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Kinetics and Mechanisms of the Reaction of $PH_2O_2^-$ with O_2, Photocatalyzed by $[Ru(bpy)_3]^{2+*}$ (bpy = 2,2′-bipyridine), Forming Peroxodiphosphate Ions in an Aqueous Solution

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The formation reaction of peroxodiphosphate (denoted by PDP and meaning $P_2O_8^{4-}$, $HP_2O_8^{3-}$ etc.) by the reaction of molecular oxygen (O_2) with the phosphinate ion ($PH_2O_2^-$) was extremely accelerated by irradiation with visible light of aqueous solutions containing the tris(2,2′-bipyridine)ruthenium(II) ion ($[Ru(bpy)_3]^{2+}$). The $[Ru(bpy)_3]^{2+}$ acted as a photocatalyst during the reaction. The reaction mechanism consists of a chain reaction being accompanied by the O_2-quenching of a photoexcited ruthenium(II) complex ($[Ru(bpy)_3]^{2+*}$) to make the superoxide ($O_2^{-\bullet}$) and $[Ru(bpy)_3]^{3+}$, followed by the reduction of $[Ru(bpy)_3]^{3+}$ by $PH_2O_2^-$ to make $[Ru(bpy)_3]^{2+}$ and $PH_2O_2^{\bullet}$. However, such PDP once formed in the presence of O_2 began to decrease with a rate law of $-d[PDP]/dt = k_{obsd}[PDP]$ after the solution was saturated with N_2 gas, and when the solution was again saturated with air, the PDP began to increase again with light irradiation and remained constant in the dark. Such behaviors are discussed while presenting the reaction mechanisms.

Previously,[1,2] we studied the PDP formation reactions by the copper(II)- and chromate(VI)-catalyzed reaction between O_2 and $PH_2O_2^-$ in aqueous media. The initiating reactions in both catalysts were different: one is $Cu^{2+} + PH_2O_2^- \rightarrow Cu^+ + PH_2O_2^{\bullet}$, being followed by the rapid reaction of $Cu^+ + O_2 \rightarrow Cu^{2+} + O_2^{-\bullet}$ (Ref. 1); the other is $O_2 + PH_2O_2^- \rightarrow O_2^{-\bullet} + PH_2O_2^{\bullet}$ (Ref. 2). In both cases, the copper(II) and chromate(VI) ions finally acted to accelerate the reaction between O_2 and $PH_2O_2^-$. It is well known that the oxidative quenching of the photoexcited $[Ru(bpy)_3]^{2+*}$ by O_2 generates $[Ru(bpy)_3]^{3+}$ and $O_2^{-\bullet}$. We have studied[3,4] the photocatalyzed reaction for $H_2C_2O_4 + O_2 \rightarrow H_2O_2 + 2CO_2$ by using such an oxygen-quenching reaction of $[Ru(bpy)_3]^{2+*}$. It is common and important for obtaining the objective reactions mentioned in the previous studies to make the superoxide ($O_2^{-\bullet}$). Considering these previous studies, a PDP formation reaction having an overall reaction of $2PH_2O_2^- + 2O_2 \rightarrow H_2P_2O_8^{2-}$ could be anticipated by the light irradiation of aqueous solutions containing $[Ru(bpy)_3]^{2+}$ and $PH_2O_2^-$ in the presence of O_2. Such a novel photocatalyzed-reaction was verified by the present study. The acid dissociation constant of HPH_2O_2 is 4.0×10^{-2} M^{-1} ($M = 1\ mol\,dm^{-3}$)[5] and those of PDP[6] are 2.0, 0.31, $(6.6\pm0.3)\times10^{-6}$, and $(2.1\pm0.1)\times10^{-8}$ M^{-1} for K_{a1}, K_{a2}, K_{a3}, and K_{a4}, respectively. Thus, the predominant species in the present study of the pH range 2—4 were $PH_2O_2^-$ and $H_2P_2O_8^{2-}$.

Experimental

Chemicals. $[Ru(bpy)_3]Cl_2\cdot6H_2O$ was prepared as described in the literature[7] and recrystallized twice. $K_4P_2O_8$ was a gift from John O. Edwards of Brown University (U.S.A.); it was standardized iodometrically by measuring the I_3^- ion formed by the oxidation of iodide ion by the peroxodiphosphate ion. Sodium phosphinate monohydrate ($NaPH_2O_2\cdot H_2O$) and other chemicals used were of guaranteed grade from Wako Pure Chemical Industries, Ltd. The phosphinate solution was freshly prepared at each moment of use. Deionized water was further distilled in a glass still.

Procedures. The reaction vessel was a colorless glass bottle (5 dl; diameter 70 mm, thickness 1 mm, with 10 mm neck) placed in thermostatted water. The sample was irradiated with light from given numbers of 100-W tungsten lamps, which were placed 3 dm to the center of the reaction vessel. The irradiation continued throughout the reaction. The reaction was started by mixing a $[Ru(bpy)_3]^{2+}$ solution with a sodium phosphinate solution, and by irradiating the mixed solution. Each solution containing $PH_2O_2^-$ or $[Ru(bpy)_3]^{2+}$ was separately saturated with gas bubbling air, O_2, or N_2 through the solution before mixing solutions. The temperature of the reaction solutions was controlled to (25.0±0.1) °C. Aliquot samples were withdrawn at appropriate times to measure the concentrations of the formed PDP and $[Ru(bpy)_3]^{2+}$. The PDP concentrations were determined by using polarography at 0.25 V vs. SCE. The procedure for the polarographic measurements is the same as that reported in a previous study.[1] The concentrations of $[Ru(bpy)_3]^{2+}$ were determined spectrophotometrically by using the molar-absorption coefficient of 1.45×10^4 $M^{-1}\,cm^{-1}$ at 452 nm with a Shimadzu UV-240 spectrophotometer. The luminescence of $[Ru(bpy)_3]^{2+*}$ was measured at 610 nm by using a Shimadzu RF-5300PC spectrofluorometer at an excitation energy of 450 nm: the $[Ru(bpy)_3]^{2+}$ solution was saturated with gas of air, O_2, N_2 or Ar by bubbling each gas through it.

Results

Under the employed conditions, the concentration of $[Ru(bpy)_3]^{2+}$ remained constant during the reaction, and was much lower than that in the PDP formed. This indicates that $[Ru(bpy)_3]^{2+}$ acted as a catalyst in the chain reaction.

Effect of Oxygen. Figure 1 shows that the PDP was not formed in the absence of O_2 (see plots ● in Fig. 1), but was greatly formed in the presence of it. The concentrations of the formed PDP in the O_2-saturated solution were larger than those in the air-saturated one.

Effect of $[Ru(bpy)_3]^{2+}$. The concentration of $[Ru(bpy)_3]^{2+}$ remained unchanged during the reaction. The formation of PDP in accordance with increasing the $[Ru(bpy)_3]^{2+}$ concentrations increased in the range of 0—0.5×10^{-5} M, and then remained constant up to around 1.0×10^{-5} M, and decreasing along with a further increase in the ruthenium(II) complex (see Fig. 2). Even in the absence of $[Ru(bpy)_3]^{2+}$, smaller amounts of PDP were formed; the cases in the air- and O_2-saturated solutions are given in Fig. 2, inset, where plots using ●, ○, and △ indicate the saturation with N_2, air, and O_2 gas, respectively.

Effect of the Light Intensity. As can be seen from Fig. 3, the PDP formation increased with increasing reaction time, being rather proportional to the reaction time at the earlier stages in the plots, [PDP] vs. t (see Fig. 3, inset), and increased with increasing the irradiation intensity. It is noted that PDP formation at the zero lx in Fig. 3 is practically the same as that in the absence of the ruthenium(II) complex (compare ▲ in Figs. 3 and 4; the value in Fig. 3 is identical with that at pH 2.52 in Fig. 4).

Effect of Acidity. PDP formation in the absence and presence of a catalyst was greatly dependent on the acidity, decreasing at either less or larger than pH ≒ 2.5 at maximum (see Fig. 4). For the purpose of a comparison, the case of a copper(II)-catalayzed reaction in a previous study[1)] is also given in Fig. 4, inset.

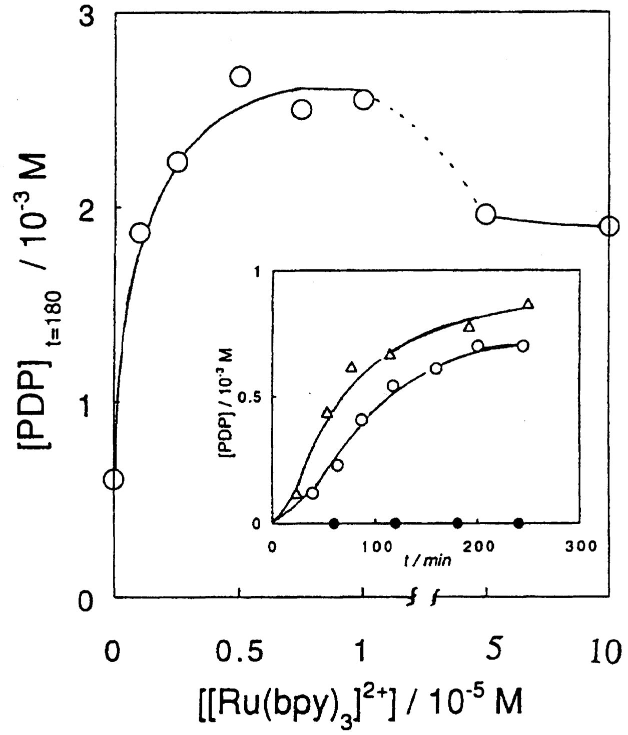

Fig. 2. Effect of concentrations of $[Ru(bpy)_3]^{2+}$.
Solutions were saturated with air at the varied concentrations of $[Ru(bpy)_3]^{2+}$. The other conditions are the same as those in Fig. 1. Inset indicates the plots [PDP] vs. t in the absence of $[Ru(bpy)_3]^{2+}$, where each symbol also means the same as each one in Fig. 1.

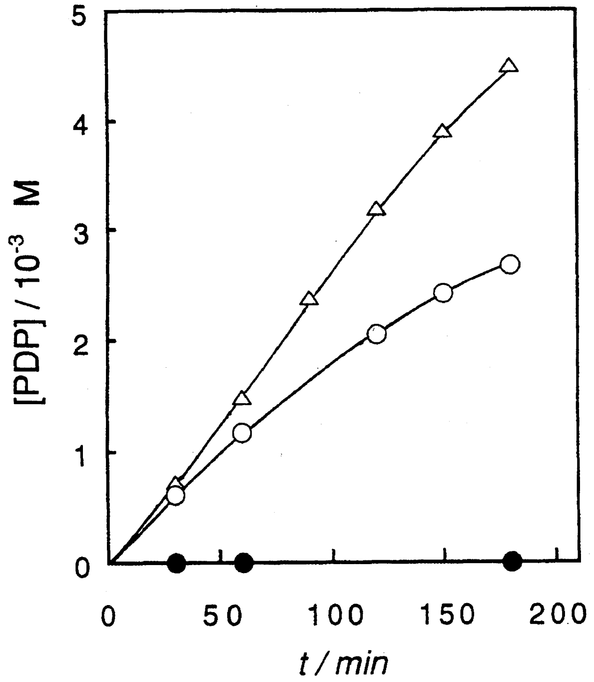

Fig. 1. Plots of [PDP] vs. t.
Conditions: 0.40 M $NaPH_2O_2$, 0.010 M H_2SO_4, 5.0×10^{-6} M $[Ru(bpy)_3]Cl_2$, pH 2.52 and 25.0 °C with irradiation with two 100-W lamps ($(5.0\pm0.3)\times10^3$ lx). Plots ●, ○, and △ indicate the solutions saturated with a gas of N_2, air, or O_2, respectively.

Effect of the Concentrations of $PH_2O_2^-$. Figure 5 shows the results obtained with different concentrations of phosphinate. PDP formation greatly increased along with increasing $PH_2O_2^-$ concentrations.

Decomposition of PDP in the Absence of Oxygen. When N_2 gas was bubbled through the reacting solution after PDP once formed in the presence of oxygen, the PDP began to decrease (see plots ● in Fig. 6). After such a PDP decrease occurred, if the solution was saturated with air PDP began to form again at almost the same rate-profile as the PDP formation curve at an earlier stage of the reaction in the air-saturated case (compare plots △ to ○ in Fig. 6A), but remained constant under dark conditions (see plots □ in Fig. 6A). As can be seen from the plots of ln [PDP] vs. t in Fig. 6B, the PDP decrease in the absence of oxygen followed a pseudo first-order rate law of $-d[PDP]/dt = k_{obsd}[PDP]$. The rate constants ($k_{obsd}$) obtained under various conditions are given in Table 1. From the results given in Table 1, the decomposition rate of PDP increased along with increasing the irradiation intensity of light, increasing the concentrations of $PH_2O_2^-$, and decreasing pH.

Quenching of $[Ru(bpy)_3]^{2+*}$ by O_2, $PH_2O_2^-$, or PDP. For clarifying electron-transfer step during the initial stage of the photocatalyzed reaction, the luminescence of [Ru-

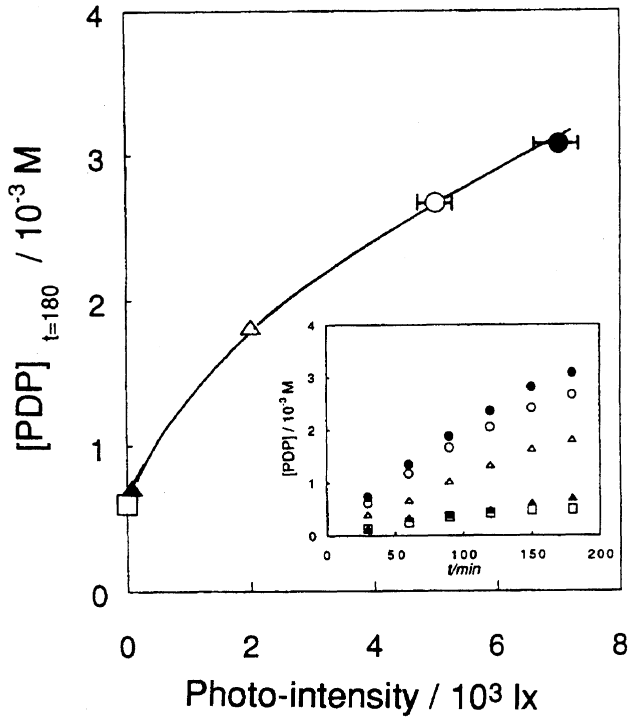

Fig. 3. Effect of the photo-intensity.

The plots of $[PDP]_{t=180}$ vs. photo-intensity with inset of [PDP] vs. *t* are given. Plots □, ▲, △, ○, and ● indicates 0.00 (dark), 60—100, (2.0±0.2)×10^3, (5.0±0.3)×10^3, and (7.0±0.5)×10^3 lx, respectively. Each solution was saturated with air at a given intensity of the light-irradiation. The other conditions are the same as those in Fig. 1. The value of (2.0±0.2)×10^3 lx corresponds to the irradiation with two tungsten lamps from 3 dm, and to 1.8×10^{-7} M s^{-1} which was determined by using a tris(oxalato)ferrate-(III) actinometer.

$(bpy)_3]^{2+*}$ at 610 nm was measured with various concentrations of O_2, $PH_2O_2^-$, or PDP. The luminescence was not appreciably affected by $PH_2O_2^-$ in the absence of O_2, but increased along with increasing the $PH_2O_2^-$ concentrations in its presence (see Fig. 7). The latter case with O_2 could occur by chemiluminescence due to such exothermal reactions as $[Ru(bpy)_3]^+ + [Ru(bpy)_3]^{3+} \rightarrow 2[Ru(bpy)_3]^{2+*}$ and $[Ru(bpy)_3]^{3+} + PH_2O_2^- \rightarrow [Ru(bpy)_3]^{2+*} + PH_2O_2^{\bullet}$. Actually, we visibly observed several chemiluminescence reactions between $[Ru(bpy)_3]^{3+}$ and such reducing agents as oxalate, ethylenediaminetetraacetate, triethylamine, and triethanolamine etc.[8] However, we could not observe analogous chemiluminescence using $PH_2O_2^-$ of 0.40 M; and the green color of $[Ru(bpy)_3]^{3+}$ did not change quickly to the orange of

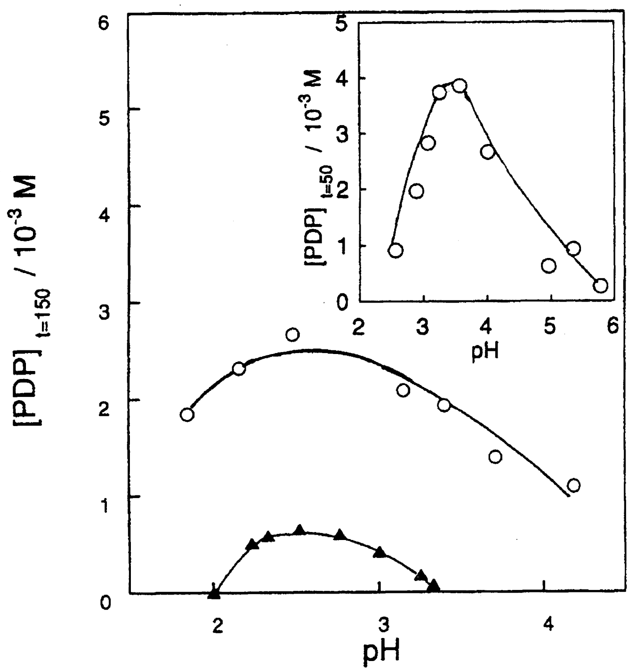

Fig. 4. Effect of acidity.

Each solution was saturated with air at a given pH. The other conditions are the same as those in Fig. 1, where the plots ▲ indicate the case in the absence of $[Ru(bpy)_3]^{2+}$ at the room light of 60—100 lx, and the inset, the case in the copper(II)-catalyzed reaction[1] of the previous study with 1.0×10^{-5} M $CuSO_4$. The pH was adjusted by adding appropriate amounts of H_2SO_4.

Table 1. Values of k_{obsd} in the Absence of O_2 (see Eq. 17)[a]

$[[Ru(bpy)_3]^{2+}]$/M	$[PH_2O_2^-]$/M	pH	Light-intensity/lx	$k_{obsd}/10^{-5}\ s^{-1}$
5.0×10^{-6}	0.20	2.44	(5.0±0.3)×10^3	3.2
	0.30			3.4
	0.40			4.0
	0.40	2.12	60—100	5.3
		2.52		3.0, 2.7, 2.8
		3.17		2.0
		2.13	(5.0±0.3)×10^3	6.3
		3.19		2.7
		3.64		1.8
		2.52	60—100	2.7, 2.8, 3.0
			(5.0±0.3)×10^3	3.5
			(7.0±0.5)×10^3	4.1

a) The other conditions are the same as those in Fig. 1.

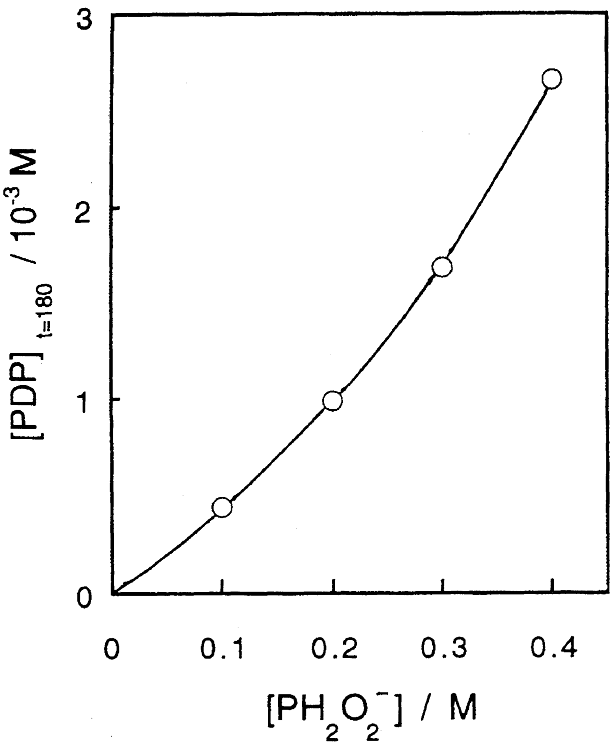

Fig. 5. Effect of the $PH_2O_2^-$ concentrations.
The plots of $[PDP]_{t=180}$ vs. $[PH_2O_2^-]$ are given. Each solution was saturated with air at a given concentration of $PH_2O_2^-$. The other conditions are the same as those in Fig. 1.

$[Ru(bpy)_3]^{2+}$. Therefore, the luminescence shown in Fig. 7 might have arisen from such reducing radicals as $PH_2O_2^{\bullet}$. Stern–Volmer plots are given in Fig. 8 for quenching experiments by PDP or O_2 in "Inset". The quenching constants in Eqs. 3 and 13 were estimated from Fig. 8 to be 3.2×10^9 and 4.8×10^8 M^{-1} s^{-1}, respectively, using 6.6×10^{-7} s[9] for the lifetime of $[Ru(bpy)_3]^{2+*}$. The quenching by PDP became stronger with decreasing pH: the emission-intensity ratio was 1.0 (8.50) : 0.71 (2.51) : 0.64 (2.39) : 0.59 (2.18), where the parentheses indicate the pH values.

Discussion

PDP formation was not found in the absence of O_2 under any conditions (● in Figs. 1 and 2), but was found in its presence even without adding $[Ru(bpy)_3]^{2+}$ (see ▲ in Fig. 4). This indicates that reactions (1), (5), (6), (7), and (8) occur as uncatalyzed reactions in which reaction (1) is an initiating reaction. However, the irradiation of a solution containing $[Ru(bpy)_3]^{2+}$ could extremely accelerate PDP formation, depending on the concentrations of $[Ru(bpy)_3]^{2+}$, O_2, $PH_2O_2^-$, and H^+, and on the irradiation intensity (see Figs. 1, 2, 3, 4, and 5). The quenching experiments given in Figs. 7 and 8 show that although the photo-excited ruthenium(II) complex $[Ru(bpy)_3]^{2+*}$ was not quenched by $PH_2O_2^-$ (see plots ● in Fig. 7), it was quenched by not only O_2, but also PDP, and that chemiluminescence occurred in the presence of oxygen (see the plots ○ in Fig. 7). Based on the plots using ● in Fig. 7, the reductive quenching reaction of $[Ru(bpy)_3]^{2+*}+PH_2O_2^-\rightarrow[Ru(bpy)_3]^{+}+PH_2O_2^{\bullet}$ does not occur, and thus, such a chemical excitation-reaction of $[Ru(bpy)_3]^{+}+[Ru(bpy)_3]^{3+}\rightarrow2[Ru(bpy)_3]^{2+*}$ should not be considered. Further, we could not directly observe chemiluminescence by the reaction between $[Ru(bpy)_3]^{3+}$ and $PH_2O_2^-$. Accordingly, the three reactions mentioned above could be excluded from considerations about the reaction mechanisms. If chemiluminescence could be found by the reaction $[Ru(bpy)_3]^{3+}+PH_2O_2^{\bullet}\rightarrow[Ru(bpy)_3]^{2+*}+PH_2O_2^{+}$ when the reacting solution of the light-irradiation in the presence of O_2 was changed to the dark, PDP formation did not stop, but continued due to co-occurrence with the reactions of

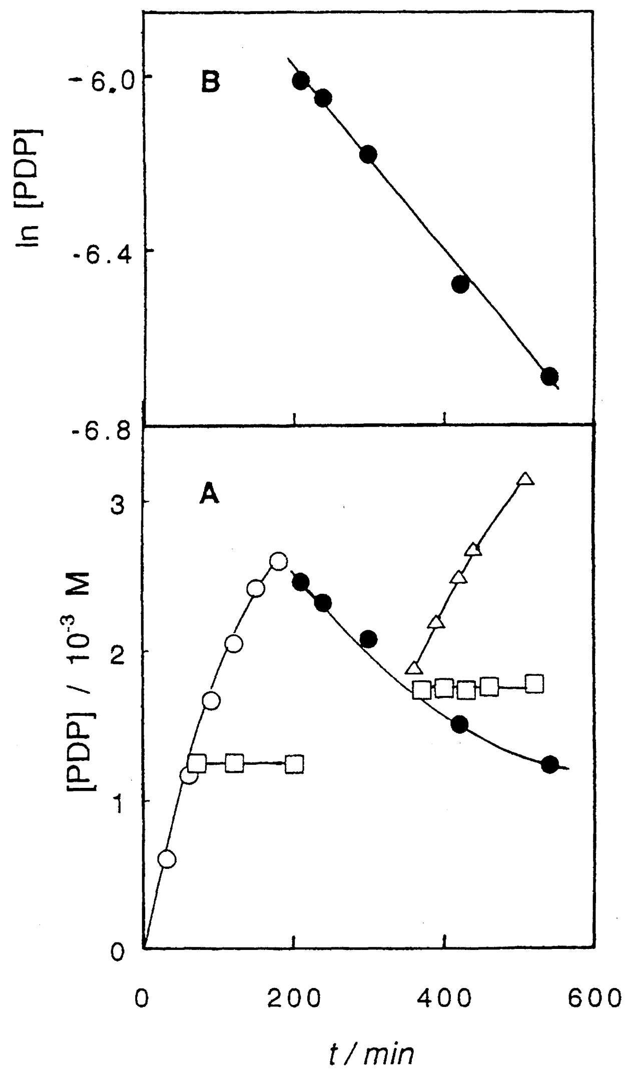

Fig. 6. Profile of the formation and decomposition of PDP.
The reaction solution was firstly saturated with air together with light-irradiation, and then, one was changed to the dark at $t=60$ min (plots □), and another was changed to the N_2-saturated at $t=180$ min (plots ●). The plots △ and □ at $t\geqq350$ min indicate cases when the reacting solution was again saturated with air, in the light-irradiation and the dark, respectively. The plots of ln [PDP] vs. *t* are given in B, using the plots ● in A. The other conditions are the same as those in Fig. 1.

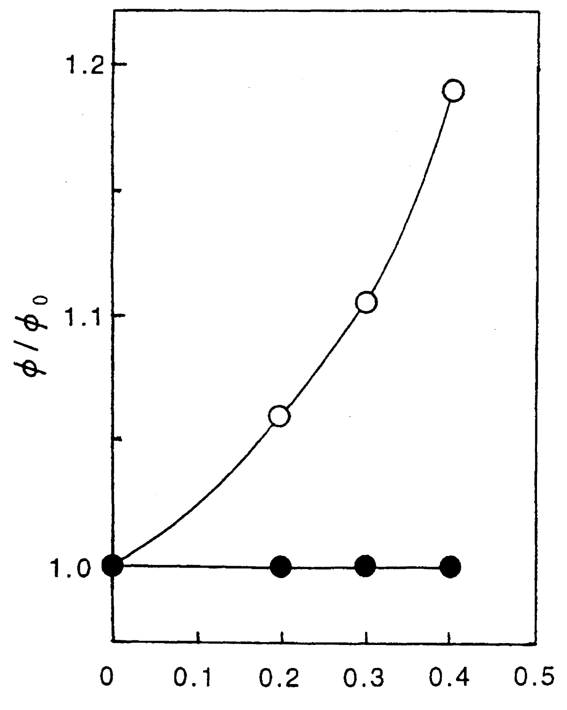

Fig. 7. Evidence of no quenching by $PH_2O_2^-$ and of chemiluminescence by $PH_2O_2^-$ with O_2.
ϕ_0 and ϕ are the emission intensities of $[Ru(bpy)_3]^{2+*}$ at 610 nm for the solutions in the absence and presence of $PH_2O_2^-$, respectively, and the plots ● and ○ indicate the reaction solution saturated with N_2 and air, respectively. The other conditions are the same as in Fig. 1.

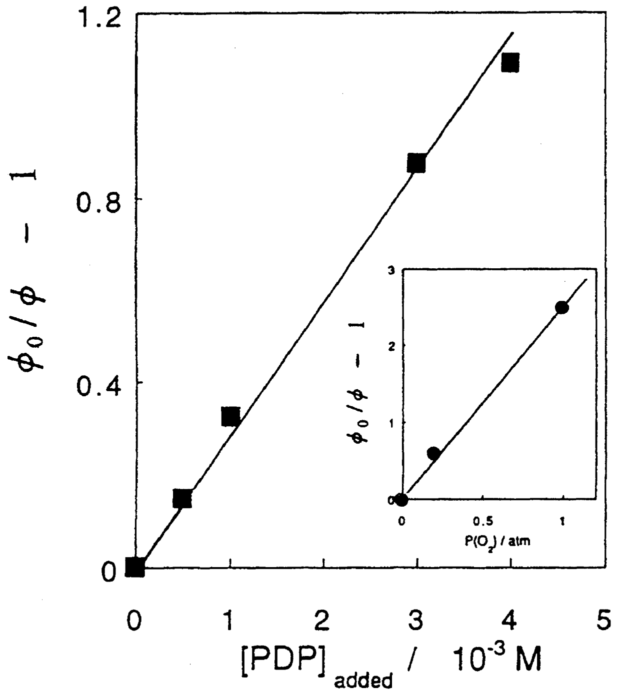

Fig. 8. Stern–Volmer plots in the quenching by PDP or O_2.
ϕ_0 and ϕ are the emission intensities of $[Ru(bpy)_3]^{2+*}$ at 610 nm for the solutions saturated with N_2 in the absence and presence of PDP, respectively. The case in the inset figure indicates ϕ_0 and ϕ to be the intensities in the absence and presence of O_2, respectively; the $P(O_2)$ indicates the partial pressures of oxygen, and the 1.0 atm in $P(O_2)$ means the O_2-saturated solution which contains 1.2×10^{-3} M. The other conditions are the same as in Fig. 1.

Eqs. 1, 7, and 8. However, such a fact could not be found at all (see □ at $t\geq 60$ min in Fig. 6A). Accordingly, it is thought that although we can observe chemiluminescence in Fig. 7, it was probably too weak to continue the PDP formation reaction, and most of the $[Ru(bpy)_3]^{3+}$ species might have been reduced to $[Ru(bpy)_3]^{2+}$ by $PH_2O_2^-$ (see Eq. 4).

Reaction Mechanisms. The following reactions are assumed to account for the obtained results (where the chemiluminescence reaction was neglected herein):

$$PH_2O_2^- + O_2 \rightleftarrows PH_2O_2^{\bullet} + O_2^{-\bullet} \quad (1)$$

$$[Ru(bpy)_3]^{2+} + h\nu \rightleftarrows [Ru(bpy)_3]^{2+*} \quad (2)$$

$$[Ru(bpy)_3]^{2+*} + O_2 \longrightarrow [Ru(bpy)_3]^{3+} + O_2^{-\bullet} \quad (3)$$

$$PH_2O_2^- + [Ru(bpy)_3]^{3+} \longrightarrow PH_2O_2^{\bullet} + [Ru(bpy)_3]^{2+} \quad (4)$$

$$HO_2^{\bullet} \rightleftarrows O_2^{-\bullet} + H^+ \quad [pK_a = 4.8^{10)}] \quad (5)$$

$$2PH_2O_2^{\bullet} \rightleftarrows PH_2O_2^+ + PH_2O_2^- \quad (6)$$

$$PH_2O_2^+ + O_2^{-\bullet}(\text{or } HO_2^{\bullet}) \longrightarrow H_2PO_4^{\bullet} \quad (7)$$

$$2H_2PO_4^{\bullet} \longrightarrow H_2P_2O_8^{2-} (\text{or PDP}) + 2H^+ \quad (8)$$

Here, the quenching constant (k_q) in Eq. 3 is 5.5×10^9 (Ref. 11) and $(3.3—5.5)\times10^9$ (Ref. 12) $M^{-1}\,s^{-1}$, which is in good agreement with 3.2×10^9 $M^{-1}\,s^{-1}$ obtained from Fig. 8, inset. An overall reaction of 4(1)+2(6)+2(7)+(8) is $2PH_2O_2^- + 4O_2 \rightarrow H_2P_2O_8^{2-} + 2HO_2^{\bullet}$, where (1) = (2)+(3)+(4). That is, the photocatalytic effect could have arisen from accelerating reaction (1) through reactions (2)—(4). The terminating reactions would include the following:

$$2HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \quad (9)$$

$$H_2O_2 + PH_2O_2^- + 2H^+ \longrightarrow PH_2O_2^+ + 2H_2O \quad (10)$$

$$H_2O + PH_2O_2^+ \longrightarrow H_2PO_3^- + 2H^+ \quad (11)$$

The overall reaction from Eq. 1 to Eq. 11 is $3PH_2O_2^- + 3O_2 \rightarrow H_2P_2O_8^{2-} + H_2PO_3^- + H_2O$ with 4(1)+2(6)+2(7)+(8)+(9)+(10)+(11), where (1) = (2)+(3)+(4). Reactions (6) and (11) are the same as those deduced in the mechanism of the reaction of $PH_2O_2^-$ with $S_2O_8^{2-}$ (Ref. 13).

Such a PDP once formed in the presence of O_2 began to decompose after the reacting solution was saturated with N_2 gas, following the rate law of $-d[PDP]/dt = k_{obsd}[PDP]$ (see the plots ● in Figs. 6A and 6B). This indicates the occurrence of the following reactions:

$$H_2P_2O_8^{2-} + PH_2O_2^- \longrightarrow HPO_4^{2-} + HPO_4^{-\bullet} + PH_2O_2^{\bullet} \quad (12)$$

$$[Ru(bpy)_3]^{2+} + h\nu \rightleftarrows [Ru(bpy)_3]^{2+*} \quad (2)$$

$$\mathrm{H_2P_2O_8^{2-}+[Ru(bpy)_3]^{2+*} \longrightarrow HPO_4^{2-}+HPO_4^{-\bullet}+[Ru(bpy)_3]^{3+}} \qquad (13)$$

$$\mathrm{[Ru(bpy)_3]^{3+}+PH_2O_2^- \longrightarrow [Ru(bpy)_3]^{2+}+PH_2O_2^{\bullet}} \qquad (4)$$

$$\mathrm{HPO_4^{-\bullet}+PH_2O_2^- \longrightarrow HPO_4^{2-}+PH_2O_2^{\bullet}} \qquad (14)$$

$$\mathrm{2PH_2O_2^{\bullet} \rightleftharpoons PH_2O_2^{+}+PH_2O_2^{-}} \qquad (6)$$

$$\mathrm{PH_2O_2^{+}+H_2O \longrightarrow H_2PO_3^{-}+2H^{+}} \qquad (11)$$

Reaction (12) could be accelerated by reactions (2), (4), and (13), i.e., (2) + (4) + (13) = (12), and the overall reaction of (2) + (13) + (4) + (14) + (6) + (11) is $\mathrm{H_2P_2O_8^{2-}+PH_2O_2^-+H_2O \rightarrow 2HPO_4^{2-}+H_2PO_3^-+2H^+}$, indicating a reaction between PDP and phosphinate. When reaction (12) is assumed to be rate-determining step, the rate law can be derived as follows:

$$-\mathrm{d[PDP]}/\mathrm{d}t = k_{12}\mathrm{[PH_2O_2^-][PDP]} \qquad (15)$$

$$= k_{\mathrm{obsd}}\mathrm{[PDP]} \quad (\text{at } \mathrm{[PH_2O_2^-]} \gg \mathrm{[PDP]}) \qquad (16)$$

$$\ln\mathrm{[PDP]} = -k_{\mathrm{obsd}}t + \ln\mathrm{[PDP]}_{t=0} \qquad (17)$$

Linear plots of ln [PDP] vs. t in the absence of $\mathrm{O_2}$ were obtained as shown in Fig. 6B. The values of k_{obsd} increased with increasing the $\mathrm{PH_2O_2^-}$ concentrations and the irradiation intensity, and also with decreasing the pH (see Table 1). If a reacting solution was again saturated with air on the way of the PDP-decomposition path, PDP began to form again (see plots △ in Fig. 6) under the conditions of light irradiation, but remained constant in the dark (see the plots □ at $t \geqq 350$ min in Fig. 6A). The former case is simply due to the reoccurrence of reactions (1)—(8), and the latter one is accounted for by the following reaction mechanism:

(Mechanism for plots □ in Fig. 6)

$$\mathrm{PH_2O_2^- + O_2 \rightleftharpoons PH_2O_2^{\bullet} + O_2^{-\bullet}} \qquad (1)$$

$$\mathrm{H_2P_2O_8^{2-}+PH_2O_2^- \longrightarrow HPO_4^{2-}+HPO_4^{-\bullet}+PH_2O_2^{\bullet}} \qquad (12)$$

$$\mathrm{HPO_4^{-\bullet}+PH_2O_2^- \longrightarrow HPO_4^{2-}+PH_2O_2^{\bullet}} \qquad (14)$$

$$\mathrm{2PH_2O_2^{\bullet} \rightleftharpoons PH_2O_2^{+}+PH_2O_2^{-}} \qquad (6)$$

$$\mathrm{PH_2O_2^{+}+O_2^{-\bullet} \longrightarrow H_2PO_4^{\bullet}} \qquad (7)$$

$$\mathrm{2H_2PO_4^{\bullet} \longrightarrow H_2P_2O_8^{2-}+2H^{+}} \qquad (8)$$

The overall reaction is $\mathrm{2PH_2O_2^-+2O_2 \rightarrow 2HPO_4^{2-}+2H^+}$ with 2(1)+(12)+(14)+2(6)+2(7)+(8), indicating the occurrence of equivalent formation and decomposition as a whole reaction. Thus, the PDP concentration remained unchanged. Such a phenomenon in plots using □ in Fig. 6 was the same as that in the case of chromate(VI) catalysis in a previous study.[2)]

For considerations of the pH effect on the formation and decomposition of PDP, the standard redox potentials[14)] are written below:

$$\mathrm{O_2 + e^- \rightleftharpoons O_2^{-\bullet}} \qquad [E^\circ = -0.56\ \mathrm{V}]\,(18)$$

$$\mathrm{O_2 + H^+ + e^- \rightleftharpoons HO_2^{\bullet}} \qquad [E^\circ = -0.13\ \mathrm{V}]\,(19)$$

$$\mathrm{H_3PO_3 + H^+ + 2e^- \rightleftharpoons HPH_2O_2 + H_2O} \qquad [E^\circ = -0.50\ \mathrm{V}]\,(20)$$

Judging from the redox potentials, the superoxide ($\mathrm{O_2^{-\bullet}}$ and $\mathrm{HO_2^{\bullet}}$) as well as the phosphinate ($\mathrm{PH_2O_2^-}$ and $\mathrm{HPH_2O_2}$) becomes a stronger reductant with increasing pH. Therefore, both conditions of increasing and decreasing the pH are not necessarily favorable for the occurrence of the forward reaction of Eq. 1. However, a pH increase is favorable for the occurrence of reactions (4), (12), and (14). Nevertheless, both reactions in the formation and decomposition of PDP became a slowdown with increasing pH (see Table 1 and Fig. 4 at pH>2.5). The rate constants for reaction (14) are reported to be 3.9×10^8, 5.9×10^7, and 7.9×10^7 $\mathrm{M^{-1}\,s^{-1}}$ for $\mathrm{H_2PO_4^{\bullet}}$, $\mathrm{HPO_4^{-\bullet}}$ and $\mathrm{PO_4^{2-\bullet}}$, respectively.[15)] The other species of $\mathrm{PH_2O_2^{\bullet}}$, $\mathrm{PH_2O_2^{+}}$ etc. would also be pH dependent on each reaction. Further, quenching reactions (3) and (13) are also dependent on the pH. Accordingly, the pH dependence in the present study was very complex; the bell-shape dependence having a maximum at around pH 2.5 (Fig. 4) would have a risen due to compensations for the increase and decrease effects by a pH change. As discussed later, such a pH-dependence as that shown in Fig. 4 was consequently thought to have mainly arisen from the pH effect on the equilibrium reaction (1), which contains in itself compensations for the forward and backward reactions' occurrence due to a pH change. The PDP formation increased along with increasing the $\mathrm{[Ru(bpy)_3]^{2+}}$ concentrations, and then reached a limiting value, showing a further decrease with larger concentrations (see Fig. 2). Such a behavior is thought to be due to a change in the amounts of light absorbed according to the concentration change of photo-catalyst $\mathrm{[Ru(bpy)_3]^{2+}}$, and is accounted for by

$$I_{\mathrm{a}} = I_0(1-\exp(-\alpha[\mathrm{[Ru(bpy)_3]^{2+}}]), \qquad (21)$$

where I_0 is the intensity of the incident light, I_{a} is the amount of light absorbed by $\mathrm{[Ru(bpy)_3]^{2+}}$, and α is an empirical constant comprising the length of the light path and the molar absorption coefficient of $\mathrm{[Ru(bpy)_3]^{2+}}$. Since the concentrations of the excited species ($\mathrm{[Ru(bpy)_3]^{2+*}}$) in Eq. 2 are proportional to I_{a}, the curve in Fig. 2 is thought to coincide with the expression of Eq. 21. Such a behavior in Fig. 2 is rather common to photoinduced electron-transfer reactions using $\mathrm{[Ru(bpy)_3]^{2+}}$ (refer to Refs. 16, 17, 18, 19, and 20).

The relatively large decrease of PDP formation at $\mathrm{[Ru(bpy)_3]^{2+}} \geqq 5.0\times10^{-5}$ M in Fig. 2 is thought to be due to an inner-filter effect and the occurrence of the reaction (13) to compete with reaction (3).

PDP formation was not proportional to I_0, showing a curve as in Fig. 3. This may indicate that the larger formation of $\mathrm{O_2^{-\bullet}}$ (or $\mathrm{HO_2^{\bullet}}$) and $\mathrm{PH_2O_2^{\bullet}}$ by photocatalyzed reactions (Eqs. 2, 3, and 4) could accelerate not only PDP formation (Eqs. 5, 6, 7, and 8), but also termination reactions (Eqs. 9, 10, and 11).

If $\mathrm{[Ru(bpy)_3]^{2+}}$ in the present study is compared to the other catalysts of copper(II)[1)] and chromate(VI),[2)] all of the behaviors in the present study are rather similar to the copper(II)-catalyzed reaction, but would be a photo-reaction. Although the catalysts concentrations remained unchanged during the reactions in the cases of the ruthenium(II)- and copper(II)-catalyzed reactions, the catalyst itself decreased in the case of Cr(VI)-catalysis according to the progress of the reaction. The bell-shape dependence of pH on PDP formation in Fig. 4 was also the same as in the case of the copper(II) catalysis, except for the pH value, to give maximum PDP formation; it was 3.5 for the copper(II) catalysis (see Fig. 4, inset). The pH value to give the maximum PDP formation in the case of Ru(II)-catalysis was 2.5, being almost the same as that of the uncatalyzed reaction (see Fig. 4). This indicates that reactions (2), (3), and (4) are practically independent of the acidity, and act to accelerate reaction (1). Consequently, such a pH dependence in the bell-shape is thought to have arisen from the opposite pH-effects on the redox capability due to the redox couples of $O_2/O_2^{-\bullet}$ and $PH_2O_2^-/PH_2O_2^\bullet$ (refer to Eqs. 18, 19, and 20). However, the pH dependence on the copper(II)-catalysis is influenced by the reaction of $PH_2O_2^- + Cu^{2+} \rightarrow PH_2O_2^\bullet + Cu^+$ (refer to Ref. 1), which is favorable for the larger pH conditions; the catalysis' activity of copper(II) diminished to nearly zero at pH 2.5, at which point PDP formation in the uncatalyzed reaction was maximum (see ▲ in Fig. 4 with inset). Thus, the bell-shape dependence of the pH in the case of the copper(II)-catalysis shifted to the right-hand side by one unit of pH (see Fig. 4, inset). Although the catalytic activity in the case of the chromate(VI) catalysis disappeared at a certain reaction time, that of both the ruthenium(II) and copper(II) catalysts did not diminish at longer reaction times, making the redox cycle of Ru^{III}/Ru^{II} or Cu^{II}/Cu^{I}. The chromate(VI)-catalyzed formation of PDP was induced or initiated by superoxide ($O_2^{-\bullet}$) formation by reaction (1) between O_2 and $PH_2O_2^-$. Namely, Eq. 1 was the sole initiating-reaction for the whole reaction; the chromate-catalyzed reactions could occur only by a reduction of Cr^{VI} to Cr^{V} by $O_2^{-\bullet}$ (refer to Ref. 2). On the other hand, Eq. 1 is not necessarily an initiating reaction in the cases of the ruthenium(II)- and copper(II)-catalyzed reactions. That is, the oxidative quenching reaction in the case of Ru(II)-catalysis (Eq. 3) and the reduction of Cu^{2+} by $PH_2O_2^-$ are very important reactions in order to accelerate reaction (1). Therefore, the pH effect on reaction (1) dominantly influenced the bell-shape dependence of pH in Fig. 4. In any case, the formation of the superoxide $O_2^{-\bullet}$ together with $PH_2O_2^+$ was absolutely necessary to make PDP (see Eqs. 7 and 8), in which the uncatalyzed reactions comprising Eqs. 1, 5, 6, 7, and 8 are always essential. It is to be noted that the turn-over numbers of $[\mathrm{PDP}]_{\mathrm{formed}}/[\mathrm{Cat}]_{\mathrm{added}}$ are as large as 10^2—10^4, depending on the conditions, where Cat = Cu^{II}, Cr^{VI}, or Ru^{II}, and that any catalysts are extremely efficient and novel for the PDP formation reaction to be accompanied by a new equilibrium reaction of Eq. 1 containing $\bullet O_2^{-\bullet}$ (or $HO_2^\bullet$) in aqueous media.

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