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# An approach to estimating photocatalytic activity of $TiO_2$ suspension by monitoring dissolved oxygen and superoxide ion on decomposing organic compounds

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## Abstract

We proposed a novel method to analyze photocatalytic reaction of $TiO_2$ suspension by measuring the consumption process of dissolved oxygen (DO). The decay rates for DO consumption could be analyzed with Langmuir–Hinshelwood (L–H) kinetics as the effects of reactants such as ethanol and *iso*-propanol. Two parameters in the L–H kinetics, the maximum consumption rate $r_{max}$ and adsorption equilibrium constant $K_D$ were obtained. The rate constants, $k_t$ and $k_p$, which express $O_2$ consumption and $O_2$ reproduction, respectively, could be estimated from dependence of $r_{max}$ on excitation intensity. Participation of $O_2^{\bullet -}$ in the decomposition of alcohols was examined by measuring the amount of $O_2^{\bullet -}$. An increase of $O_2^{\bullet -}$ concentration was observed by the addition of a small amount of the reactants, and a decrease was observed for the reactant concentration of more than few mM. Based on these results, we analyzed the DO consumption process and suggested the applicability that the DO consumption efficiency can be used as a relative photonic efficiency to compare the differences in the photocatalytic activities and in the stabilities of reactants.
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*Keywords:* Photocatalysis; Dissolved oxygen; Active oxygen; Activity; Limonol chemiluminescence

## 1. Introduction

$TiO_2$ photocatalysis is developing into a popular technology to decompose and mineralize undesirable compound and pollutant in our surroundings [1]. On these decomposition and mineralization, $TiO_2$ photocatalysis consumes $O_2$. In earlier study on photocatalysis, this $O_2$ consumption was studied as "photo-adsorption" of $O_2$ [2]. The photo-adsorption of $O_2$ has been a general term of the consumption of $O_2$ by photocatalytic reaction. Actually, photocatalytic reaction should proceed simultaneously by reduction and oxidation. In general photocatalysis, $O_2$ in air is reduced to give $O_2^{\bullet -}$, while organic compounds are oxidized to form organic radicals which consume $O_2$ as well for further oxidation [3–5].

The formation of $O_2^{\bullet -}$ contributes to improving the photocatalytic activity to promote $e^-$–$h^+$ charge separation [6,7]. The details of the behavior of $O_2^{\bullet -}$ have been studied by luminol chemiluminescent (CL) probe method [8,9] and ESR spectroscopy [10]. According to the studies, the produced $O_2^{\bullet -}$ is adsorbed at the surface of $TiO_2$ and it becomes a steady amount during the irradiation [8,9]. The lifetime of $O_2^{\bullet -}$ after stopping UV irradiation was few seconds in air and several hundred seconds in water [8e, 9a,b] Some of the $O_2^{\bullet -}$ decay processes in different pH solution were observed by MIR-IR spectroscopy technique [11].

On disproportionation of $O_2^{\bullet -}$ and/or further reduction of $O_2^{\bullet -}$, $H_2O_2$ is produced from $O_2$ in the $TiO_2$ photocatalysis [7–14]. In addition, $H_2O_2$ can be also produced by a chain reaction of $O_2$ with the intermediate radicals of alcohol [3,4]. Details of the formation and reaction processes of $H_2O_2$ in $TiO_2$ photocatalysis have been studied more extensively than the behavior of $O_2$ and $O_2^{\bullet -}$. The produced $H_2O_2$ is oxidized to form $O_2^{\bullet -}$ and reduced to $OH^\bullet$. Although $H_2O_2$ has relatively

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high reactivity, $OH^{\bullet}$ is likely more considerable species to oxidize organic compounds [7,8,10,12–15].

As introduced above, despite we know that $O_2$ is necessary species as an electron donor to promote charge separation and as an oxidant to decompose organic molecules in $TiO_2$ photocatalysis, the behavior of $O_2$ has not been correlated with the photocatalytic activity of $TiO_2$ suspension. Although, oxygen consumption focusing on $O_2$ reduction was kinetically studied [16], the study on the kinetics of $O_2$ consumption process under whole photocatalysis with a reactant has not been fully carried out yet. In addition, since the behavior of active oxygen species in the photocatalytic oxidation with a reactant has not been analyzed from the quantitative points of view, the detailed reaction mechanism involving $O_2$ and active oxygen species in photocatalysis carries still unclear points.

In the present study, the amount of dissolved oxygen (DO) in $TiO_2$ photocatalytic system with a reactant is kinetically analyzed to obtain the information of reaction mechanism including $O_2$. Furthermore, we also report here the reaction of $O_2^{\bullet -}$ with the organic reactant as one of the DO consumption processes by observing the amount of $O_2^{\bullet -}$ produced in the $TiO_2$ photocatalysis. As model organic compounds, we employed ethanol and *iso*-propanol because the reaction mechanism of these alcohols has been widely studied [17–21] and their oxidation processes are different; ethanol oxidation process contains a chain reaction with $O_2$, whereas no chain reaction takes place in *iso*-propanol decomposition process [3,17–21].

## 2. Photocatalytic reaction model for oxygen consumption

The DO decay process in $TiO_2$ photocatalysis with a reactant was considered to obey the following reaction steps as illustrated in Scheme 1. Firstly, conduction band electron ($e^-$) and valence band hole ($h^+$) are induced by UV-light excitation (reaction (1)). Though some of them recombine each other in a $TiO_2$ particle (reaction (2)), the produced $e^-$ and $h^+$ react with $O_2$ (reaction (3)) and alcohols (ROH) (reaction (4)), respectively:

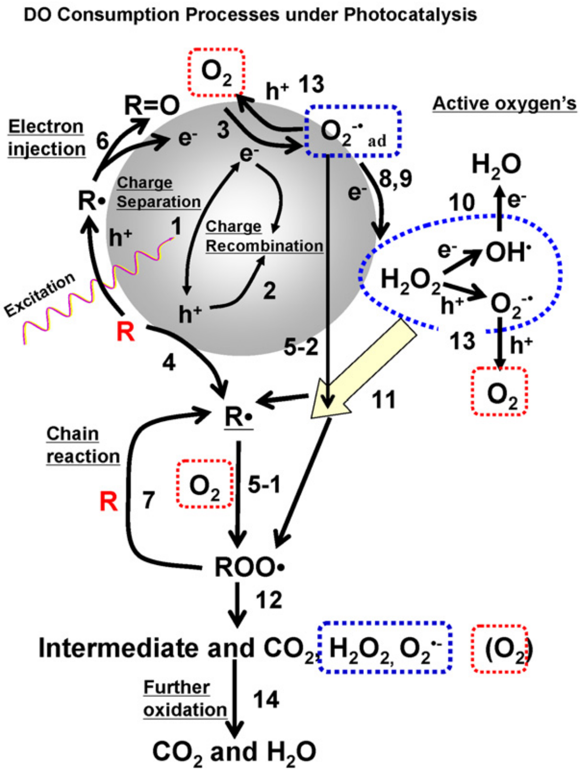
$$TiO_2 + h\nu \rightarrow Ti^{3+}(e^-) + h^+ \quad (1)$$

$$Ti^{3+}(e^-) + h^+ \rightarrow h\nu\,(\text{heat}) \quad (2)$$

$$O_2 + Ti^{3+}(e^-) \rightarrow Ti^{4+}\text{–}O_2^{\bullet -} \quad (3)$$

$$h^+ + ROH \rightarrow R^{\bullet}OH \quad (4)$$

where $R^{\bullet}OH$ is an intermediate radical of the reactant and reacts with $O_2$ to produce oxygenated radical intermediate, $ROO^{\bullet}$ (reaction (5.1)) [2–5]. Though a lot of researchers consider so-called OH radical reaction path, the formation of $OH^{\bullet}$ radical was not supported from EPR [22,23], and IR measurements [24]. We have also discussed the detection method of $OH^{\bullet}$ radicals previously [25]. Then we think that in $TiO_2$ photocatalytic reactions, $OH^{\bullet}$ radical is minor oxidative reaction species, and instead, valence band hole and trapped hole are major oxidative reaction species, especially, in the present condition as ethanol adsorption at the surface of $TiO_2$.



Scheme 1. DO consumption processes under photocatalysis.

It has been suggested that the reaction of $O_2^{\bullet -}$ with ROH is relatively disregarded. However, the $O_2^{\bullet -}$ produced by reaction (3) can react with $R^{\bullet}OH$ directly (reaction (5.2)) as has been reported [2–5]:

$$R^{\bullet}OH + O_2 \rightarrow ROO^{\bullet} \quad (5.1)$$

$$R^{\bullet}OH + O_2^{\bullet -} \rightarrow ROO^{\bullet} \text{ or other oxygenated radical intermediate} \quad (5.2)$$

Actually, radical intermediates $R^{\bullet}OH$ on $TiO_2$ photocatalytic oxidation of ethanol and *iso*-propanol produce $CH_3(CH^{\bullet})OH$ and $(CH_3)_2C^{\bullet}OH$, respectively [3,17–26]. The reaction rate of these radical intermediates with $O_2$ (reaction (5.1)) is very fast. That is, the bi-molecular rate constants are of diffusion limit; $k\,({}^{\bullet}CH_2OH + O_2) = 4.9 \times 10^9\,M^{-1}\,s^{-1}$ and $k\,((CH_3)_2C^{\bullet}OH + O_2) = 4.2 \times 10^9\,M^{-1}\,s^{-1}$ [26]. This reaction may compete with an electron injection into $TiO_2$ solid as expressed by reaction (6):

$$R^{\bullet}OH + TiO_2 \rightarrow R{=}O + H^+ + TiO_2\,(e_{CB}{}^-) \quad (6)$$

The redox potential $E_{1/2}$ for $CH_3CH^{\bullet}OH$ and $(CH_3)_2C^{\bullet}OH)$ are −0.94 and −1.06 V (versus NHE: at pH 7) [27], respectively, while the potential of the conduction band of $TiO_2$ is −0.81 V (versus NHE) calculated from −0.13 to 0.059 pH with a pH of 11.5 [28]. Then, the radical intermediates could inject an electron to the conduction band. The electron injection from intermediate radical is much faster than the reaction with $O_2$ since the surface of photocatalysts locates near the radical. In the present study, we supposed that the injected electrons increase the reduction of $O_2$

because there is no any other electron acceptor in the system. Thus, the reaction (6) produces $TiO_2$ ($e_{CB}^-$) which becomes $Ti^{3+}(e^-)$ in reactions (2) and (3). This process corresponds to the current doubling effect in photo-electrochemistry [29].

In addition, the $ROO^\bullet$ radical formed from $R^\bullet OH$ can induce $R^\bullet OH$ as reaction (7). That is, a chain reaction takes place [3], and $O_2$ is consumed with producing $H_2O_2$:

$$ROO^\bullet + ROH \rightarrow R{=}O + R^\bullet OH + H_2O_2 \qquad (7)$$

$H_2O_2$ ($HO_2^-$) is also produced by further reduction of $O_2^{\bullet-}$ (reactions (8) and (9)) [7–14]:

$$O_2^{\bullet-} + O_2^{\bullet-} + 2H^+ \rightarrow H_2O_2 + O_2 \qquad (8)$$

$$O_2^{\bullet-} + Ti^{3+}(e^-) + 2H^+ \rightarrow H_2O_2 \qquad (9)$$

Although the chain reaction originated from $H_2O_2$ has been suggested [3,4,7,12–16,21], we assume in the present stage that the chain reaction has no contribution to the decomposition because $H_2O_2$ diffuse from $TiO_2$ surface to the bulk solution [30]. However, some $H_2O_2$, which is produced from adsorbed $O_2$ as reactions (8) and (9) at the surface, might produce $OH^\bullet$ (reaction (10)) by the photocatalytic reduction. Then, this $OH^\bullet$ might react with the reactant and the intermediate (reaction (11)) [7–15].

$$H_2O_2 + Ti^{3+}(e^-) + H^+ \rightarrow OH^\bullet + H_2O \qquad (10)$$

$$\begin{aligned} &OH^\bullet + \text{reactant (and the intermediate)} \\ &\quad \rightarrow \text{further decomposition} \end{aligned} \qquad (11)$$

As mentioned above, the consumption of DO on photocatalytic reaction arises from a series of the reactions from (1) to (11). Notice here that the intermediate radicals $ROO^\bullet$ produced in reaction (5) and the intermediates produced by further decomposition (reaction (11)) have to be decomposed to $CO_2$ (reaction (12)):

$$\begin{aligned} &ROO^\bullet + \text{active oxygen}/h^+ \text{ and } e^- \\ &\quad \rightarrow CO_2 + \text{other intermediate} \end{aligned} \qquad (12)$$

Against to the consumption, $O_2$ molecule could be reproduced in $TiO_2$ photocatalysis according to reactions (13) and (14) [3–9]:

$$Ti^{4+}\text{–}O_2^{\bullet-} + h^+ \text{ (and trapped } h^+) \rightarrow O_2 + Ti^{4+} \qquad (13)$$

$$ROO^\bullet \rightarrow O_2 + \text{intermediate} \qquad (14)$$

This reaction (13) would be the main reaction to deactivate $O_2^{\bullet-}$ in the $TiO_2$ photocatalysis. To confirm the presence of reaction (13), it is necessary to analyze $O_2^{\bullet-}$. Based on the reactions from (1) to (14), which are shown in Scheme 1, the DO consumption process in $TiO_2$ photocatalysis with the reactant was kinetically analyzed in the present study.

## 3. Experimental

### 3.1. Materials and properties

P25 (Nippon Aerosil) $TiO_2$ was used as a photocatalyst in the present study. In order to remove the organic contaminates, $TiO_2$ photocatalyst was thinly placed on glass plate and exposed to a black light lamp at 354 nm for 120 h under ambient condition. After the treatment, $TiO_2$ powder was stocked in glass bottle under dark condition. MilliQ-water was used to prepare aqueous suspension. Every chemical reagent was used as received without further purification.

Adsorption coefficient $\alpha$ of $TiO_2$ suspensions was measured by UV–vis–NIR spectrophotometer (Shimadzu, UV-3600) equipped with integrating sphere assembly (Shimadzu, ISR-3100), which contains $BaSO_4$ as a reflectance reference. A 1 cm quartz cell of 1-mm path length was used according to the method reported by Bolton and co-worker [15].

### 3.2. Monitoring the consumption of dissolved oxygen (DO)

The behavior of DO under photocatalysis of $TiO_2$ suspension was monitored with a DO sensor (Central Kagaku Co., UC-12-SOL), which was connected to a computer. One hundred milliliters of long colorimetric bottle (as-one) was used to effectively irradiate UV-light to $TiO_2$ suspension.

Experimental procedure is as follows. $TiO_2$ suspension was prepared in 100 mL of 0.01 M NaOH solution (pH 11.5) in a flask. This suspension was sonicated for 10 min, and then transferred to the colorimetric bottle and was stirred vigorously for 30 min under ambient condition to attain an equilibrium DO condition. The DO sensor was then immersed into the suspension. The suspension was sealed by using a silicon cap. Since the suspension occupies fully the bottle, there is no space for air. This suspension was stirred vigorously during the experiment. UV-irradiation was carried out with four black light bulbs (Toshiba, FL10B). The light intensity up to 2.8 mW cm$^{-2}$ was changed by changing the number of UV-lamps. An electric fan was used to prevent the suspension from the temperature increase, and the bottle temperature was kept at 295–300 K.

### 3.3. Luminol chemiluminescent (CL) probe method

The formation of $O_2^{\bullet-}$ was observed by using luminol CL probe method with photon-counting system. Fifteen milligrams of $TiO_2$ powder was added into 3.5 mL of 0.01 M NaOH (4.3 g L$^{-1}$) solution of pH 11.5. This suspension was stirred vigorously for 10 min before UV irradiation and this stirring was continued during the UV irradiation. A Hd–Cd Laser (KIMMON, IK5652R-G) of a 30-mW specified power at the wavelength of 325 nm was used as an excitation light source. The laser beam was guided to the side face of the cell. After 10 s of laser irradiation, 50 μL of 7 mM luminol solution (0.01 M NaOH) was immediately injected by a micro syringe into the irradiated $TiO_2$ suspension. The CL intensity was measured with a photomultiplier tube which was mounted in a Peltier cooling box. The concentration of $O_2^{\bullet-}$ was estimated from the CL intensity, which was calibrated with $KO_2$ by the following procedure. DMSO solution of 18-crown-6-ether and $KO_2$ in the concentration ratio of 1.5:1 was injected into 3.5 mL of $TiO_2$ suspension containing 0.1 mM luminol under the dark. The temperature of the DMSO solution was tightly held to 296 K using water bath. Other details in the CL measurements have been described elsewhere [8].

## 4. Results

### 4.1. Effect of reactants on DO consumption

Fig. 1 shows decay of DO on photocatalytic decomposition of ethanol for various concentrations. The DO decay process obeyed zero-order reaction kinetics since the rate was constant during the decay. The DO decay rate, $r_{DO}$, was increased with increasing the concentration of ethanol added. When ethanol concentration was 5 mM, the DO was completely consumed in 20 min. The similar experiments were carried out for *iso*-propanol as a reactant. The decay process is composed of the reaction (5)–(14) as $O_2$ consumption and reproduction process.

In Fig. 2, the $r_{DO}$ was plotted as a function of the concentration of each reactant added. The obtained data apparently obeyed the Langmuir–Hinshelwood (L–H) kinetics (Eq. (15)):

$$\frac{1}{r_{DO}} = \frac{1}{r_{max}} + \frac{1}{r_{max} K_D [\text{Reactant}]} \tag{15}$$

Two parameters, maximum consumption rate ($r_{max}$) and an adsorption equilibrium constant ($K_D$) could be calculated by using the inverse plot of $r_{DO}$ against the inverse of the reactant concentration as shown at the inset in Fig. 2. The $r_{max}$ and $K_D$ obtained were 20 μM min$^{-1}$ and 6424 M$^{-1}$ for ethanol, 22 μM min$^{-1}$ and 4684 M$^{-1}$ for *iso*-propanol, respectively. By using these parameters, $r_{DO}$ are calculated and shown by curves in Fig. 2. The $r_{max}$ obtained from each reactant showed almost similar values. In contrast to the similarity of $r_{max}$, the $K_D$ obtained on the ethanol addition was slightly larger than that for *iso*-propanol. This may be attributable to an individual oxidation mechanism with each reactant.

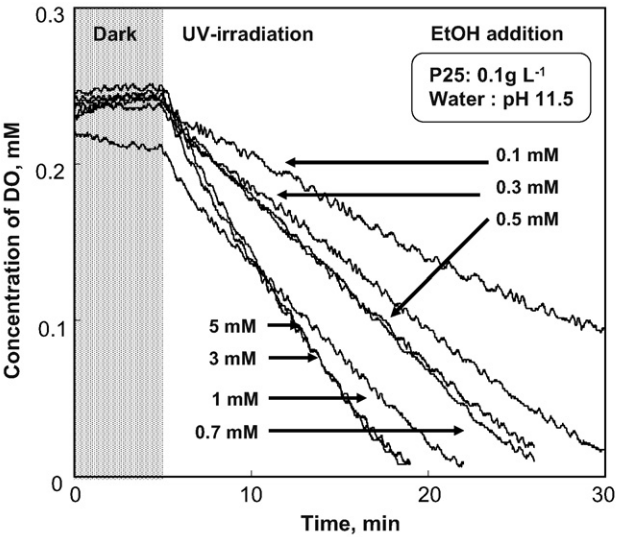


Fig. 1. Dissolved oxygen consumption during P25 photocatalysis in aqueous suspension containing ethanol. The 0.1 g L$^{-1}$ of $TiO_2$ was suspended in 0.01 M NaOH solution at 11.5 of pH. Before UV-irradiation, $TiO_2$ suspension was kept for 5 min in the dark condition under stirring.

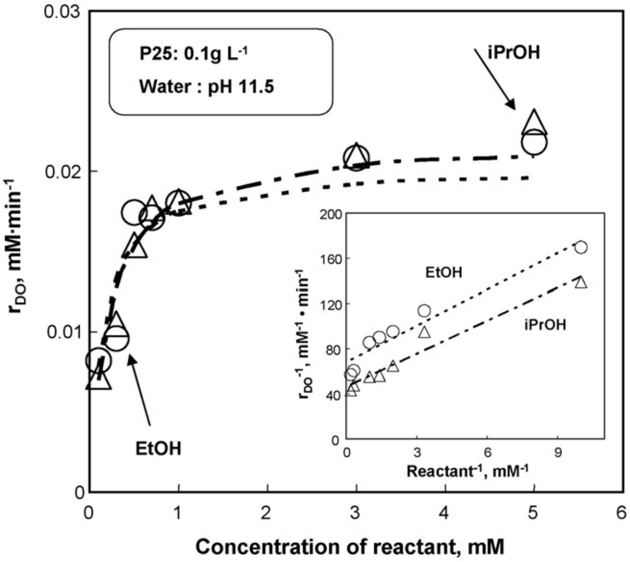


Fig. 2. Consumption rate of dissolved oxygen $r_{DO}$ obtained from photocatalysis with ethanol (○) and *iso*-propanol (□) were plotted as a function of the reactant concentration added. The broken and dashed curves were calculated by using $r_{max}$ and $K_D$ obtained from the inverse plots shown in the inset. 0.1 g L$^{-1}$ of $TiO_2$ in 0.01 M NaOH solution at pH 11.5.

### 4.2. Effect of photon flux on the DO consumption

Because the photocatalytic activity is influenced by the photon flux adsorbed, a dependency of light intensity was examined. The light intensity was changed from 2.8 to 1.2 and 0.54 mW cm$^{-2}$. The experimental results were plotted for $1/r_{DO}$ against 1/[ethanol] and 1/[*i*-PrOH] in Fig. 3(A and B), respectively. From these figures, we can see that $r_{DO}$ is increased with increasing the light intensity. In Fig. 4(A and B), the L–H parameters, $r_{max}$ and $K_D$, were plotted as a function of the light intensity, respectively. These parameters obtained were averaged values for the measurements of two to three times. As seen in Fig. 4(A), the dependence of the $r_{max}$ on the light intensity was almost the same for ethanol (open circle) and *iso*-propanol (open diamond), but not a linear dependence. The reason for the non-linear increase will be discussed later as the increase of net recombination process.

In contrast to the $r_{max}$, the $K_D$ shows different dependence on light-intensity for each reactant. In the case of ethanol addition, the $K_D$ was increased with increasing the light intensity, while in the case of *iso*-propanol addition an opposite tendency was observed. Since equilibrium constant is generally un-changed during the irradiation in a certain reaction mechanism, the change of $K_D$ indicates that the consumption of DO consists of some reaction pathways and the contribution of each pathway changed with the light intensity.

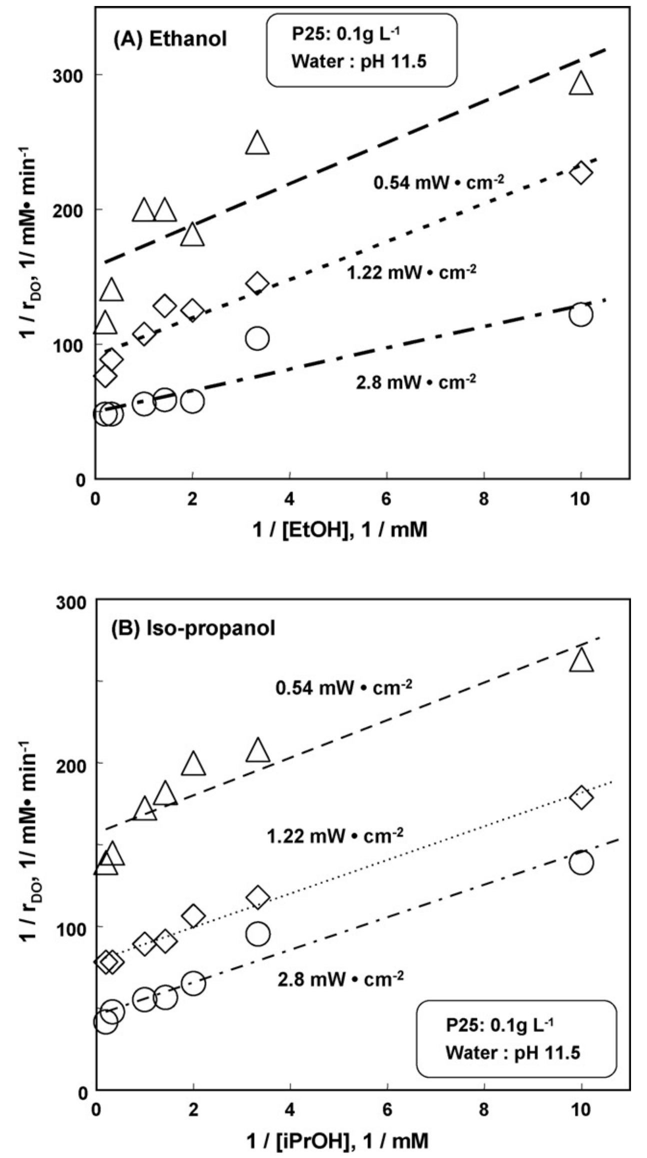


Fig. 3. Dependence of light intensity on $r_{DO}{}^{-1}$ were plotted as a function of $[\text{reactant}]^{-1}$. The light intensity was 0.54 (△), 1.22 (◊) and 2.8 (◯) mW cm$^{-2}$. (A) Ethanol addition; (B) *iso*-propanol addition.

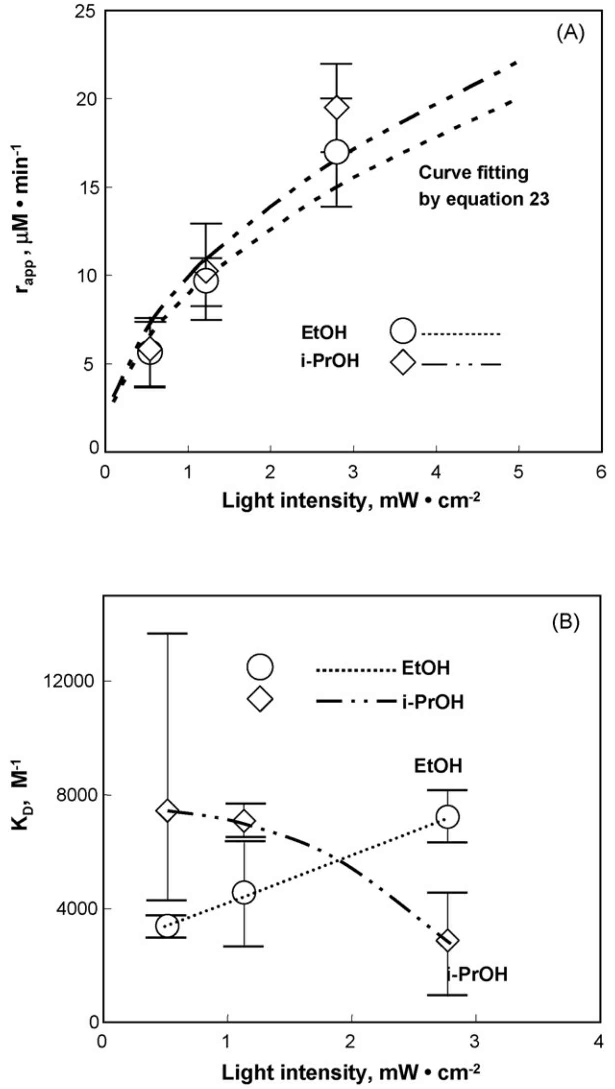


Fig. 4. Light-intensity dependence of (A) $r_{\max}$ and (B) $K_D$ obtained from plot of $r_{DO}{}^{-1}$ vs. $[\text{reactant}]^{-1}$. The single and double dashed lines in (A) were calculated by using Eq. (23). Each data in the plot was average of two to three measurements.

### 4.3. Measurements of absorption coefficient of $TiO_2$ suspension

For quantitative analysis of reaction kinetics, the light absorption coefficient ($\alpha$) at 365 nm of $TiO_2$ suspension was evaluated by spectroscopic method using an integrated sphere and a 1-mm quartz cell for several amount of P25 in 0.01 M NaOH solution. Since the absorbance below 0.01 g L$^{-1}$ showed the Lambert–Beer behavior as the inset in Fig. 5, the $\alpha$ of $TiO_2$ suspension was calculated to be $9.0 \times 10^4$ cm$^2$ g$^{-1}$ from the slope.

### 4.4. Effect of reactants on the $O_2{}^{\bullet-}$ formation

In the photocatalytic oxidation, the chain reaction with $O_2{}^{\bullet-}$ as reaction (5.2) is also carried out. Since this chain reaction might accelerate the whole DO consumption, the reaction of $O_2{}^{\bullet-}$ with alcohols was studied to observe whether $O_2{}^{\bullet-}$ participates in alcohol oxidation. The behavior of $O_2{}^{\bullet-}$ in the photocatalysis was monitored by the luminol CL probe method which is proved to be useful in the previous studies [8,9]. In the present study, the CL intensity observed was converted into the amount of $O_2{}^{\bullet-}$ by using $KO_2$ as a standard. The integrated number of photons (INP) counted for the CL intensity is plotted in Fig. 6 as a function of the concentration of $KO_2$ added into $TiO_2$ suspension containing 0.1 mM luminol without UV-irradiation. In our experimental setup, the concentration of $O_2{}^{\bullet-}$ (μM unit) was calculated by $(\text{INP})/(9 \times 10^6)$ based on the calibration plot in Fig. 6.

In Fig. 7(A), the concentration of $O_2{}^{\bullet-}$ which is produced in the $TiO_2$ photocatalysis on 10-s laser irradiation was plotted as a function of the concentration of ethanol. Ethanol was added in $TiO_2$ suspension before the UV-irradiation to equilibrate the surface adsorption. The concentration of $O_2{}^{\bullet-}$ increased with up to 1 mM of ethanol addition and decreased with a higher

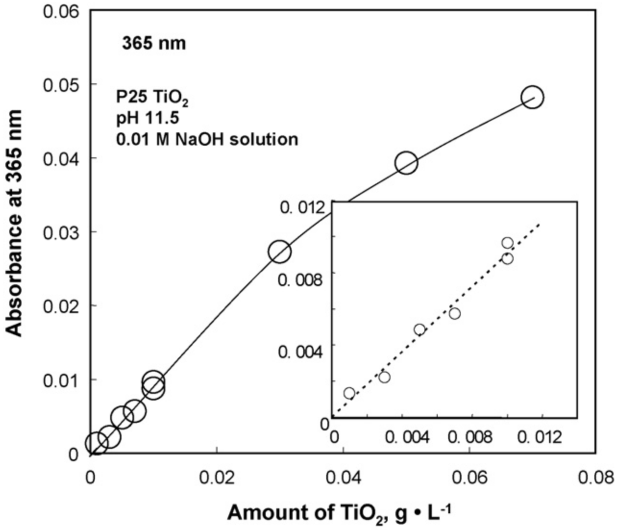


Fig. 5. Absorbance at 365 nm vs. $TiO_2$ concentration in 0.01 M NaOH solution at pH 11.5. The 1 mm for light path length and an integrating sphere were used. The inset shows an expansion of small part that shows the Lambert–Beer behavior.

concentration. The decrease of the concentration of $O_2^{\bullet -}$ was observed up to 20 mM of ethanol.

Fig. 7(B) shows the change of the $O_2^{\bullet -}$ concentration by *iso*-propanol addition. The maximum concentration of $O_2^{\bullet -}$ was approximately 40 μM, which is similar to the case of ethanol. However, the increase of $O_2^{\bullet -}$occurs at low concentration of *iso*-propanol and the decrease was observed at a higher concentration than the case of ethanol. Although the direct reaction of $O_2^{\bullet -}$ with *iso*-propanol was actually reported [30], the chain reaction as reaction (5.2) is deemed to be unlikely for *iso*-propanol.

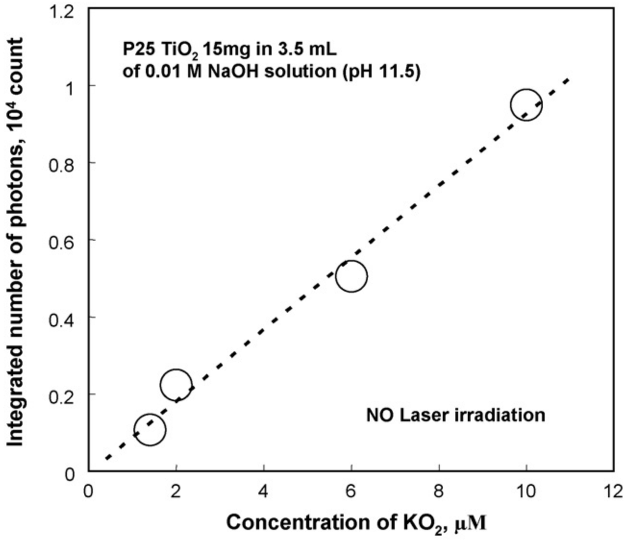


Fig. 6. Integrated number of photons of the chemiluminescence observed by the addition of various concentrations of $KO_2$ stabilized by 18-crown-6-ether into 4.3 g $L^{-1}$ $TiO_2$ suspension in the presence of 0.1 mM luminol without UV-irradiation. Suspension temperature and $KO_2$ solution was kept at 295 K.

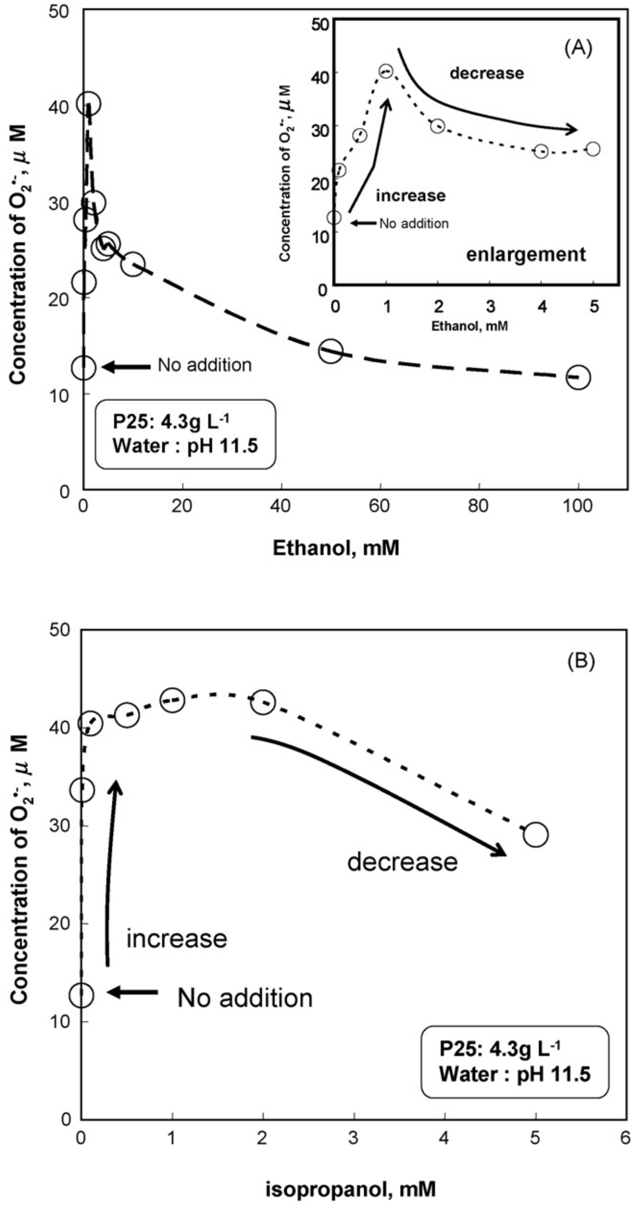


Fig. 7. (A) The concentration of $O_2^{\bullet -}$ produced by addition of ethanol in the $TiO_2$ suspension. Inset shows enlargement. (B) The concentration of $O_2^{\bullet -}$ produced in the presence of various amount of *iso*-propanol is plotted. The amount of $TiO_2$ was 4.3 g $L^{-1}$. pH of the suspension was 11.5.

## 5. Discussion

### 5.1. Zero-order reaction kinetics of DO consumption

We showed that the DO consumption process in $TiO_2$ photocatalytic reaction of alcohols obeyed zero-order reaction (Fig. 1) and could be analyzed as L–H kinetics (Figs. 2 and 3). The zero-order reaction rate kinetics by adding ethanol indicates that the amount of ethanol was larger than that of the photo-induced active site of $TiO_2$ particle. We could confirm this quantitatively as follows. The amount of ethanol adsorbed on the surface of $TiO_2$ in water is reported at around 3.3 $nm^{-2}$ [17,18a–c], which corresponds to that the ratio of water displacement on P25 is 50% [18a]. In 0.1 mM ethanol solution, the number of ethanol molecules is $6.02 \times 10^{19}$ L$^{-1}$. Since the specific surface area of P25 is 49 m$^2$ g$^{-1}$, 12.3 ethanol molecules in average are ready to be adsorbed per nm$^2$ for 0.1 g L$^{-1}$ $TiO_2$. Then, above 0.1 mM of ethanol addition, the number of ethanol is enough to occupy the adsorption sites. The number of ethanol molecules adsorbed per one $TiO_2$ particle is calculated from the diameter of 32 nm to be about 5000. On the other hand, the number of photons irradiated on $TiO_2$ particle could be calculated as follows. When the light intensity at 354 nm is 2.8 mW cm$^{-2}$, the number of photons are $5.4 \times 10^{15}$ cm$^{-2}$ s$^{-1}$. Then 36.1 photons s$^{-1}$ in average are absorbed by one $TiO_2$ particle. Therefore, even when all the photons are absorbed in $TiO_2$ particle and the quantum efficiency is assumed to be unity, the number of active species for the photocatalytic reaction is much lower than the number of ethanol molecules adsorbed. Thus, the photocatalytic reaction rate is determined by the rate of light absorption, which explains the results of the zero-order reaction kinetics for DO consumption (Fig. 1).

### 5.2. L–H kinetics model for DO consumption

The DO consumption rate $r_{DO}$ in $TiO_2$ photocatalysis could be fitted by L–H kinetics for the reactant concentration as shown in Figs. 2 and 3. We will interpret here the $r_{max}$ and $K_D$ by considering the details of the photocatalytic DO consumption process described in the previous section. Because the L–H kinetics is based on the adsorption of the reactant molecules on the surface of the catalyst, we assume simply the adsorption equilibrium of reactant molecules as Eq. (16).

$$TiO_2 + \text{Reactant} \leftrightarrow TiO_2\text{–Reactant}_{ad} \tag{16}$$

Considering that the $O_2$ consumption is controlled by the adsorption of the reactant on the $TiO_2$ surface, we can lead Eq. (17) for equilibrium constant $K_D$:

$$K_D = \frac{[TiO_2\text{–Reactant}_{ad}]}{[TiO_2][\text{Reactant}]} \tag{17}$$

Here, $[TiO_2\text{–Reactant}_{ad}]$ represents the concentration of adsorption sites occupied with the reactants and $[TiO_2]$ defines the concentration of residual adsorption sites. When $[TiO_2]_0$ is the initial concentration of the adsorption site of $TiO_2$ on which alcohol can be adsorbed, $[TiO_2]$ is expressed by $[TiO_2] = [TiO_2]_0 - [TiO_2\text{–Reactant}_{ad}]$. Then the amount of $[TiO_2\text{–Reactant}_{ad}]$ is given by the following simple equation (Eq. (18)):

$$[TiO_2 - \text{Reactant}_{ad}] = \frac{K_D[TiO_2]_0[\text{Reactant}]}{1 + K_D[\text{Reactant}]} \tag{18}$$

Since the observed DO consumption rate, $r_{DO}$, would be proportional to the amount of reactant adsorbed, $[TiO_2\text{–Reactant}_{ad}]$, Eq. (15′) is given:

$$r_{DO} = \frac{r_{max} K_D[\text{Reactant}]}{1 + K_D[\text{Reactant}]} \tag{15′}$$

where $r_{max}$ is $r_{DO}$ when the adsorption site was fully occupied by the reactant. By taking the reciprocals of both terms, this Eq. (15′) becomes Eq. (15). Since the experimental result in Fig. 2 showed that the observed $r_{DO}$ fits to Eq. (15), the presumption of equilibrium 16 is verified.

### 5.3. Effect of light intensity on the L–H parameters

Generally, the rate $R$ of photocatalytic reaction for adsorbed molecules can be represented by three parameters; light intensity ($I$), absorption coefficient ($\alpha$), and quantum efficiency ($\Phi$). Namely, $R = \alpha I \Phi$. In photocatalytic reactions, $\Phi$ depends on the light intensity as expressed by Eq. (19) [31]:

$$\frac{1 - \Phi}{\Phi^2} = \frac{k_r \alpha I}{k_h k_e [D_{ad}][A_{ad}]} \tag{19}$$

where $k_h$, $k_e$ and $k_r$ are oxidation, reduction, and recombination rate constants, and $D_{ad}$ and $A_{ad}$ are a donor and an acceptor adsorbed at the surface of $TiO_2$, respectively. This equation is based on the reaction rate equations: $d[e^-]/dt = \alpha I - k_e[e^-][A_{ad}] - k_r[e^-][h^+]$ and $d[h^+]/dt = \alpha I - k_h[h^+][D_{ad}] - k_r[e^-][h^+]$ and $\Phi = ([h^+]/dt)/(\alpha I)$ [32].

Since the $\Phi$ of $TiO_2$ photocatalysis is usually much smaller than 1 ($\Phi \ll 1$), the photocatalytic reaction rate $R$ given by $R = \alpha I \Phi$ could be calculated with the following Eq. (20):

$$R = \left\{ \frac{k_h k_e [D_{ad}][A_{ad}]\alpha I)}{k_r} \right\}^{0.5} \tag{20}$$

By applying the steady state approximation for the concentrations of $e^-$ and $h^+$, $[e^-]$ is equal to $[h^+]$, and $k_e[A_{ad}] = k_h[D_{ad}]$ is obtained. This relationship simplifies Eq. (20) to give Eq. (21):

$$R = k_h[D_{ad}] \left\{ \frac{\alpha I}{k_r} \right\}^{0.5} \tag{21}$$

Although Eq. (21) is for photocatalytic oxidation, the similar equation for reduction can be obtained by replacing $k_h[D_{ad}]$ with $k_e[A_{ad}]$. Since the total photocatalytic reaction rate $R_t$ concerns both reduction and oxidation, Eq. (22) is obtained:

$$R_t = (k_h + k_e)[TiO_2\text{–Reactant}_{ad}] \left\{ \frac{\alpha I}{k_r} \right\}^{0.5} \tag{22}$$

By substituting Eq. (18) for $[TiO_2\text{–Reactant}_{ad}]$, Eq. (22) could be comparable with Eq. (15) which shows the simple L–H kinetics equation for DO consumption. Then, $r_{max}$ in Eq. (15′) can be expressed by Eq. (23):

$$r_{max} = k_t[TiO_2]_0 \left\{ \frac{\alpha I}{k_p} \right\}^{0.5} \tag{23}$$

where $k_t$ and $k_p$ correspond to $k_h + k_e$ and $k_r$ in Eq. (22), respectively. Notice here that in the present L–H model, the $k_h$ and $k_e$ do not simply mean the reaction rate constants for ($h^+$ + reactant) and ($e^- + O_2$), respectively, but the $k_h$ and $k_e$ include a whole DO consumption processes observed under steady state UV-light condition as exhibited in Scheme 1. Then, the $k_h$ in Eq. (22) corresponds the sum of the reaction rate constants which concern with the oxidation processes; $k_4$ as the reaction of the valence band $h^+$ with the reactant (reaction (4)), $k_{5.1}$ and $k_{5.2}$ as the reaction of the intermediate of the reactant (reaction (5.1) and (5.2)). In addition, $k_{11}$ and $k_{12}$ of reaction (11) and (12) which includes several oxidation steps have to be added when we assume that the produced $ROO^{\bullet}$ is decomposed to $CO_2$ without producing $O_2$. Therefore, $k_h = k_4 + k_{5.1} + k_{5.2} + k_{11} + k_{12}$. In the case of ethanol, the radical transfer reaction (reaction (7)) should also be added to $k_h$. On the other hand, the $k_e$ is composed of several reactions such as $k_3$ of reaction (3), $k_{5.2}$ of reaction (5.2), $k_8$ or/and $k_9$ of reaction (8) and (9), $k_{10}$, $k_{11}$ and $k_{12}$ of reaction (10)–(12) as shown in Scheme 1. Therefore, $k_e = k_3 + k_{5.2} + k_8$ (or/and $k_9$) $+ k_{10} + k_{11} + k_{12}$. In a word, $k_t$ as the sum of $k_h$ and $k_e$ can be defined by the DO consumption rate constant. Though $k_r$ in Eq. (22) means originally the reaction rate constant for charge recombination between $e^-$ and $h^+$, $k_p$ in Eq. (23) contains the reproduction of $O_2$ and any other reaction against $O_2$ consumption. Notice here that $k_2$ as the direct charge recombination can be disregarded since $k_2$ is usually induced within μs time scale. Then $k_p$ would be composed of $k_{12} + k_{13}$.

Eq. (19) has usually been employed for analyzing the results of laser flash photolysis with a high photon density [31,32]. As seen in Fig. 4(A), the data obtained from the L–H kinetics of DO decay could be fitted by Eq. (23), which is based on Eq. (19). In our experimental conditions, since the photon flux is too small to excite $TiO_2$ more than one pair of $e^-$–$h^+$ at some instance, Eq. (19) seems not to be adoptable. However, the indirect charge recombination processes that stem from the long lifetime of trapped $e^-$ or $O_2^{\bullet-}$ strongly influence the $TiO_2$ photocatalysis under steady state UV light. Actually, the lifetime of trapped $e^-$ was reported to be 500 ms as half-life time when alcohol reacted as sacrificial reagent [16]. Even without alcohol, long lifetime of about 1 s was indicated from our previous report [33]. By current doubling effect, the injected $e^-$ can also have long life as trapped $e^-$. In addition, $O_2^{\bullet-}$ produced at the surface of $TiO_2$ has also long lifetime of 17 s [8a] to hundred seconds [8e] for P25 suspension. Since 36 photons per second are absorbed by a particle, $TiO_2(e^-)$ and $O_2^{\bullet-}$ can be oxidized back to $TiO_2$ and $O_2$, respectively, with the $h^+$ produced by the photons absorbed in the same particle later. By taking these net recombination reactions into account of the $e^-$–$h^+$ recombination, Eq. (19) could be applied for the continuous light excitation. Notice here that the indirect charge recombination as $O_2^{\bullet-}$ with $h^+$ can be counted for $k_p$ but recombination as trapped $e^-$ cannot be in the present study of DO consumption.

### 5.4. Analysis of photocatalytic DO consumption process using L–H model

Based on Eq. (23), the values of $k_t$ and $k_p$ were evaluated from Fig. 4(A). In $TiO_2$ photocatalysis with ethanol, the $k_t$ and $k_p$ were $5.1 \times 10^{-3}$ and $11 \times 10^{-3}\ s^{-1}$, respectively. While those with *iso*-propanol were $2.1 \times 10^{-3}$ and $0.5 \times 10^{-3}\ s^{-1}$, respectively. The $k_p$ for ethanol is approximately 20 times higher than that for *iso*-propanol, while the $k_t$ is approximately twice higher. This result can be interpreted by considering a difference in the decomposition mechanisms of ethanol and *iso*-propanol.

On the ethanol oxidation, reaction of $O_2$ by a radical chain reaction is well known (reaction (5)) [3b,c]. This $O_2$ consumption of ethanol is much larger than *iso*-propanol because no radical chain reaction is brought about in the case of first oxidation process of *iso*-propanol [3b,c,19–21]. As the oxidation intermediate acetaldehyde and acetone are produced from ethanol and *iso*-propanol, respectively [17–21]. It has known that the $O_2$ consumption in acetone decomposition process is smaller than acetaldehyde [3b,c,21]. Based on this interpretation, the larger $k_t$ of ethanol oxidation could be explained [34]. The reason for the larger $k_p$ of ethanol addition can be also interpreted by $O_2$ reproduction from the chain reaction, while no $O_2$ reproduction process could be assumed in the first oxidation process of *iso*-propanol. Thus, the $O_2$ reproduction on *iso*-propanol oxidation could reflect the smaller $k_p$. This means that the measured $r_{DO}$ exactly is composed of the balance of $k_t$ and $k_p$. We have to notice here that $k_p$ include charge recombination by trapped $e^-$. Therefore, the propriety of the scale of $k_p$ could not be verified in the present stage.

In the L–H kinetics model for DO consumption, the $K_D$ represents the ratio of forward and backward rate constants of reaction (16), that is, $K_D = k_{16}k_{-16}^{-1}$. Since the $K_D$ reflects the irreversible $O_2$ consumption processes on the alcohol decomposition, it is not simply defined by the adsorption equilibrium of the reactant but influenced by the adsorption equilibrium of $O_2$. The $K_D$ shown in Fig. 4(B) is appreciably larger than the adsorption coefficient $K$ reported for alcohol decomposition. For instance, the reported $K$ for *iso*-propanol is 87 and $1.8\ M^{-1}$ at pH 6 and 2, respectively [20c–e]. By using P25 suspension, $K$ for ethanol and *iso*-propanol at pH 3.6 are reported to be 47.6 and $28.6\ M^{-1}$, respectively [4b]. Although the value of $K_D$ includes the consumption of $O_2$ by chain reactions, the larger $K_D$ is presumable for the case of ethanol.

With increasing the light intensity, the $K_D$ of ethanol addition was increased, while it was decreased in the case of *iso*-propanol addition as shown in Fig. 4(B). The increase in $K_D$ is attributed to the increase of the intermediate reactants with the light intensity. The intermediates such as acetaldehyde and acetone are produced and are also oxidized to consume $O_2$. The amount of adsorption of acetaldehyde is 3-fold higher than acetone at the surface of $TiO_2$ and the water displacement ratio is 70% for acetaldehyde and 30% for acetone [18,19,35]. Furthermore, acetaldehyde adsorption is stronger than acetone adsorption on the surface of P25 [35a]. Therefore, at a higher light intensity, the larger $K_D$ of ethanol addition is attributable to larger adsorption of acetaldehyde. At a lower light intensity, the $K_D$ varied widely. Especially, the data were fluctuated largely at the higher alcohol concentration. Thus, we are now supposing that $K_D$ of *iso*-propanol addition may be independent on the light intensity. Besides, we are planning to employ some carbon hydrates those have much different adsorption properties and decomposition rates.

### 5.5. Reactant dependence of the amount of $O_2^-$

Since $O_2$ is first converted to $O_2^{\bullet-}$ in photocatalysis, monitoring of $O_2^{\bullet-}$ is important to understand the DO consumption mechanism. The steady state concentration of $O_2^{\bullet-}$ in $TiO_2$ photocatalysis without reactant may be determined by the reactions (2), (3), (8), (9) and (13). Shortly, the concentration of $O_2^{\bullet-}$ on the steady state depend mainly on the reaction of $O_2^{\bullet-}$ with $h^+$.

As seen in Fig. 7(A), the concentration of $O_2^{\bullet -}$ had an apex at 1 mM of ethanol addition, though the amount of ethanol adsorbed was calculated to be abundant as stated above. Approximately 40 μM of steady state concentration of $O_2^{\bullet -}$ observed at 1 mM ethanol addition, which was four times higher than that without ethanol addition. Since this large increase in the amount of $O_2^{\bullet -}$ cannot be explained by the current doubling effect via reactions (4), (6) and (3), the other reason for the increase has to be marked. Reaction of alcohol with $h^+$ causes the decreases in the direct recombination of $e^-$ and $h^+$ (Eq. (2)) and the oxidation of $O_2^{\bullet -}$ by $h^+$ (Eq. (13)). Since the quantum yield of $O_2^{\bullet -}$ formation under very weak light is very high [9], the direct recombination could be of minor process in the case of continuous light irradiation. Therefore, we may conclude that the increase of the steady state concentration of $O_2^{\bullet -}$ with alcohol addition is attributed to the synergy effect of current doubling effect and the decrease of the indirect recombination between $O_2^{\bullet -}$ and $h^+$.

As seen in Fig. 7(A), the decrease of the steady concentration of $O_2^{\bullet -}$ by adding ethanol has apparently two phases. One phase is rapid decrease until 5–10 mM ethanol addition and other one is slow decrease above 5–10 mM. To explain the rapid decrease in the $O_2^{\bullet -}$ concentration, two possible reasons could be considered. First one is the decrease of the $O_2$ molecules adsorbed at the surface because $O_2$ is adsorbed at the same $Ti^{4+}$ site as alcohol [10,17–20]. If the number of $O_2$ adsorbed were decreased with the ethanol adsorption, the amount of $O_2^{\bullet -}$ produced should be decreased with increasing the concentration of ethanol. However, the amount of $O_2^{\bullet -}$ in the presence of 5 mM ethanol is twice of that without ethanol. The similar tendency was observed from *iso*-propanol addition as shown in Fig. 7(B). Therefore, the desorption of $O_2$ by the alcohol will be ruled out to explain the decrease of $O_2^{\bullet -}$. Instead, we can suggest here that the chain reaction as reaction (5.2) might be carried out at the high ethanol adsorption because an effective $TiO_2$ photocatalytic oxidation of ethanol attained (reaction (4)). In fact, as seen in Fig. 7(A), the decrease of the concentration of $O_2^{\bullet -}$ was observed above 1 mM of ethanol, where a large amount of ethanol is adsorbed. Thus, the plausible process on the decrease in the $O_2^{\bullet -}$ concentration is the chain reaction route as reaction (5.2) in Scheme 1 [3], because the lifetime of $O_2^{\bullet -}$ is 17 to several hundred second as stated above.

Above 10 mM of ethanol addition, there may be two candidates as the cause for decreasing the steady state concentration of $O_2^{\bullet -}$. First possible cause is a diminution of CL intensity of luminol with increasing the concentration of ethanol. However, in separate blank experiments using $KO_2$, ethanol in $TiO_2$ suspension did not decrease the luminol CL intensity, then, this is not the cause of the decrease. Second possible cause is a decrease of an adsorbed $O_2$ at the surface of $TiO_2$ by increasing the amount of ethanol adsorption. Although some effort to elucidate the role of $O_2$ is reported under gas phase, the adsorption equilibrium of $O_2$ with $TiO_2$ surface has not been established yet under aqueous phase [17–19]. Therefore, the precise reason for the slow decrease above 10 mM of ethanol addition is unclear in the present stage. However, the luminol CL probe method employed to elucidate the amount of $O_2^{\bullet -}$ for the reaction intermediate of $O_2$ has been successfully used to understand the photocatalytic reaction mechanism with organic compound.

### 5.6. Estimation of photocatalytic efficiency from the DO consumption rate

Based on the results of the L–H plot (Fig. 3) obtained from the DO consumption, we could know that the $r_{DO}$ was composed of $r_{max}$ and $K_D$. From these parameters, the photocatalytic activity for alcohol decomposition could be estimated. In this section, from the view point of DO consumption, the photocatalytic efficiency for the decomposition of alcohol is discussed.

Quantum efficiency ($\Phi_{DO}$) for DO consumption is calculated by Eq. (24):

$$\Phi_{DO} = \frac{r_{DO}}{\alpha I} \tag{24}$$

Here, $\alpha I$ stands for the excitation rate. The values of $\Phi_{DO}$ for the excitation with 0.54, 1.22, and 2.80 mW cm$^{-2}$ were 0.67, 0.54, and 0.42% with ethanol and 0.75, 0.55, and 0.42% with *iso*-propanol, respectively. The $\Phi_{DO}$ was increased with decreasing $I$ for both ethanol and *iso*-propanol. This increase is consistent with that obtained from laser photolysis and so on [32,36].

Eq. (24) gives Eq. (25) by using Eqs. (15) and (17). Where $\Phi_{max}$ is the maximum efficiency obtained with the maximum $r_{DO}$, or $\Phi_{max} = r_{max}/(\alpha I)$:

$$\frac{1}{\Phi_{DO}} = \frac{1}{\Phi_{max}} + \left(\frac{1}{\Phi_{max}}\right)\frac{[TiO_2]}{[TiO_2\text{–Reactant}_{ad}]} \tag{25}$$

As shown in Fig. 8, the plot of $1/\Phi_{DO}$ as a function of $I^{0.5}$ shows a straight line. This experimental result indicates that, in Eq. (25), following relationship (Eq. (26)) holds:

$$\frac{[TiO_2]}{[TiO_2\text{–Reactant}_{ad}]} = \left(\frac{I}{I_0}\right)^{0.5} \tag{26}$$

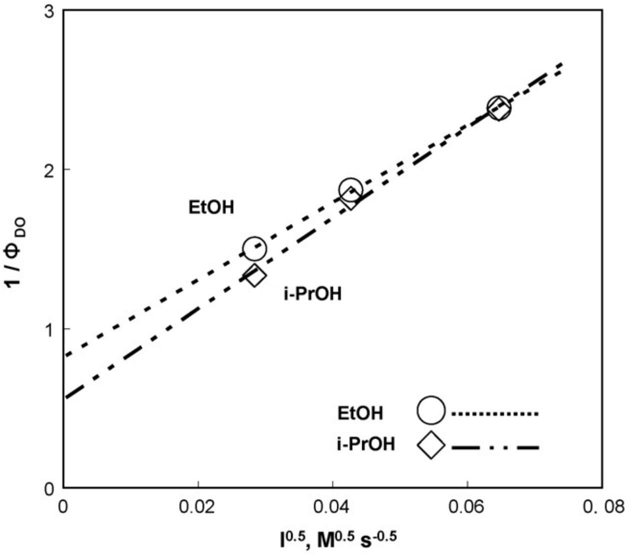


Fig. 8. The inverse of quantum efficiency of oxygen consumption $\Phi_{DO}$ was plotted as a function of $I^{0.5}$ for the photocatalytic decomposition with ethanol and *iso*-propanol.

The value of $I_0$ corresponds to the light intensity at which half of the adsorption site of $TiO_2$ surface is occupied by reaction intermediates and reactant alcohols. From Fig. 8, the $\Phi_{max}$ is 2.4% with $I_0 = 0.12\,mW\,cm^{-2}$ for ethanol addition and 1.8% with $I_0 = 0.24\,mW\,cm^{-2}$ for *iso*-propanol addition. The $\Phi_{max}$ is comparable to $\Phi$ for the decomposition of ethanol and *iso*-propanol, which have been reported to 2.8 and 1.2%, respectively, at pH 3.5 [4b]. Then we may conclude in the present study that the relative photonic efficiency $\Phi_{DO}$ for DO consumption is suitable as a convenient parameter to compare photocatalysts and reactants [37].

## 6. Conclusions

In the present study, we could demonstrate that the measurement of DO consumption is a powerful method to obtain much information of photocatalytic reaction and to estimate the photocatalytic activity.

By adopting the L–H kinetics model for the DO consumption rate with various amounts of reactants, ethanol and *iso*-propanol, two parameters $r_{max}$ and $K_D$ were evaluated. We found that the dependence of $r_{max}$ on the light intensity ($I$) obeyed the term of $\{(\alpha I)/k_p\}^{0.5}$ and could estimate two rate constants, $k_t$ and $k_p$, which were defined for the DO consumption and the $O_2$ reproduction. Though this analysis originated from on the high $e^-$–$h^+$ recombination rate with a high photon density such as laser flash photolysis, it could be formally applicable because the trapped $e^-$ and $O_2^{\bullet -}$ having a long lifetime cause a slow charge recombination with the $h^+$ produced by the photons absorbed in the same particle later.

The values of $K_D$ obtained for ethanol and *iso*-propanol showed quite different tendency with increasing the light intensity. Change of $K_D$ with increasing the light intensity stems from the different photocatalytic oxidation rate of the produced intermediates. In the present study, though the $K_D$ was defined by the oxygen uptake from the solution, it is exactly influenced by the association constant of the reactant on the photocatalysts. We suggested here the $K_D$ can be used as one of the index to estimate the progress level on photocatalytic reaction with a reactant.

The reaction of alcohol and intermediate with $O_2^{\bullet -}$ produced in photocatalysis was detected by means of luminol chemiluminescence (CL) method. The quantitative observation of the behavior of $O_2^{\bullet -}$ in a $TiO_2$ photocatalysis with alcohol concentration is first reported as far as we know. With increasing the concentration of alcohol addition, the steady state concentration of $O_2^{\bullet -}$ was increased as the result of a synergy effect of the current doubling effect and the prolonged lifetime of $O_2^{\bullet -}$ with the decrease of the $h^+$ oxidation. Decrease of $O_2^{\bullet -}$ at a higher concentration of reactants suggested that radical intermediates react with $O_2^{\bullet -}$ (Eq. (5.2)).

We suggested also that the relative photonic efficiency $\Phi_{DO}$ for DO consumption can be used as an convenient parameter to compare photocatalysts and reactants.

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[34] Notice here that the $O_2$ consumption reported is focused on the chain reaction at the first oxidation process but not on the total amount of DO consumption. From its chemical structure, *iso*-propanol consumes higher amount of $O_2$ than ethanol to achieve the complete decomposition into $CO_2$ and $H_2O$. Hence, total DO consumption for complete decomposition of *iso*-propanol might be higher than ethanol.

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