# Application of Chemiluminescent Probe to Monitoring Superoxide Radicals and Hydrogen Peroxide in TiO<sub>2</sub> Photocatalysis

## Yoshio Nosaka,\* Yoshifumi Yamashita, and Hiroshi Fukuyama

Department of Chemistry, Nagaoka University of Technology, Kamitomioka, Nagaoka 940-21, Japan Received: January 31, 1997; In Final Form: April 23, 1997<sup>®</sup>

A chemiluminescent probe, luminol, was successfully applied to monitoring superoxide ions  $(O_2^{\bullet-})$  and hydrogen peroxide  $(H_2O_2)$  produced on photocatalytic reaction in aqueous TiO<sub>2</sub> suspension. Two chemiluminescent reactions were distinguished from the decay profile after the end of the irradiation, and the reaction mechanism was analyzed. The fast decay component gives information about  $O_2^{\bullet-}$  and the slow one provides the amount of  $H_2O_2$ . The rate constant for the reaction of  $O_2^{\bullet-}$  with luminol was found to be  $1 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ . The amount of  $O_2^{\bullet-}$  during the irradiation on TiO<sub>2</sub> in alkaline solution could be estimated to be on the order of  $10^{-13}$  M. Detection of  $H_2O_2$  in concentrations as small as  $10^{-9}$  M was demonstrated in the photocatalytic water oxidation.

Photocatalytic reaction by using semiconductor powders has been paid much interest because of its possible applications to solar energy storage and mineralization of waste water. On band-gap irradiation of semiconductor powder in photocatalysis, electrons and holes are produced in the conduction band and valence band, which reduce and oxidize the molecules at the surface, respectively. In photocatalysis in air, active oxygen species such as hydroxyl radical (OH), superoxide ions  $(O_2^{\bullet-})$ , and hydrogen peroxide  $(H_2O_2)$  have been noticed as key species to initiate the reaction.<sup>1,2</sup> The efficiency of the photocatalytic reaction is limited by the reduction kinetics of dissolved  $O_2$ .<sup>3</sup> The formation of  $O_2^{\bullet-}$  in the photocatalytic system was certified by means of spin-trapping ESR spectroscopy.<sup>4</sup> Although, the lifetime of O<sub>2</sub><sup>•-</sup> is rather long in alkaline solution,<sup>5</sup> Gerischer assumed the steady concentration of O<sub>2</sub><sup>•-</sup> to be negligible.<sup>6</sup> The spin-trapping method gave no information on the lifetime of  $O_2^{\bullet^-}$ .

As an alternative method of detecting the active oxygen, it is interesting to use chemiluminescence (CL) in semiconductor photocatalytic reactions. Luminol is a representative CL probe, which is known to be sensitive to any oxidation reaction and the presence of hydrogen peroxide. Merenyi and co-workers investigated the mechanism of CL of luminol,<sup>7–9</sup> where  $O_2^{\bullet-}$ takes an important role of producing the electronically excited state. Since the luminescence detection is more sensitive than the ESR method, new information is obtained on the behavior of superoxide ions in photocatalysis. As far as we know, the present article is the first report of utilizing CL probes in the investigation of semiconductor photocatalytic reactions.

### **Materials and Method**

The sample was an aqueous solution of 3.5 mL (L = dm<sup>3</sup>) containing typically 0.01M (M = mol dm<sup>-3</sup>) NaOH and 15 mg of TiO<sub>2</sub> powder (Ishihara Sangyo, Ltd., ST-01). The pH was usually 11.0. The solution was stirred with a magnetic bar in a Pyrex cell 1 cm × 1 cm in size, and the cell was placed in a dark box. An aqueous solution (50  $\mu$ L) of 7 mM luminol (5-amino-2,3-dihydro-1,4-phthalazinedione, Nacalai Tesque, Ltd.) was added with a syringe into the solution before or after the irradiation. We distinguish this experimental procedure as

preaddition or postaddition. In some postaddition experiments, MCLA (methoxy *cypridina* luciferin analogue, 2-methyl-6-(*p*-methoxyphenyl)-3,7-dihydroimidazo[1,2-*a*]pyrazin-3-one, To-kyo Kasei, Ltd.)<sup>10,11</sup> was employed in place of luminol to detect superoxide ions.

Irradiation at the wavelength of  $387 \pm 11$  nm (fwhm) was performed with a 150-W xenon lamp through two glass filters (Hoya, U-330 and L39). The intensity of light incident on the cell was measured with a power meter to be 13 mW. After switching off the light irradiation, CL was measured at a side of the cell through a light guide, which was connected to a photon-counting photomultiplier tube (Hamamatsu Photonics Ltd., R2693P) mounted in a cooled housing (C659-S). Between the sample cell and the light guide, an interference filter and another shutter were set. The shutter placed in front of the light guide is to reduce the remaining signal of the photomultiplier tube associated with the activation by scattered light during the irradiation. In place of the interference filter, a sharp-cut filter of 420 nm (Hoya, L42) was used in some experiments. The photon-counting apparatus used was assembled with a discriminator (Hamamatsu, C3866) and a counting board (Hamamatsu, M3949) controlled by a personal computer. Photons were counted every 20 ms until 20 s after the end of the irradiation. The two shutters were driven with the personal computer through a digital pulse programmer (Stanford Research System, DG535).

#### **Results and Discussion**

**Postaddition of Probe Reagents.** Figure 1 is a superposition of the time profiles of the CL intensity on three batches of experiments where the addition of luminol was performed at 1, 21, and 41 s after the end of each 60-s irradiation. The weak signal observed in the short time region near 0 s is attributable to the luminescence of  $TiO_2$  powder. Although the irradiation duration was 60 s for Figure 1, a similar intensity of CL was observed for the duration of more than 10 s. In order to confirm that the observed light originates from the CL of luminol, the luminescence at 1 s after the irradiation was measured at various wavelengths. Figure 2 is the plot of the summation of the counted photons at each wavelength. The curve in Figure 2 is the photoluminescence spectrum of 3-aminophthalate (AP), which has been identified as the light-emitting species in luminol CL.

<sup>&</sup>lt;sup>®</sup> Abstract published in Advance ACS Abstracts, July 1, 1997.



**Figure 1.** Superposition of three traces of CL intensity, where the times of adding 0.1 mM luminol are 1, 21, and 41 s after the end of the 60-s irradiation on 3.5 mL of an aqueous solution containing 15 mg of TiO<sub>2</sub> and 0.01 M NaOH.



Figure 2. Spectrum of CL measured by changing interference filters ( $\bigcirc$ ) in postaddition experiments as shown in Figure 1 with the mark  $\times$ . The curve is the fluorescence spectrum with excitation wavelength at 350 nm for aqueous solution of 3-aminophthalic acid containing 0.01 M NaOH.

The excited state of 3-aminophthalate, AP\*, can be induced by the two reactions (eq 1 and 2).<sup>7</sup>

$$L^{\bullet-} + O_2^{\bullet-} \xrightarrow{k = 2.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}} \rightarrow AP^*$$
(1)

$$L + HO_2^{\bullet - \xrightarrow{k = 5 \times 10^7 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}}} \to AP^*$$
 (2)

where  $L^{\bullet-}$  is luminol radicals and L is two-electron-oxidized luminol or 5-aminophthalazine-1,4-dione. Reaction 2 is equivalent stoichiometrically to the reaction 1, although the yield of AP\* is rather low ( $\Phi = 0.012$ ).<sup>7</sup> Hydroperoxide ion HO<sub>2</sub><sup>-</sup> is formed by the acid—base equilibrium of H<sub>2</sub>O<sub>2</sub> in alkaline solution, where H<sub>2</sub>O<sub>2</sub> is formed by oxidation of H<sub>2</sub>O or reduction of O<sub>2</sub> in photocatalytic reaction.<sup>12</sup>

$$H_2O_2 \xrightarrow{pK_a = 11.7} HO_2^- + H^+$$
(3)

Figure 1 suggests that the amount of the chemical species inducing the CL decreased in the time range of 10 s without luminol. In order to know the lifetime of this species, the luminescence intensity was measured for other delay times of luminol mixing, and all obtained data were plotted in Figure 3. Each datum is the average of more than three experiments. The decay could be fit with an exponential function by a usual least-squares method. The lifetime of the chemical species was 17 s at pH 11. Since the lifetime was rather long, it is plausible that the active species is  $O_2^{\bullet-}$ , which disappears by a second-



**Figure 3.** Integrated intensity of CL of luminol  $(\Box)$  and MCLA  $(\bigcirc)$  as a function of the delay time of probe mixing in postaddition experiments at pH 11, as shown in Figure 1. The curve is the exponential function fitted to the data of luminol.

order process in pure aqueous solution with the rate constant of  $6 \times 10^{12}$ [H<sup>+</sup>] M<sup>-1</sup> s<sup>-1</sup> at pH > 6.<sup>5</sup> The concentration of O<sub>2</sub><sup>•-</sup> is less than the amount of incident photons, which is estimated to be  $10^{-4}$  M. The lifetime of O<sub>2</sub><sup>•-</sup> is then expected to be larger than  $10^2$  s. The observed decay time may originate from the reaction with TiO<sub>2</sub> particles.

The life time of the active species was measured at different pH. At pH 10 and 12, the lifetimes were 13 and 18 s, respectively. Increase in the luminescence intensity with pH was observed as well. This observation is consistent with the fact that the active species is  $O_2^{\bullet-}$ .

In order to confirm the existence of  $O_2^{\bullet-}$ , MCLA was used in place of luminol, because its CL occurs in the reaction with  $O_2^{\bullet-}$  and singlet molecular oxygen,  ${}^{1}O_2$ .<sup>10,11</sup> In Figure 3 is plotted the integrated number of photons observed on the addition of MCLA at different delay times after the end of the each irradiation. Since MCLA suffers autoxidation with air in alkaline solution, a constant CL was observed. Then the sharp peak of the CL observed immediately after the mixing was counted. The decay of the reactant shows a rate similar to that observed with luminol. Since luminol CL with  ${}^{1}O_2$  was not reported, the present observation shows that the CL in postaddition experiments is caused by  $O_2^{\bullet-}$ .

The two-electron-oxidized form of luminol, L, rapidly decomposes on reaction with  $OH^{-}$ , as eq 4.<sup>13</sup>

$$L + OH^{-} \xrightarrow{k = 4 \times 10^{6} M^{-1} s^{-1}} decomposition$$
(4)

Reaction 2 then appears to be less plausible as the CL mechanism in the postaddition experiment where the amounts of L and  $HO_2^-$  are small.

There are several possible routes for the formation of L<sup>•-</sup> radicals in eq 1. Although OH<sup>•</sup> radicals or surface holes are candidates of L<sup>•-</sup> formation, the following experiment denied the possibility.<sup>14</sup> Figure 4 shows the integrated CL intensity as a function of I<sup>-</sup> concentration. By adding I<sup>-</sup> the CL intensity increased at first and reached a steady value, indicating that the steady-state concentration of the oxidizing species increased with I<sup>-</sup> ions. Since I<sup>-</sup> is oxidized by OH<sup>•</sup> radicals or surface holes, then if these species oxidize luminol, the CL intensity should be decreased. The life time of these oxidants is too short to react with the luminol added after the end of the irradiation. The increase in the CL with I<sup>-</sup> is explained by the increase of O<sub>2</sub><sup>•-</sup> concentration, which originates from the suppression in the oxidation of O<sub>2</sub><sup>•-</sup>.

Other possible processes for the formation of  $L^{\bullet-}$  radicals in the postaddition experiments are the autoxidation of luminol in



Figure 4. Effect of the presence of NaI in an aqueous  $TiO_2$  suspension on the integrated CL intensities observed in the postaddition experiments.



Figure 5. Decay rate of CL as a function of the concentration of luminol added after the irradiation on an aqueous  $TiO_2$  suspension at pH 11.

alkaline solution (eq 5), $^9$  the oxidation with  $O_2{}^{\bullet-}$  (eq 6), $^8$  and the oxidation with  $H_2O_2$  (eq 7). $^{15}$ 

$$LH^{-} + O_{2} + OH^{-} \xrightarrow{k = 1.1 \times 10^{-8} M^{-1} s^{-1}} L^{\bullet -} + O_{2}^{\bullet -} + H_{2}O$$
(5)

$$LH^{-} + O_2^{\bullet-} \xleftarrow{K=10^{-4} M^{-1}} L^{\bullet-} + H_2O_2 + OH^{-}$$
(6)

$$LH^{-} + H_2O_2 \rightarrow L^{\bullet-} + OH^{\bullet} + H_2O$$
(7)

where  $LH^-$  is an ionized form of luminol in alkaline solution under the equilibrium of eq 8.<sup>9,16</sup>

$$LH2 \xrightarrow{pK_a = 6.7} LH^- + H^+$$
(8)

In the presence of 0.1 M  $H_2O_2$ , luminol solution shows continuous CL. This observation seems to justify the contribution of eq 7. However, since  $HO_2^{-1}$  is in equilibrium with  $O_2^{-1}$  at pH 11 (eq 9),<sup>17</sup>

$$\mathrm{HO}_{2}^{-} + \mathrm{O}_{2} + \mathrm{OH}^{-} \xleftarrow{K=4 \times 10^{-9}} 2\mathrm{O}_{2}^{\bullet-} + \mathrm{H}_{2}\mathrm{O} \qquad (9)$$

a small amount of  $O_2^{\bullet-}$  may be produced with a large amount of  $H_2O_2$ . Then oxidation can be attributable to the reaction with  $O_2^{\bullet-}$  (eq 6). Furthermore, reaction 7 has not been referred to by Merenyi *et al.*,<sup>9</sup> because of the energetical point of view. Thus the reaction 7 is ignored in the further discussion.

Figure 5 shows the dependence of decay rate on the concentration of luminol. Since the CL intensity is proportional



**Figure 6.** Integrated CL intensity observed after the end of the irradiation of  $1 \le (\times)$ ,  $5 \le (\diamondsuit)$ ,  $10 \le (\bigcirc)$ ,  $20 \le (\blacktriangle)$ ,  $40 \le (\blacksquare)$ , and  $80 \le (\textcircled{O})$ , as a function of the number of repeated irradiation on the sample under aerobic conditions (preaddition experiment). The irradiated sample was 3.5 mL of an aqueous suspension of 15 mg of TiO<sub>2</sub> containing 0.1 mM luminol and 0.01 M NaOH.



**Figure 7.** Typical time profile of the CL intensity in the preaddition experiment. The two curves are the components of the decay obtained from the curve fitting. See text for the details of the fitting procedure.

to the rate of AP\* formation, the intensity is proportional to the product of concentrations  $[O_2^{\bullet-}][L^{\bullet-}]$  based on eq 1 for fastdecay CL. This means that when  $[O_2^{\bullet-}] \ll [L^{\bullet-}]$ , the decay of CL is controlled by the decay of  $[O_2^{\bullet-}]$ , and the decay rate is proportional to  $[L^{\bullet-}]$ . In another case, when  $[L^{\bullet-}] \ll [O_2^{\bullet-}]$ , the decay rate is proportional to  $[O_2^{\bullet-}]$  or the concentration of other reactants for  $L^{\bullet-}$ . The decay rate of CL is unchanged with the amount of  $O_2^{\bullet-}$ , as shown in Figure 1. Figure 5 indicates a linear relationship between the decay rate and  $[LH^-]$ . Then the forward reaction of eq 6 is most plausible as the reaction controlling the decay of CL intensity. Since the decay rate is about 1 s<sup>-1</sup> with 0.1 mM LH<sup>-</sup>, the rate constant of reaction 6,  $k_6$ , is estimated to be about 10<sup>4</sup> M<sup>-1</sup> s<sup>-1</sup>. Further discussion including the estimation of radical concentration will be described in the last section.

**Preaddition of Luminol.** Figure 6 shows the total number of photons observed 20 s after the end of the irradiation for various durations ranging from 1 to 80 s. The abscissa of the figure is the number of repeated irradiations. With the repeat of irradiation, the CL intensity increased, indicating that some species contributing to the CL is accumulated during the irradiation of  $TiO_2$ .

Figure 7 shows a time profile of luminescence in the preaddition experiments. In the analysis of the data, the region later than 7 s was fitted first. This part of the data lies on the second-order decay curve. The calculated value of the fitted



**Figure 8.** Integrated CL intensity (a) and rate constants (b) of the fast ( $\Box$ ) and slow ( $\bigcirc$ ) decay components in the preaddition experiment as a function of the number of repeated 60-s irradiations, where 0.2 mM H<sub>2</sub>O<sub>2</sub> was added at the end of 5 irradiations.

curve was subtracted from the observed data. Then, the remaining fast part of CL decay can be fit by an exponential decay curve. Both components originate from luminol CL, because the spectra of each component fit to that of the photoluminescence of AP. The integrated number of photons was calculated from the amplitude and decay rate for each component.

Figure 8a shows the integrated CL intensity of each component as a function of the number of repeated irradiations. The component of slower decay increased with the number of repeated irradiations, while the increment of the fast component is small. When 0.2 mM  $H_2O_2$  was added after the five 10-s irradiations, only the intensity of the slow component increased. The decay rate constant of each CL is shown in Figure 8b, where the left-side scale is the pseudo-first-order rate constant of the fast decay. In the right-side scale,  $C_0$  is the initial concentration of the reactant, and k' is the second-order rate constant. The reactant will be identified in the later discussion. The rate for the slow component  $C_0k'$  decreased with the addition of  $H_2O_2$ , while that for the fast component remains almost constant. The relatively large scattering of rate constants in the preaddition experiment may be caused by possible adsorption of reaction products on the TiO<sub>2</sub> surface.

Since the decay rate of the fast component is similar to that observed in the postaddition experiment, CL of this component is probably induced by  $L^{\bullet-}$  with  $O_2^{\bullet-}$  (eq 1). On the other hand, Figure 8a shows that the chemiluminescent reaction of slow decay may involve the accumulated species, and it may be  $H_2O_2$  as indicated by eq 2. Thus, CL observed as the slow component is attributable to the reaction of L with  $HO_2^{-}$  (eq 2).

When luminol is present during the irradiation of  $TiO_2$ , it may suffer oxidation to L by the reaction with surface holes or OH• radicals. The luminescence intensity of two components



**Figure 9.** Effect of the presence of NaI in an aqueous  $TiO_2$  suspension on the integrated CL intensity of the fast ( $\Box$ ) and slow ( $\bigcirc$ ) decay components in the preaddition experiment.

was measured in the presence of the oxidizable agent I<sup>-</sup>. Figure 9 shows each CL intensity as a function of the concentration of NaI. The CL intensity of both components increased with the addition of I<sup>-</sup> similarly to that observed in the postaddition experiment. This observation indicates that L in the present observation was produced by another route than that with OH<sup>•</sup> radicals or surface holes.

Since luminol is present during the irradiation in the preaddition experiments,  $L^{\bullet-}$  is formed by photocatalytic reaction and the amount of  $L^{\bullet-}$  may be enough for producing L by disproportionation (eq 10).<sup>7</sup>

$$L^{\bullet-} + L^{\bullet-} + H_2 O \xrightarrow{k = 5 \times 10^8 \,\mathrm{M}^{-1} \,\mathrm{s}^{-1}} L + L H^- + O H^- \quad (10)$$

Since the amount of  $H_2O_2$  is on the order of  $10^{-4}$  M and then  $[HO_2^{-1}] \cong 10^{-5}$  M at pH 11, the time scale of reaction 2 is on the order of 1 ms. Then, the rate-determining step in CL of the slow-decay component is reaction 10. Since the CL intensity is proportional to [L], the second-order decay profile of the CL can be explained by reaction 10. From the observed rate constant of  $C_0k'$  in Figure 8b, the initial concentration of L<sup>•-</sup> is estimated by equating the reported rate constant of eq 10 to k'. They are  $6 \times 10^{-10}$  and  $2 \times 10^{-10}$  M before and after the addition of 0.2 mM H<sub>2</sub>O<sub>2</sub>, respectively. This decrease in the amount of  $H_2O_2$  during the irradiation.

In aqueous solution at pH 11, the rate constants for the reaction of OH<sup>•</sup> radicals with LH<sup>-</sup> (eq 11)<sup>18</sup> and HO<sub>2</sub><sup>-</sup> (eq 12)<sup>19</sup> are the same order of magnitude.

$$OH^{\bullet} + LH^{-} \xrightarrow{k = 9 \times 10^9 M^{-1} s^{-1}} L^{\bullet -} + H_2O$$
 (11)

$$OH^{\bullet} + HO_2^{-} \xrightarrow{k = 5.6 \times 10^9 M^{-1} s^{-1}} O_2^{\bullet^-} + H_2O$$
 (12)

For  $HO_2^-$  of reaction 12, the rate constant reported is larger than that for  $H_2O_2$  by 2 orders of magnitude.<sup>19</sup> Then, the amount of  $H_2O_2$  added (0.2 mM) is effective as  $HO_2^-$ , of which amount is calculated to be 0.03 mM at pH 11 from eq 3. Then the rate of reaction 12 is calculated to be  $2 \times 10^5 \text{ s}^{-1}$ . Provided that  $[LH^-] = 0.1 \text{ mM}$ , the rate of reaction 11 is  $9 \times 10^5 \text{ s}^{-1}$ . In the experimental observation in Figure 8, the amount of  $L^$ decreased by a factor of 3 in the presence of  $H_2O_2$ . Then, the rate of reaction (12) is expected to be twice that of reaction 11. The difference in the ratio of the competitive reactions by the factor 9 shows that the environment of OH• radicals at the catalyst surface is different from that in the bulk solution or the species were oxidized by surface holes.



**Figure 10.** Total CL intensity in the preaddition experiment for an aqueous  $TiO_2$  suspension containing 0.1 mM luminol and 0.01 M NaOH in the absence of oxygen plotted as a function of the number of repeated 60-s irradiations. An interference filter of 430 nm was used for observation.

Although the slow-decay component of CL is attributable to the reaction of L with  $HO_2^-$  (eq 2), this reaction competes with the decomposition of L with  $OH^-$  in alkaline solution (eq 4). Then the CL intensity of the slow component is related to the solution pH and concentrations of  $H_2O_2$  and L<sup>•-</sup>, in a complex manner.

As mentioned above, in the postaddition experiment where luminol was mixed after the photoirradiation, CL of the slowdecay component was not observed. This was attributed to the small amount of L and  $H_2O_2$ . Then, in the presence of  $H_2O_2$ , the slow-decay component of CL should be observed even in the postaddition experiment. When 0.2 mM  $H_2O_2$  was added before irradiation in the postaddition experiment, a part of the fast-decay changed to the slow-decay component.

Although most of the present experiments were performed in aerated condition, the reaction may be sensitive to the existence of oxygen. Then, we tried a preaddition experiment under vacuum to detect the oxygen formation from water by photocatalytic reaction. The sample cell was evacuated by freeze-and-thaw cycles. Although the intensity was very low, CL of the slower decay was observed. Figure 10 shows that the total CL increases with the repeat of the 10-s irradiation. The increment of the number of photons is smaller by a factor of  $10^4$  than that observed in the addition of 0.2 mM H<sub>2</sub>O<sub>2</sub> of Figure 8a. Then, the amount of produced H<sub>2</sub>O<sub>2</sub> is calculated to be on the order of  $10^{-9}$  M or  $10^{-11}$  mol. This means that the chemiluminescent probe is useful to detect the oxidation of water in photocatalytic reaction.

**Estimation of Radical Concentration.** Since the rate constants of related reactions have been reported, we can estimate steady-state concentration in the dark for the chemical species involved in the CL. When the steady-state approximation was applied to eqs 1, 5, 6, and 10 for  $O_2^{\bullet-}$  radicals, we obtain

$$[O_2^{\bullet}] = (k_5[LH^-][O_2] + 2k_9[HO_2^-][O_2])/(k_1[L^{\bullet}] + k_6[LH^-] + k_8)$$
(13)

where  $k_{\rm S}$  is decay rate constant of  $O_2^{\bullet-}$  in the absence of luminol. The forward rate constant for reaction 9,  $k_9$ , is calculated to be  $7 \times 10^{-11}$  M<sup>-1</sup> s<sup>-1</sup>, from the equilibrium constant reported<sup>17</sup> and the backward rate constant of 60 M<sup>-1</sup> s<sup>-1</sup> at pH 11.0.<sup>5</sup> Since  $[L^{\bullet-}] < 10^{-9}$  M and  $k_6 \approx 10^4$  M<sup>-1</sup> s<sup>-1</sup>, by adopting  $[O_2] = 3 \times 10^{-4}$  M,  $[HO_2^{--}] = 3 \times 10^{-5}$  M, and  $[LH^{--}] = 10^{-4}$  M in eq 13, the concentration of  $O_2^{\bullet-}$  is calculated to be  $3 \times 10^{-16}$  M before the irradiation. When we applied the steady-state



**Figure 11.** Simulated time profile of the amount of unstable species in a 0.1 mM luminol solution of pH = 11.0 after mixing with 5 ×  $10^{-13}$  M O<sub>2</sub><sup>•-</sup>: (a) d[AP\*]/dt in units of  $10^{-16}$  M s<sup>-1</sup>, (b) [O<sub>2</sub><sup>•-</sup>] in units of 5 ×  $10^{-13}$  M, (c) [L<sup>•-</sup>] in units of 5 ×  $10^{-12}$  M, and (d) [L] in units of  $10^{-19}$  M.

approximation to eqs 5 and 10 for  $[L^{\bullet-}]$  and then eqs 2, 4, and 10 for [L], the following relations were obtained.

$$[L^{\bullet-}] = \{(k_5[O_2] + k_6[O_2^{\bullet-}])[LH^-]/k_{10}\}^{1/2}$$
(14)

$$[L] = k_{10}[L^{\bullet}]^2 / (k_2[HO_2^-] + k_4[OH^-])$$
(15)

By adopting the above mentioned parameters to eqs 14 and 15, the steady-state concentrations for the unstable intermediates were obtained to be  $[L^{\bullet-}] = 1 \times 10^{-12} \text{ M}$  and  $[L] = 9 \times 10^{-20} \text{ M}$ .

The formation rate of AP\*, which is proportional to the observed CL intensity, is obtained from eqs 1 and 2.

$$d[AP^*]/dt = k_1[L^{\bullet-}][O_2^{\bullet-}] + \Phi k_2[L][HO_2^{-}]$$
(16)

By using the radical concentrations obtained for 0.1 mM luminol with 0.2 mM  $H_2O_2$  at pH 11.0, the steady-state formation rate of AP\* is calculated to be  $1.6 \times 10^{-18}$  M s<sup>-1</sup>. In the dark, the number of photons observed for this solution was 72 count/(20 ms) in the present experimental setup. Since it was 0.3 count/ (20 ms) in the absence of oxygen and  $H_2O_2$ , the 72 count/(20 ms) observed corresponds to the formation rate of  $1.6 \times 10^{-18}$ M s<sup>-1</sup>. Thus the formation rate of AP\* in the postaddition experiment in Figure 1 is calculated to be  $5.6 \times 10^{-17}$  M s<sup>-1</sup>, based on the CL intensity of 2500 count/(20 ms) at 1 s after the end of the irradiation. Although the second term in eq 16 is dominant in the CL for the solution containing  $H_2O_2$  in the dark, the first term is dominant in the postaddition experiment because of low  $H_2O_2$  concentration. Then, from eq 16 the product of the concentration  $[L^{\bullet-}][O_2^{\bullet-}]$  is estimated to be about  $2.4 \times 10^{-25}$  M<sup>2</sup>. Based on these considerations, the time profile of CL in the postaddition experiment was simulated for the AP\* formation rate as shown in Figure 11. The parameters newly introduced in the simulation are only  $k_6$  and the initial  $[O_2^{\bullet-}]$ ; the others are reported in the literature. Thus, the concentration of O2<sup>•-</sup> during the TiO2 irradiation in water at pH 11 is estimated to be about  $5 \times 10^{-13}$  M.

Acknowledgment. The authors are grateful to Prof. N. Suzuki for his stimulating discussion. The present work is partly defrayed by the Grant-in-Aid for Scientific Research on Priority-Area-Research (Nos. 07228223 and 08218223) from the Japanese Ministry of Science, Education and Culture.

## **References and Notes**

(1) Serpone, N.; Pelizzetti, E.; Hidaka, H. In *Photocatalytic Purification and Treatment of Water and Air*; Ollis, D. F., Al-Ekabi, H., Eds.; Elsevier: London, 1993; pp 225–250.

(2) Bahnemann, D.; Cunningham, J.; Fox, M. A.; Pelizzetti, E.; Pichat, P.; Serpone, M. In *Aquatic Surface Photochemistry*; Helz, G., Zepp, R., Crosby, D., Eds.: CRC: Boca Raton, FL, 1993; pp 261–316.

(3) Gerischer, H.; Heller, A. J. Electrochem. Soc. 1992, 139, 113-118.

(4) (a) Jaeger, C. D.; Bard, A. J. J. Phys. Chem. 1979, 82, 31463152.
(b) Harbour, J. R.; Hair, M. L. Adv. Colloid Interface Sci. 1986, 24, 103–141.

(5) Bielski, B. H. J.; Cabeli, D. E.; Arudi, R. L.; Ross, A. B. J. Phys. Chem. Ref. Data 1985, 14, 1041-1051.

- (6) Gerischer, H. Electrochim. Acta 1993, 38, 3-9.
- (7) Merenyi, G.; Lind, J.; Eriksen, T. E. J. Phys. Chem. 1984, 88, 2320-2323.
- (8) Merenyi, G.; Lind, J.; Eriksen, T. E. Photochem. Photobiol. 1985, 41, 203–208.
- (9) Merenyi, G.; Lind, J.; Shen, X.; Eriksen, T. E. J. Phys. Chem. 1990, 94, 748-752.

(10) Takahashi, A: Totsune-Nakano, H.; Nakano, M.; Mashiko, S.; Suzuki, N.; Ohma, C.; Inaba, H. *FEBS Lett.* **1989**, *246*, 117.

- (11) Suzuki, N. Spectrum 1993, 6, 21-25.
- (12) Ilan, Y. A.; Czapski, G.; Meisel, D. Biochim. Biophys. Acta 1976, 430, 209–224.
- (13) Eriksen, T. E.; Lind, J.; Merenyi, G. J. Chem. Soc., Faraday Trans. 1 1981, 77, 2125–2135.
- (14) Gutierrez, C.; Salvador, P. J. Electrochem. Soc. 1986, 133, 924-929.
- (15) Miller, E. K.; Fridovich, I. J. Free Radicals Biol. Med. 1986, 2, 107-110
- (16) Babko, A. K.; Lukovskaya, N. M. Ukr. Khim. Zr. (Russ. Ed.) 1963, 29, 479.
  - (17) Sawyer, D. T.; Gibian, M. J. Tetrahedron 1979, 35, 1471-1481.
  - (18) Wuerzberg, E.; Haas, Y. J. Phys. Chem. 1979, 83, 2687-2692.
  - (19) Baxton, G. V. Trans. Faraday Soc. 1969, 65, 2150-2158.