation (12)[20b]

$$\alpha = \frac{\%\text{abs.}^{t=0}}{\varepsilon^{\cdot+}}\cdot\frac{1}{n_{ad}} \tag{12}$$

The α values were determined from the initial slopes of the solid lines shown in Figure 6 because the linearity for the actual absorptions can be satisfied only when %abs. is below 10% as suggested elsewhere.[16]

In terms of the semiclassical ET theory,[30] the rate constant (k_{ET}) for a nonadiabatic ET reaction can be expressed as a product of the thermally averaged Franck-Condon (FC) factor and an electronic factor which is proportional to the square of the H_{DA} between the electron donor and acceptor as shown by Equation (13),

$$k_{ET} = \frac{4\pi^2}{h}(H_{DA})^2\,\mathrm{FC} \tag{13}$$

The thermally averaged FC factor, which depends on the driving force (ΔG_{ET}) for ET and the reorganization energy (λ) accompanying ET, is given by Equation (14) in the classical limit,

$$\mathrm{FC} = \frac{1}{\sqrt{4\pi\lambda RT}}\exp\left[-\frac{\lambda+\Delta G_{ET})^2}{4\lambda R}\right] \tag{14}$$

Therefore, we examined the ΔG_{HT} dependence on the α values. As given by Equations (9), (13), and (14), it is expected that the α values increase with the decreasing of the ΔG_{HT} values, that is, with the increasing of the driving force for the HT reactions. However, as shown in Figure 8, the α values decreased with the decreasing of the ΔG_{HT} values estimated from Equation (9) and E_{ox} of 2.66 V versus NHE for h^+_{VB},[36] while those previously obtained for the hydroxyl-substituted biphenyls increased with the decreasing of the ΔG_{HT} values, although we have no data for E_S values for S adsorbed on the TiO_2 surface under the same conditions. As reported elsewhere, the redox potential of adsorbate strongly depends on the electronic interaction between S and TiO_2 surface.[22c] If E_S decreases or increases with increasing H_{DA}, however, the significant difference in the α values cannot be explained by E_S.

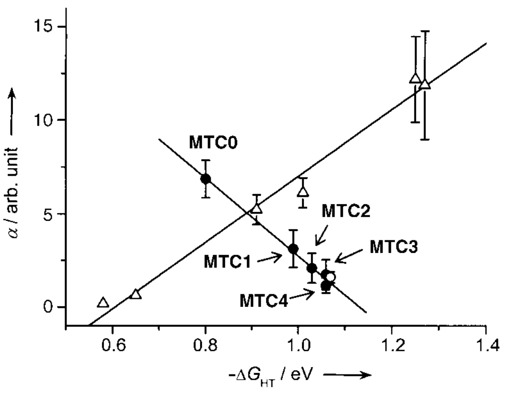

Figure 8. The relationship between the efficiency factor (α) determined for **MTC0–4** (●), 4-(methylthio)phenyl methanol (○),[20a] and biphenyl derivatives (△)[20b] and the free energy change for HT (ΔG_{HT}) estimated from $\Delta G_{HT} = E_S - E_{ox}$, where E_S and E_{ox} are the oxidation potentials of S and h^+_{VB}, respectively.

Next, we examined the relationship between H_{DA} and α. As shown in Figure 9, the α values significantly increased with the increasing of the H^2_{DA} values at H_{DA} < 2000 cm^{-1} and were insensitive to H^2_{DA} values at H_{DA} > 2000 cm^{-1}. In the non-adiabatic regime,[30] it is expected that the HT rate depends on E_S as well as H_{DA}. In fact, as shown in Figure 8, the α values obtained for **MTC3** and **MTC4** are much higher than those for 4-biphenylmethanol and 4-biphenylethanol which have high E_S values (2.01 and 2.08 V vs NHE, respectively) in spite of similar H_{DA} values (730 and 430 cm^{-1}, respectively).[20b] Therefore, the increase in the α values at H_{DA} < 2000 cm^{-1} provides evidence for the non-adiabatic mechanism.

An alternative description of the ET rate constant is required when H_{DA} is large enough and is referred to the adiabatic limit. In this limit, the rate constant is no longer controlled by the magnitude of H_{DA}, but rather by the frictional coupling between the changing charge distribution of the reactants and the polarization of the surrounding medium. This frictional coupling is most often characterized by the characteristic relaxation time of the medium, τ_s, or the viscosity, η, of the medium.[40] When the frictional coupling to the medium is very strong, the rate constant decreases by $1/\tau_s$ or $1/\eta$. The strong coupling, or adiabatic regime, is often used to describe short-range electron transfer and is viewed as solvent-controlled motion in a single electronic state. Unfortunately, we cannot easily discuss the solvent effects on the H_{DA} dependence on the α values, because the CT band character significantly depends on the nature of the solvents.

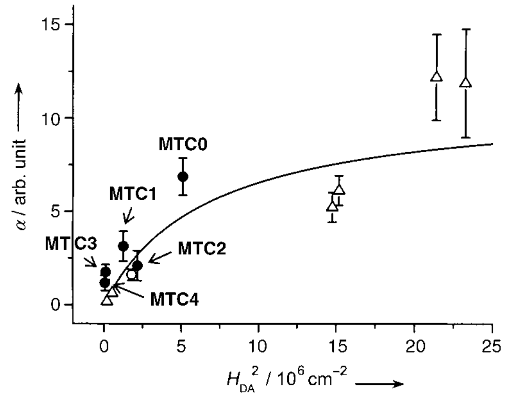

Figure 9. The relationship between the efficiency factor (α) determined for **MTC0–4** (●), 4-(methylthio)phenyl methanol (○), and biphenyl derivatives (△) and the electronic coupling element between the hole donor–acceptor (H_{DA}) estimated from Equation (2). The lines are arbitrarily.

Although it is difficult to know all the facts concerning the one-electron oxidation mechanisms due to the heterogeneity in the systems, We believe that the observed H_{DA} dependence of the α values clearly suggest a gradual transition of the one-electron oxidation mechanisms from the non-adiabatic to the adiabatic regime or other influences on the one-electron oxidation mechanisms such as a significant shift in the flat band potentials of TiO_2 particles due to the strong interaction between adsorbates and the TiO_2 surface.

Conclusion

In summary, we have investigated the TiO_2 photocatalytic one-electron oxidation mechanisms of aromatic sulfides involving -COOH terminal groups adsorbed on the surface of a TiO_2 powder slurried in MeCN by using TDR spectroscopy. The H_{DA} estimated from the spectroscopic characteristics and structures of the CT complexes of S and the TiO_2 surface, exhibited an exponential decline with the increasing of the d_{DA} value, although a slight oscillation between the even and odd n was observed. The determined β value of $9 \pm 1\,nm^{-1}$ clearly suggests that the 4-(methylthio)phenyl chromophore is separated from the TiO_2 surface with the increasing of the methylene number. The efficiencies of the one-electron oxidations of S adsorbed on the TiO_2 surface determined from the relationship between the amount of adsorbates and the concentration of the generated radical cations significantly depended on H_{DA}, but not E_S. Along with the reported ones, the α values dramatically increased with the increasing of the H_{DA}^2 values at $H_{DA} < 2000\,cm^{-1}$ and were insensitive to the H_{DA}^2 values at $H_{DA} > 2000\,cm^{-1}$. These experimental results suggest that H_{DA} plays an important role in the efficiency of the one-electron oxidation of S adsorbed on the TiO_2.

Experimental Section

Materials: The TiO_2 powder (P25, Japan Aerosil) was a mixture of rutile (20%) and anatase (80%) with a BET surface area of $50\,m^2g^{-1}$ and an average primary particle size of 21 nm. 4-(Methylthio)benzoic acid (**MTC0**) and 4-(methylthio)phenyl acetic acid (**MTC1**) were purchased from Aldrich and recrystallized from ethanol. The synthetic procedures of 3-(4-methylthiophenyl)propionic acid (**MTC2**), 4-(4-methylthiophenyl)butyric acid (**MTC3**), and 5-(4-methylthiophenyl)pentanoic acid (**MTC4**) are described below. Fresh MeCN (Nakarai Tesque, spectral grade) was used as the solvent without further purification.

Synthetic procedures: 3-(4-Methylthiophenyl)propionic acid (**MTC2**), 4-(4-methylthiophenyl)butyric acid (**MTC3**), and 5-(4-methylthiophenyl)-pentanoic acid (**MTC4**) were synthesized by the following procedures. Melting points (mp) were determined with a Yanaco micro-melting point apparatus and are uncorrected. NMR spectra were recorded on a JEOL JMN EX-270 (270.05 MHz) spectrometer using tetramethylsilane as internal standard; J values in Hz. Mass spectra were obtained on a JEOL JMS-M600 mass spectrometer.

3-(4-Methylthiophenyl)propionic acid (MTC2): A mixture of 4-(methylthio)benzaldehyde (Tokyo Kasei) (15.79 g), malonic acid (12.57 g), and piperidine (5 drops) in anhydrous pyridine (30 mL) was heated at 100 °C for 2 h. The mixture was then heated under reflux for 1 h to remove the excess malonic acid and cooled to room temperature. The reaction mixture was added to hydrochloric acid, and a pale yellow precipitate (olefin, **2a**) formed. Compound **2a** (16.85 g) was collected by filtration. A suspension of palladium-activated carbon (Pd 10%) (Wako) (2.0 g) in ethyl acetate (20 mL) and ethanol (60 mL) was stirred overnight at room temperature under a hydrogen atmosphere. To the suspension was added a solution of the olefin (2 g) in ethyl acetate (60 mL) and the mixture was stirred under a hydrogen atmosphere for 7 d at room temperature. After the Pd catalyst was filtered off, the solvents were removed under vacuum. The crude product was purified by distillation under reduced pressure (175–185 °C) to yield **MTC2** as a colorless solid (100 mg). M.p. 100.5–101.5 °C; ^{1}H NMR (270 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 7.17$ (AA′BB′ type signals, 4H, ArH), 2.92 (t, $J = 7.6$ Hz, 2H, CH_2), 2.66 (t, $J = 7.6$ Hz, 2H, CH_2), 2.47 (s, 3H, SCH_3); MS: m/z: calcd for $C_{10}H_{12}O_2S$: 196.27, found 196.2; elemental analysis calcd (%) for $C_{10}H_{12}O_2S$: C 61.20, H 6.16, S 16.34; found: C 61.16, H 6.03, S 16.36.

4-(4-Methylthiophenyl)butyric acid (MTC3): A solution of **MTC2** (160 mg), sulfuric acid (20–30 drops), and methanol (5 mL) in dichloromethane (20 mL) was heated under reflux overnight. The reaction mixture was washed with a saturated aqueous solution of $NaHCO_3$ and then dried over anhydrous sodium sulfate. The solvents were removed under vacuum to yield a liquid (methyl ester, **3a**) (4.25 g). $LiAlH_4$ (830 mg) was added in portions to a solution of the methyl ester (5.15 g) in anhydrous Et_2O (40 mL). After stirring overnight, the usual workup gave a yellow liquid (alcohol, **3b**) (2.72 g). A solution of PBr_3 (2 g) in a small amount of carbon tetrachloride was added dropwise into a solution of **3b** (2.72 g) in carbon tetrachloride (10 mL). The mixture was stirred overnight at room temperature, and water was then dropwise added to the reaction mixture. The ethereal extract was concentrated by using a vacuum evaporator and the residue was distilled under reduced pressure (175–185 °C) to yield yellow liquid (bromide, **3c**) (1.18 g). A solution of **3c** (780 mg) and a small amount of iodine in anhydrous ether (15 mL) was added to magnesium turnings (for Grignard) (100 mg) with a syringe under an argon atmosphere, and the mixture was stirred overnight at room temperature. The reaction mixture was powered onto crushed dry ice (300 g) in anhydrous Et_2O (50 mL). Evaporation of the ethereal solution gave a crude pale yellow solid. The crude acid was dissolved in an aqueous NaOH solution and the solution was filtered. Upon the addition of hydrochloric acid to the filtrate, a colorless solid formed. The precipitate was collected by filtration to yield **MTC3** as a colorless solid (160 mg). M.p. 82.0–82.5 °C; ^{1}H NMR (270 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 7.15$ (AA′BB′ type signals, 4H, ArH), 2.64 (t, $J = 7.7$ Hz, 2H, CH_2), 2.47 (s, 3H, SCH_3), 2.37 (t, $J = 7.4$ Hz, 2H, CH_2), 1.94 (q, $J = 7.4$ Hz, 2H, CH_2); MS: m/z: calcd for $C_{11}H_{14}O_2S_1$: 210.30, found 210.2; elemental analysis calcd (%) for $C_{11}H_{14}O_2S$: C 62.83, H 6.71, S 15.25; found: C 62.92, H 6.65, S 15.16.

5-(4-Methylthiophenyl)pentanoic acid (MTC4): A solution of *n*-butyl lithium (Nakarai Tesque, about 1.6 M (15 %) in hexane) (26 mL) under an argon atmosphere was dropwise added to a solution of 4-bromothioanisole (Tokyo Kasei) (4.06 g) in anhydrous Et_2O (50 mL). The mixture was stirred for 2 h. The reaction mixture was then dropwise added to a solution of 1,4-dibromobutane (Tokyo Kasei, 98 %) (21.6 g) in anhydrous Et_2O (15 mL) for 30 min with a syringe under an argon atmosphere, and the mixture was stirred overnight. An ether solution of an NH_4Cl saturated aqueous solution was dropped into the reaction mixture and the mixture was extracted with Et_2O. The extract was washed with a saturated aqueous NaCl solution, and dried over anhydrous sodium sulfate. The solvent and an excess of 1,4-dibromobutane were removed under vacuum, and the residue was distilled under reduced pressure (175–185 °C). The product was purified by column chromatography (hexane) to yield of pale yellow liquid (bromide, **4a**) (1.843 g). **MTC4** (150 mg) as a colorless solid was prepared from the bromide (907.2 mg) following the same procedure as **MTC3**: M.p. 79.0–80.0 °C; ^1H NMR (270 MHz, $CDCl_3$, 20 °C, TMS): $\delta = 7.14$ (AA′BB′ type signals, 4 H, ArH), 2.60 (t, $J = 6.9$ Hz, 2 H, CH_2), 2.47 (s, 3 H, SCH_3), 2.38 (t, $J = 6.9$ Hz, 2 H, CH_2), 1.66 (m, 4 H, CH_2CH_2); MS: *m/z*: calcd for $C_{12}H_{16}O_2S$: 224.32, found 224.2; elemental analysis calcd (%) for $C_{12}H_{16}O_2S$: C 64.25, H 7.19, S 14.29; found: C 64.12, H 7.07, S 14.26.

Cyclic voltammetry measurements: Cyclic voltammograms were obtained by using a conventional three-electrode system (BAS, CV-50W) in MeCN solution at room temperature. A platinum electrode was used as the working electrode and an $Ag/AgNO_3$ electrode was used as the reference electrode.

Steady-state UV/Vis absorption and diffuse reflectance spectral measurements: The steady-state UV/Vis absorption and diffuse reflectance spectra were measured by UV/Vis-NIR spectrophotometers (Shimadzu, UV-3100 and Jasco, V-570, respectively) at room temperature. The sample solutions containing TiO_2 powder (20 g dm^{-3}) were sonicated for 10 min, and the TiO_2 particles in solution were then completely removed by centrifugation (10 000 rpm, 10 min) using a high-speed microcentrifuge (Hitachi, himac CF16RX) at 22 °C for the UV absorption measurements. All procedures for the sample preparation were performed with shielding from the UV light.

The concentrations of the adsorbates in MeCN containing TiO_2 powder (20 g dm^{-3}) after reaching an adsorption equilibrium ($[S]_{eq}$) were determined from the steady-state UV absorption measurements. The amounts of adsorbates (n_{ad}, in mol g^{-1}) were estimated by using Equation (15),

$$n_{ad} = [S] \times \frac{\text{Abs.} - \text{Abs.}_{\text{-TiO}_2}}{\text{Abs.}} \tag{15}$$

where [S] is the concentration of S in the bulk MeCN, and Abs. and Abs.$_{\text{-TiO2}}$ represent the absorbances of S in the absence and presence of the TiO_2 powder, respectively.

Time-resolved diffuse reflectance (TDR) measurements: The TDR measurements were performed using the third harmonic generation (355 nm, 5 ns full width at half-maximum) from a Q-switched Nd^{3+}:YAG laser (Continuum, Surelite II-10) for the excitation operated with temporal control by a delay generator (Stanford Research Systems, DG535). In these experiments, the spot irradiated on the sample cell with a thickness of 2 mm was approximately 1 cm$^{“2}$. The reflected analyzing light from a pulsed 450-W Xe-arc lamp (Ushio, XBO-450) was collected by a focusing lens and directed through a grating monochromator (Nikon, G250) to a silicon APD (Hamamatsu Photonics, S5343). The transient signals were recorded by a digitizer (Tektronix, TDS 580D). The reported signals are averages of 20–30 events.

The absorption values (% absorption) were obtained by subtracting the absorption value observed in the absence of S from that observed in the presence of S. Here, % absorption (% abs.) is given by Equation (16),

$$\%\text{abs.} = \frac{R_0 - R}{R_0} \times 100 \tag{16}$$

where R and R_0 represent intensities of the diffuse reflected monitor light with and without excitation, respectively.[16]

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