Kinetics of Photocatalytic Reactions under Extremely Low-Intensity UV Illumination on Titanium Dioxide Thin Films

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The photocatalytic decomposition efficiency of gaseous 2-propanol was studied using a titanium dioxide thin film under very weak UV light; the incident UV light intensity was 36 nW−45 μW·cm^{-2}. Under such low-intensity UV illumination, the value of the quantum yield (QY) increased gradually with decreasing number of absorbed photons and finally saturated (28%) for a number of absorbed photons less than 4×10^{11} quanta·cm^{-2}·s^{-1} for an initial 2-propanol concentration of 1000 ppmv. Thus, purely light-limited conditions were reached. For lower initial concentrations, the QY values decreased, but the same maximum QY value as that for 1000 ppmv was also approached with decreasing light intensity. We discuss these results in terms of the normalized absorbed photon number (I_{norm}/s^{-1}), a parameter that we have defined as the ratio of the number of absorbed photons ([photon]$_{ab}$) to the number of adsorbed 2-propanol molecules ([M]$_{ad}$). When all of the experimental QY values were plotted as a function of I_{norm}, all of the points appeared on a single line for a wide range of initial 2-propanol concentrations. On the basis of these results, we conclude that either $^{\bullet}$OH radicals or 2-propanol molecules must be able to diffuse at least ca. 11 nm on the titanium dioxide surface in order to react with each other. We also conclude that the maximum QY value of 28% represents the intrinsic charge-separation efficiency for this photocatalyst.

Introduction

It is well-known that when photons with energies greater than the bandgap are absorbed by semiconductors such as ZnO, CdS, and TiO$_2$, electron−hole pairs are generated and are then transferred to the surface, where they are trapped and can react with surface-adsorbed molecules. TiO$_2$ in particular has beneficial characteristics, such as its chemical and physical stability, as well as the strong oxidizing power of the photogenerated holes, with which most organic compounds can be oxidized to carbon dioxide at ambient temperature and pressure. Therefore, the photocatalytic destruction of harmful and toxic materials using TiO$_2$ powders and films has great promise for the purification of air and water.[1−3] Traditionally, high-pressure mercury and xenon lamps have been used in most photocatalytic research for the purpose of high-rate photodecomposition and also to compensate for the low photocatalytic efficiency of TiO$_2$ itself.[4−6] In recent years, since Heller et al. reported the oxidative stripping of oil sheens from the surface of sea water with buoyant photocatalyst-coated ceramic microbubbles,[7] the field of environmental purification has been devoting increasing attention to photocatalysis using sunlight and black-light-type fluorescent lamps as UV light sources, i.e., at the several mW·cm^{-2} level, which is safe for human exposure.[8−11]

In contrast, we have been devoting our attention to a unique type of passive-type purification system for indoor working and living environments. These systems incorporate deodorizing, antibacterial, and self-cleaning functions under lower level illumination from room light. In connection with this concept, many different types of TiO$_2$ materials that exhibit higher photocatalytic activities than P-25 powder, which is known for its highly photocatalytic activity, have been prepared.[12−15] For example, quantum yields (QY) of close to 100% have been achieved under 0.5 mW·cm^{-2} irradiance for 1000 ppmv gaseous acetaldehyde decomposition using TiO$_2$-containing paper[12] and semitransparent TiO$_2$ thin films formed on glass.[13,14] In addition, we have found that *Escherichia coli* cells can be completely killed on TiO$_2$-coated glass tiles even under room light.[15] Using these materials, we can also investigate the kinetics of photocatalytic reactions under even lower-intensity UV illumination, e.g., at nW·cm^{-2} levels. Using this approach, new aspects of photocatalysis, distinct from those associated with the higher-intensity UV illumination employed in many other reports, can be expected to be discovered.

In the present work, we have examined the stationary photocatalytic decomposition of dilute gas-phase 2-propanol on a TiO$_2$ thin film under extremely low-intensity UV illumination, from as little as 10 nW·cm^{-2} and ranging up to 10 μW·cm^{-2}, for the first time. We have paid particular attention to the dependence of the QY values on the number of absorbed photons ([photon]$_{ab}$) and on the number of 2-propanol molecules ([M]$_{ad}$) adsorbed on the surface of the film. Consequently, we found that the ratio of [photon]$_{ab}$/[M]$_{ad}$ uniquely determines QY, even with a wide range of different initial concentrations, i.e., 1−1000 ppmv. We have discussed the diffusion length of $^{\bullet}$OH radicals on the TiO$_2$ surface and the charge-separation efficiency of the TiO$_2$ film on the basis of these results.

The reasons that 2-propanol was chosen as a reactant for these experiments were that (i) it is efficiently photodecomposed to acetone, which undergoes further reactions at a much slower rate, (ii) acetone can be detected sensitively using gas chromatography (GC), (iii) a single photon is considered to participate in the generation of each acetone molecule, and (iv) its self-oxidation is negligible. The latter aspect is distinct from the aldehydes, which are decomposed via free radical chain reactions involving reduced oxygen species,[16,17] and therefore, the reaction dynamics cannot be accounted for in a simple fashion. It should also be noted that, under very low-intensity illumination

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conditions, the adsorption of the reactant on the TiO_2 surface is essentially at equilibrium. We are currently examining mass transport effects at higher UV light intensities.

Experimental Section

TiO_2 thin films were prepared on soda lime glass by a conventional spin-coating process, using a commercial TiO_2 anatase aqueous sol (Ishihara Sangyo Kaisha, Ltd., STS-21, 20 nm particle diameter, 50 $m^2 \cdot g^{-1}$ surface area). A 7 cm × 7 cm piece of glass was spun at 1500 rpm for 10 s. After air-drying, a second coating was applied in the same manner over the coated gel. The resulting sample was calcined at 450 °C for 1.5 h in air. The thickness of the semitransparent film was about 1.7 μm, according to cross-sectional observation by atomic force microscopy. The weight of the film was 0.40 $mg \cdot cm^{-2}$. The roughness factor of the film was estimated to be about 150 cm^2/cm^2 , by measuring the amount of adsorbed cyanine dye (1-(2-carboxyethyl)-2-[7-[1-(2-carboxyethyl)-1,3-dihydro-3,3-dimethyl-2*H*-indol-2-ylidene]-1,3,5-heptatryenyl]-3,3-dimethyl-3*H*-indolium hydroxide, inner salt, NK3422, Nippon Kankoh-Shikiso Kenkyusyo Co., Ltd.) on the sample surface. Scanning electron micrographic observation showed that the film consisted of particles with diameters of about 50−100 nm due to particle growth during the sintering step.

An O_2 (20%)−N_2 gas mixture, which was passed through a 16 °C water humidifier in order to adjust the relative humidity to 50%, was used to fill the 1-L Pyrex glass photocatalytic reaction vessel. For purposes of preparing the gas mixtures containing various concentrations of 2-propanol, the nonhumidified O_2−N_2 mixture gas was first saturated with 2-propanol (Kosou Kagaku Yakuhin) by passage through a 2-propanol liquid reservoir at room temperature, resulting in a concentration of 5 vol %, as measured using GC (see below) after dilution. Measured quantities of the 2-propanol-saturated gas were then injected into the 1-L vessel using a syringe.

For the photocatalytic decomposition of gaseous 2-propanol, the TiO_2 thin film was illuminated with a Hg−Xe lamp (Hayashi Tokei, Luminar Ace 210). To obtain monochromatic UV light, a 365 nm band-pass filter (fwhm = 2 nm, Kenko, BP-W1-365) was used. To control the intensity, poly(ethylene terephthalate) sheets were used as neutral density filters. The UV intensity was measured using a UV power meter (TOPCON UVR-1) that had previously been corrected against a thermopile meter (No. 30198E6, The Eppley Laboratory, Inc.). Because the detection limit of the power meter was 1 $\mu W \cdot cm^{-2}$, we used extrapolated values below 10 $\mu W \cdot cm^{-2}$ incident UV light. Illumination was conducted at room temperature after equilibrium between gaseous and adsorbed 2-propanol on the TiO_2 thin film was achieved, as evidenced by a constant 2-propanol concentration.

The 2-propanol concentration was measured using a GC (Shimadzu Model GC-8A) equipped with a 5-m PEG1000 column and a flame ionization detector, using N_2 as the carrier gas. The CO_2 concentration was measured using the same GC, equipped with a 2-m Porapak-Q column, with a methanizer and a flame ionization detector, also using N_2 as the carrier gas. The detection limits for both acetone and CO_2 were approximately 0.1 ppmv.

All of the data were collected using the same TiO_2 thin film in order to avoid variations in activity caused by the difference of the surface area and thickness. The photocatalytic activity of the film was able to be fully regenerated by illumination with 5 $mW \cdot cm^{-2}$ UV light in fresh humid air for 120 min.

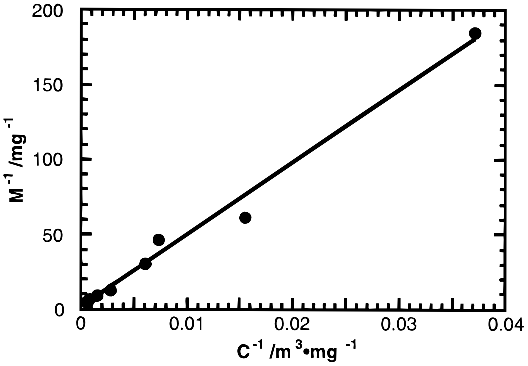

Figure 1. Inverse plots of the gaseous concentration (C/$mg \cdot m^{-3}$) and the weight of adsorbed 2-propanol (M/mg) on the TiO_2 thin film used for analysis of the Langmuir-type isotherm.

The absorbed photon flux was estimated as follows. The incident photon flux (I_0) can be expressed as follows[18]

$$I_0 = I_a + I_t + I_f + I_b \qquad (1)$$

where I_a is the intensity of light absorbed in the film, I_t is the transmitted intensity, I_f is the forward-scattered intensity, and I_b is the backscattered intensity. I_0 was measured directly using the UV power meter. However there was some degree of nonuniformity of intensity over the illuminated area because of passage of the UV light though a 1-m glass fiber light pipe. Therefore I_0 was estimated in a manner analogous to that described by Hill et al.[19] for the measurement of I_b. This involves the establishment of a contour map of light intensity and subsequent calculation of the average intensity over the illuminated area. The full-strength intensity of I_0, after passing through the light pipe, was 45 $\mu W \cdot cm^{-2}$. The sum of I_t and I_f was determined using a conventional integrating sphere (Shimadzu ISR-260). The modified method of Bolton et al.[20] was not used, because I_b was measured separately (see below). The sample was placed at the sample position of the integrating sphere with a piece of glass plate similar to that used as a support for the TiO_2 film as the reference. The apparent transmission factor, $(I_t + I_f)/I_0$, reading of the instrument was 0.30 at 365 nm. I_b from the sample was estimated using a method similar to that of Hill et al.[19] I_b at normal incidence was extrapolated by measuring I_b as a function of the incident light angle. The factor I_b/I_0 evaluated following this methodology was 0.05. The factor I_a/I_0 for the sample TiO_2 film was calculated to be 0.65. The UV absorption by 2-propanol on the film (365 nm) was considered to be negligible.

The amount of physically adsorbed water on the TiO_2 surface was estimated using a differential thermobalance (Shikuu Riko TGD 7000RH) for the TiO_2 powder (Ishihara Sangyo Kaisha, Ltd., ST-21), the commercial powder corresponding to that dispersed in STS-21 sol, which was used after it was subjected to the same heat treatment that was used to prepare the film (see above).

The amount of 2-propanol adsorbed on the TiO_2 sample was estimated by measuring the decrease in the balance of 2-propanol gas concentration in the glass vessel containing the TiO_2 film sample versus that in a separate empty glass vessel. The concentrations were measured 1 h after a given concentration gas mixture was introduced into each glass vessel.

Results

Figure 1 shows the experimental data for the adsorption isotherm in the form of an inverse plot, the weight of adsorbed 2-propanol on the TiO_2 thin film (M/mg) vs the gaseous

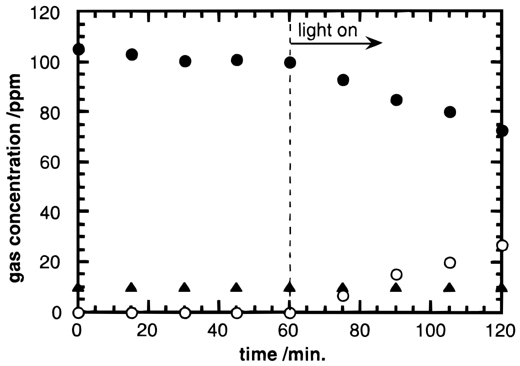

Figure 2. Concentration changes of gaseous 2-propanol, acetone, and CO_2 as a function of time in the decomposition of gaseous 2-propanol (incident UV intensity, 45 μW·cm^{-2}; initial 2-propanol concentration, 100 ppmv; ● 2-propanol, ○ acetone, ▲ carbon dioxide).

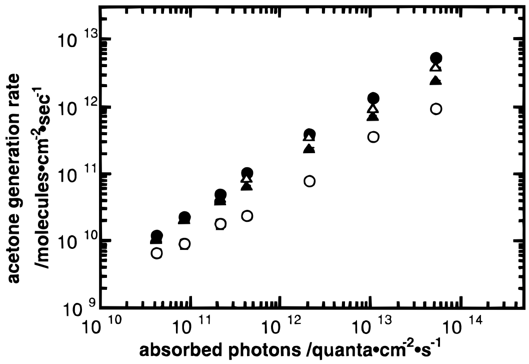

Figure 3. Dependence of the acetone generation rate on the absorbed photons (initial 2-propanol concentration: ● 1000 ppmv, △ 100 ppmv, ▲ 10 ppmv, ○ 1 ppmv).

2-propanol concentration (C/mg·m^{-3}). These data were analyzed in terms of a Langmuir-type isotherm, which is described as follows

$$1/M = 1/\mu + 1/(\mu TC) \tag{2}$$

where μ is the maximum weight of molecules in an adsorbed monolayer, for a given TiO_2 sample, and T is the adsorption binding constant. The values of μ and T were ca. 0.33 mg and 0.000 63 m^3·mg^{-1}, respectively. These results will be used in the discussion of the QY values for 2-propanol decomposition in the next section.

Figure 2 shows a typical experimental data set for the concentration changes of gaseous 2-propanol, acetone, and CO_2 as a function of time in the decomposition of gaseous 2-propanol (incident UV intensity, 45 μW·cm^{-2}; initial 2-propanol concentration, 100 ppmv). After 60 min, when equilibrium between gaseous and adsorbed 2-propanol on the TiO_2 thin film had been achieved, UV light illumination was initiated. The amount of generated acetone was equivalent to that of the decomposed 2-propanol, and the generation of CO_2 and other stable intermediates was not detected, within experimental error. Under the present experimental conditions, i.e., 1−1000 ppmv initial 2-propanol concentration and 36 nW−45 μW·cm^{-2} incident UV light intensity, only acetone was generated stoichiometrically.

Figure 3 shows log−log plots of the acetone generation rates (R) versus the number of absorbed photons (I). R decreased with decreasing I, in essentially a linear fashion, with slopes that were almost constant regardless of the initial 2-propanol concentration. The higher the initial 2-propanol concentration, the higher the value for the same UV intensity. The value of the slope, i.e., the exponent α in the $R = KI^{\alpha}$ relation, is ca. 0.7−0.8. It is well-known in heterogeneous photocatalysis that, under light-rich conditions, the reaction rate is often characterized by an α value of 0.5 due to domination by the second-order-dependent carrier-recombination process.[21,22] Conversely, the light-limited reaction rate is represented as $\alpha = 1$.[23,24] Thus the present experimental regime is in a transition region between the two asymptotic values. α values of ca. 0.7 were also reported in the photodecomposition of formic acid by Hill et al.[19] and of acetone by Ollis et al.[25] under several mW·cm^{-2} UV irradiation. For 365 nm light, an incident UV light intensity of 1 μW·cm^{-2} corresponds to a photon flux of 1.8×10^{12} quanta·cm^{-2}·s^{-1}, of which the TiO_2 film absorbs 1.2×10^{12} quanta·cm^{-2}·s^{-1}. We calculated the initial rates using the conventional least-squares method over the first 1 h and used the least-squares statistics to calculate the error ranges, based on a 50% confidence level. Only for the plots in which 2-propanol was exponentially decomposed, i.e., at the highest light intensity, the initial amount of acetone generated in 15 min was used as the initial rate.

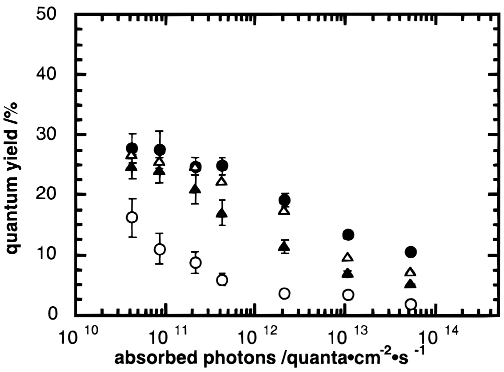

Figure 4. Dependence of QY on absorbed photons (initial 2-propanol concentration: ● 1000 ppmv, △ 100 ppmv, ▲ 10 ppmv, ○ 1 ppmv). Error bars for 100 ppmv are omitted for clarity.

Figure 4 shows semilog plots of I versus the apparent QY values for acetone generation. The apparent QY values were calculated using the following equation:

$$\mathrm{QY} = \frac{\text{number of generated acetone molecules}}{\text{number of absorbed photons}} \tag{3}$$

Error bars associated with the QY values were evaluated on the basis of the total error of measuring the acetone concentration and extrapolating the value of the UV light intensity. However, good repeatability, within 7% , was obtained even for the lowest I values. The QY values increased gradually with decreasing I and finally saturated for the highest initial 2-propanol concentration (1000 ppmv) for I less than 4×10^{11} quanta·cm^{-2}·s^{-1}, and thus a purely light-limited condition ($\alpha = 1$) was reached, where the maximum QY value was 27.8 ± 2.5%. This maximum QY value also appeared to be approached for lower initial concentrations. Moreover, the curve shapes for the different initial 2-propanol concentrations are similar regardless of the initial concentration. For a given QY value, increasing the initial 2-propanol concentrations by a factor of 10 leads to an increased value of I. However, the increases became smaller with increasing concentration: 10 times, 6 times, and only 2 times for 1−10 ppmv, 10−100 ppmv, and 100−1000 ppmv, respectively.

Discussion

The mechanisms for the photocatalytic decomposition of 2-propanol to acetone has been described.[16,26] The photocatalytic processes prior to the initiation of 2-propanol decomposition are well-known:

$$h\nu \rightarrow h^+ + e^- \tag{4}$$

$$h^+ + OH^-(s) \rightarrow {}^\bullet OH, \quad \text{or } h^+ + H_2O \rightarrow {}^\bullet OH + H^+ \tag{5}$$

$$e^- + O_2(s) \rightarrow O_2^{\bullet -} \tag{6}$$

$$O_2^{\bullet -} + H^+ \rightarrow HO_2^\bullet \tag{7}$$

The generated $^\bullet$OH radical reacts with 2-propanol, abstracting its hydrogen atom to form a radical:

$$CH_3CH(OH)CH_3 + {}^\bullet OH \rightarrow CH_3C\cdot(OH)CH_3 + H_2O \tag{8}$$

This $CH_3C^\bullet(OH)CH_3$ radical is decomposed to acetone through several reaction pathways. One of these is the so-called current-doubling reaction, expressed by

$$CH_3C^\bullet(OH)CH_3 \rightarrow CH_3COCH_3 + H^+ + e^-(C.B.) \tag{9}$$

where e^- (C.B.) represents an electron in the TiO_2 conduction band.[27] Under ambient conditions, however, O_2 can attack the radical, producing an unstable peroxo radical, which decomposes to acetone:

$$CH_3C^\bullet(OH)CH_3 + O_2 \rightarrow CH_3COO^\bullet(OH)CH_3 \tag{10}$$

$$CH_3COO^\bullet(OH)CH_3 \rightarrow CH_3COCH_3 + H^+ + O_2^- \tag{11}$$

In the same manner, $HO_2^\bullet$ radicals generated via eqs 6 and 7 may also react with the $CH_3C^\bullet(OH)CH_3$ radical

$$CH_3C^\bullet(OH)CH_3 + HO_2^\bullet \rightarrow CH_3COOH(OH)CH_3 \tag{12}$$

$$CH_3COOH(OH)CH_3 \rightarrow CH_3COCH_3 + H_2O_2 \tag{13}$$

Note that there is no chain reaction involved in the above processes. Overall, only one photon participates in generating one molecule of acetone, and therefore QY values were calculated using eq 3. Considering that no radical chain reactions are involved, the maximum QY value obtained (28%) is very high. We have previously reported that QY values for the decomposition of gaseous acetaldehyde ranged up to nearly 100%,[12−14] but this reaction involves chain reactions.[28]

In the present experiments, in which very low-intensity UV light was used, the frequency of the reaction of each adsorbed molecule with photoproduced reactive species such as $^\bullet$OH is very low. Let us estimate the frequency, for example, for the case of a light intensity of 1 $\mu W\cdot cm^{-2}$ and a gaseous 2-propanol concentration of 1000 ppmv. From the Langmuir adsorption isotherm in Figure 1, the area occupied by each molecule is estimated to be 0.3 nm^2. One $\mu W\cdot cm^{-2}$ of 365 nm UV light corresponds to 2×10^{12} $quanta\cdot cm^{-2}\cdot s^{-1}$. Therefore on the average, each 2-propanol molecule can encounter a photogenerated $^\bullet$OH radical only once every $\sim 10^3$ s if a single photon always generates a $^\bullet$OH radical. Conversely, the time scale of one series of photocatalytic processes including charge-separation and charge-transfer processes is very short. The time scale of electron−hole pair generation is on the order of 100 fs.[29,30] Thus, hole-trapping and electron-trapping at the TiO_2 surface, in other words, the charge-transfer processes to the surface, are completed in the picosecond−nanosecond region.[31,32] For example, electron migration to the TiO_2 surface is estimated to be 0.83 ns using $D = 0.02$ $cm^2\cdot s^{-1}$ in a 100-nm-TiO_2 particle.[33] $^\bullet$OH radicals are formed in on the order of 10 ns, and 2-propanol oxidation occurs in on the order of 100 ns. Electron−hole recombination proceeds in the 10−100 ns range.[34,35] Electron transfer to O_2 molecules is usually assumed to proceed more slowly[20,35] but still much faster than the time interval of the overall reaction frequency. These processes are schematically summarized in Figure 5. As seen in Figure 5, the charge-separation efficiency must be independent of I. Therefore, the maximum QY value of 28% can be considered to represent the intrinsic charge-separation efficiency of this TiO_2 film. The remaining 72% must be converted into heat in a charge-recombination process, as shown below.

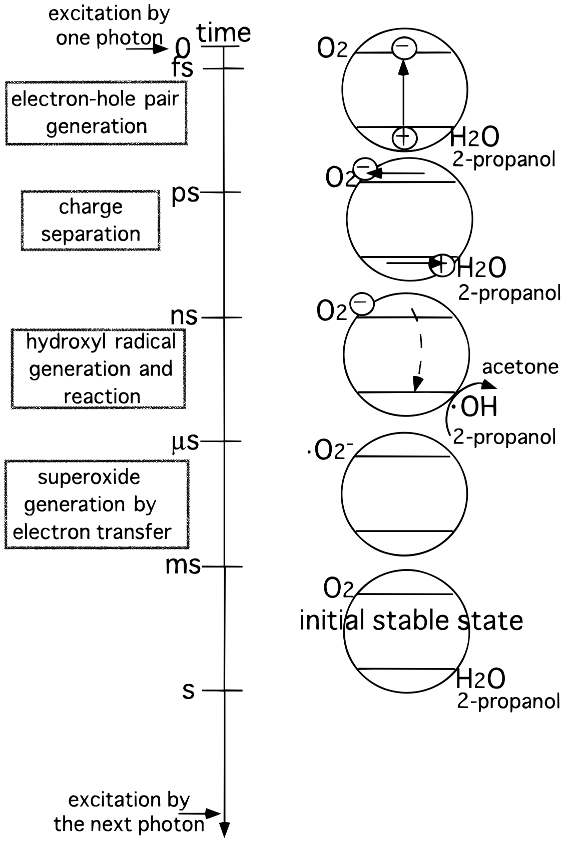

Figure 5. Schematic diagram of a series of photocatalytic processes along the time axis. The time interval of excitation by photons in this figure is assumed to be that for an experimental condition of 1 $\mu W\cdot cm^{-2}$ incident UV intensity and 1000 ppmv initial 2-propanol concentration.

$$h^+ + e^- \rightarrow \text{heat} \tag{14}$$

On a photoirradiated TiO_2 surface, various types of active oxygen species exist. These species react with each other, forming stable products, as follows:

$${}^\bullet OH + HO_2^\bullet \rightarrow H_2O + O_2 \tag{15}$$

$${}^\bullet OH + {}^\bullet OH \rightarrow H_2O_2 \tag{16}$$

Therefore, when the 2-propanol concentration is low, these reactions predominate. Conversely, with decreasing light intensity, these recombination reactions proceed less efficiently, and the QY values for 2-propanol decomposition increase. Because $^\bullet$OH radicals are much more reactive than $HO_2^\bullet$ radicals, the steady-state $^\bullet$OH concentration is probably much less than that of $HO_2^\bullet$. Moreover, the reaction rates of $^\bullet$OH with $HO_2^\bullet$ and with $^\bullet$OH were estimated to be 1.1×10^{-10} and 1.8×10^{-12} $cm^3\cdot mol^{-1}\cdot s^{-1}$, respectively.[36] Therefore, we can

TABLE 1: Correlation of the Initial 2-Propanol Concentration, Its Adsorbed Amount, and Absorbed Photons at a QY Value of 15%

initial concentration of 2-propanol/ppmv	adsorbed amount of 2-propanol/ molecules·cm^{-2}	adsorbed photons/ quanta·cm^{-2}·s^{-1}
1000	4.4×10^{16}	1×10^{13}
100	9.6×10^{15}	3×10^{12}
10	1.1×10^{15}	5×10^{11}
1	1.1×10^{14}	5×10^{10}

assume that reaction 15 is the main recombination process on the TiO_2 surface.

Next, let us consider the variation of the QY-absorbed photon curves on the reactant concentration in Figure 4. When the reactant concentration in the gas phase was decreased, the curve shifted to the lower light intensity direction. If we assume that both incident photon and reactant molecule flux arriving at the TiO_2 surface react immediately, the QY values should be determined by the ratio of the light intensity to the gas concentration. In other words, when the gas concentration increases by a factor of 10, the same QY value should be obtained with a factor of 10 higher light intensity. As can be seen in Figure 4, however, the experimental results do not support this model, showing that the factor correlating the QY values with the photon flux is not the flux of 2-propanol molecules under the present experimental conditions.

It is reasonable to consider that the adsorbed amount of 2-propanol is more important in determining the QY values. For example, in Table 1 are shown the initial 2-propanol concentrations (ppmv), the amounts of adsorbed 2-propanol molecules on TiO_2 (molecules·cm^{-2}), and the numbers of absorbed photons (quanta·cm^{-2}·s^{-1}) at a QY of 15% , as determined from Figure 4. The adsorbed amounts of 2-propanol were estimated from the Langmuir isotherm in Figure 1. A good proportionality between the amount of adsorbed 2-propanol molecules and the number of absorbed photons is suggested in this table. Even over the wide range of QY values shown in Figure 4, this relationship is satisfied. In other words, QY values appear to be determined by the ratio between the number of adsorbed 2-propanol molecules ($[M]_{ad}$) and the number of absorbed photons ($[photon]_{ab}$).

Here we define the normalized photon number (I_{norm}) as $[photon]_{ab}$ divided by $[M]_{ad}$ and have replotted the QY values as a function of I_{norm} in Figure 5. Despite the wide range of different initial concentrations of 2-propanol, the plots fall on the same curve. The value of QY increases as I_{norm} decreases and finally becomes constant at 28% for I_{norm} values below 10^{-4} (s^{-1}). Because $[photon]_{ab}$ is defined as the number of photons being absorbed in 1 s, I_{norm} has the dimension of s^{-1} in Figure 5.

This result indicates that either reactive species ($^{\bullet}OH$) or reactant (2-propanol) diffuses on the TiO_2 surface and the decomposition reaction efficiency is determined by the collision probability of these species. Moreover, it is suggested that the oxidation rate of 2-propanol by $^{\bullet}OH$ (eq 7) is much faster than the deactivation rates of $^{\bullet}OH$ (eqs 14 and 15). In other words, in the region where the QY value is constant with respect to I_{norm}, the $^{\bullet}OH$ produced by one photon always reacts with 2-propanol, not with either $HO_2^{\bullet}$ or $^{\bullet}OH$. From Figure 6, for 1 ppmv, i.e., of the lowest initial 2-propanol concentration in this study, we might also expect that QY approaches 28%. On the basis of this concentration, an intermolecular distance of adsorbed 2-propanol of ca. 11 nm can be calculated from the adsorption isotherm in Figure 1, making use of the surface area of this film (roughness factor of 150 cm^2·cm^{-2}) Therefore the possible diffusion length of either $^{\bullet}OH$ radicals or 2-propanol may be at least 11 nm. However, when the average 2-propanol intermolecular distance becomes greater than the $^{\bullet}OH$ radical diffusion length, the QY values can decrease against totally I_{norm} in Figure 6.

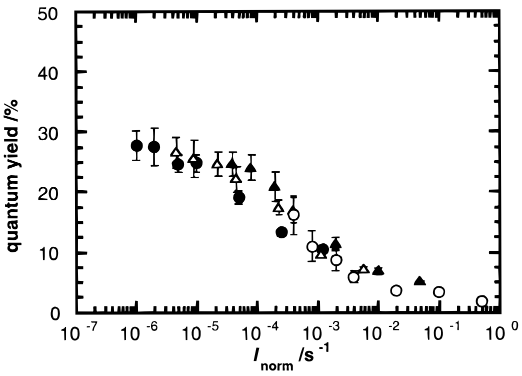

Figure 6. Plots of QY values vs log I_{norm} (/s^{-1}), a parameter that is defined as the ratio of the number of absorbed photons to the number of adsorbed 2-propanol molecules (initial 2-propanol concentration: ● 1000 ppmv, △ 100 ppmv, ▲ 10 ppmv, ○ 1 ppmv).

In the present study, we used a pure anatase TiO_2 sintered thin film, which has sufficient surface adsorbed water and oxygen[10] for electron−hole pairs to transfer at the TiO_2 interface. However, some lattice defects or doping transition metals exist in the bulk of TiO_2. These behave as trapping sites or recombination sites for electron−hole pairs.[34,37,38] Thus the variable amounts of these in different samples could influence the QY values vs I_{norm} in Figure 6. In addition, the variation of the amounts of surface hydroxyl groups, water, and oxygen molecules can also influence the charge-transfer process at the surface, and thus the $^{\bullet}OH$ radical diffusion distance.

Conclusion

From the present kinetic study of the photocatalytic decomposition efficiency of gaseous 2-propanol using purely anatase TiO_2 sintered thin film under very weak UV light, it can be concluded for the first time that QY values are determined by the ratio of the number of adsorbed 2-propanol molecules to the number of absorbed photons. This phenomenon indicates that either $^{\bullet}OH$ radicals or 2-propanol can diffuse on the TiO_2 surface at least ca. 11 nm. The decrease in QY is attributed to increases in the rates of reaction for $^{\bullet}OH$ radicals with $HO_2^{\bullet}$ radicals and $^{\bullet}OH$ with itself, relative to that with 2-propanol. The maximum QY value of 28% represents the intrinsic charge-separation efficiency of this sample. It is interesting that we can apply this reaction dynamics for such a wide 2-propanol concentration range. We believe that these findings can become significant models for photocatalysis involving more complex reactions, for example, in the case of reactants that are easily oxidized via radical chain reactions.

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