

Water Photolysis by Means of Visible Light with a System Composed of Prussian Blue and the Tris(2,2'-bipyridine)ruthenium(II) Complex

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A water-photolysis system composed of Prussian Blue (PB) and the tris(2,2'-bipyridine)ruthenium(II) complex ($[\text{Ru}(\text{bpy})_3]^{2+}$) which evolves hydrogen and oxygen simultaneously was studied. Both the components worked catalytically in the photolysis. PB provides active sites for both H_2 and O_2 evolution. The dependence on the pH showed optimum conditions at pH 2. The photolysis required the presence of a cation, and only such cations as K^+ and Rb^+ whose hydrated ions are smaller than the pore size of the PB lattice were active for the reaction. The dependence on the KCl concentration showed an optimum point at 0.5 mol dm^{-3} . The oxidative quenching of $[\text{Ru}(\text{bpy})_3]^{2+}$ by PB was suggested, but its ratio in the total quenching process was estimated to be only 8.5%. The static quenching of $[\text{Ru}(\text{bpy})_3]^{2+}$ by PB was demonstrated, and an interaction between the two components was shown by NMR spectroscopy. The effect of oxygen on the photolysis suggested that the reduction sites are located inside the PB lattice. A mechanism for the photolysis was proposed.

Water photolysis by visible light is attracting much attention in the chemical conversion of solar energy. Many studies of solar-energy conversion have been related to this subject.^{1,2)} The tris(2,2'-bipyridine)ruthenium(II) complex ($[\text{Ru}(\text{bpy})_3]^{2+}$) is the most promising photocatalyst for decomposing water photochemically.^{1,3,4)} Water photolysis with this complex requires, though, both electron mediator and catalysts. Methylviologen (MV^{2+} ; 1,1'-dimethyl-4,4'-bipyridinium dichloride) has been studied as a promising electron mediator; however, the cation radical formed in its reaction system is too sensitive to oxygen oxidation for it to be used in a system evolving oxygen simultaneously. Moreover, the rather complicated system composed of $[\text{Ru}(\text{bpy})_3]^{2+}$, MV^{2+} , and two kinds of catalysts for hydrogen and oxygen evolution (*e.g.*, Ref. 5) involves the problem of getting reproducible results.

It was found by the present authors⁶⁾ that Prussian Blue (PB) induces water photolysis to give hydrogen and oxygen simultaneously with the combination of $[\text{Ru}(\text{bpy})_3]^{2+}$. PB is a polynuclear mixed-valent iron complex whose composition has been proposed to be $\text{Fe}^{\text{III}}_4[\text{Fe}(\text{CN})_6]_3$; ⁷⁾ it forms a colloidal aqueous solution. The studies of this simple photolysis system have shown that the PB works as a kind of electron mediator as well as a catalyst for both hydrogen and oxygen evolution.⁶⁾ Such multifunctionalities of PB must be due to its polynuclear and mixed-valent structure. In this paper the factors affecting the photochemical reaction as well as the reaction mechanism are reported.

Experimental

Materials. The potassium hexacyanoferrate(III), $\text{K}_3[\text{Fe}(\text{CN})_6]$, and iron(II) chloride, $\text{FeCl}_2 \cdot 3.8 \text{ H}_2\text{O}$, were the purest commercially available grade. The PB was prepared by mixing aqueous solutions of both the iron salts at an equimolar ratio. The molar concentration ($M = \text{mol dm}^{-3}$) of PB in the text represents the concentration of each of the iron salts contained in the solution. The colloidal solution of PB thus prepared was stirred continuously before use in order to prevent the aggregation of the colloids, and used within 1 d. The $[\text{Ru}(\text{bpy})_3]^{2+}\text{Cl}_2$ was prepared by the reaction of ruthenium(III) chloride and 2, 2'-bipyridine in methyl alco-

hol, and recrystallized twice from methyl alcohol.

Photochemical Reaction. A 10-ml aqueous solution of 5 mM PB and $10 \mu\text{M} [\text{Ru}(\text{bpy})_3]^{2+}$ containing 0.5 M KCl at pH 2 (HCl–KCl buffer) was stirred and irradiated with visible light under argon atmosphere in a sealed vessel with a volume of about 20 ml equipped with a silicone stopper for the gas sampling. The irradiation was made with a 500-W Xenon lamp through UV and IR cutoff filters (Toshiba VY-42 and IRQ-80). The light intensity at the illuminated surface was 78 mW cm^{-2} .

Measurements. The gases formed were analyzed mainly by gas chromatography with a column consisting of a Molecular Sieve 5 A, using argon as the carrier gas. The O_2 evolved by the photochemical reaction was calculated by subtracting the content of O_2 coming from the air. For this calculation, the blank O_2/N_2 ratio was obtained by measuring the ratio (O_2/N_2) in the same vessel containing the same solution without irradiation. The errors in the determinations were $\pm 0.01 \mu\text{l}$ for H_2 and $\pm 0.02 \mu\text{l}$ for O_2 . The lifetime was measured by a single-photon-counting method, with an exciting light pulse of about 1 ns from a 12-atm hydrogen lamp. The particle size of the PB colloids was studied by means of transmission electron microscope (Hitachi H-3000), using phosphotungstic acid as the negative staining agent.

Results and Discussion

The mass spectrum of the gases evolved by the reaction of water containing D_2O and H_2^{18}O in the presence of PB, $[\text{Ru}(\text{bpy})_3]^{2+}$, and KCl showed that hydrogen and oxygen came from water.⁶⁾ The ratio of H_2 to O_2 was almost 2 to 1, corresponding to the theoretical value of water decomposition.⁶⁾ The time dependencies of the water photolysis, as represented by the amount of H_2 evolved at various concentrations of PB and $[\text{Ru}(\text{bpy})_3]^{2+}$, are shown in Fig. 1. The photolysis occurs almost linearly with the time. The turnover number of $[\text{Ru}(\text{bpy})_3]^{2+}$ in the photolysis with $1 \mu\text{M} [\text{Ru}(\text{bpy})_3]^{2+}$ and $500 \mu\text{M}$ PB is calculated to be 11 after 90 h. The visible spectrum of the solution after that reaction showed no actual change in the absorptions of either PB or $[\text{Ru}(\text{bpy})_3]^{2+}$ indicating that both the reactants work as catalysts.

As has been described in the previous paper⁶⁾ the excitations of both the complexes were required for the water photolysis to occur. The irradiation of an aque-

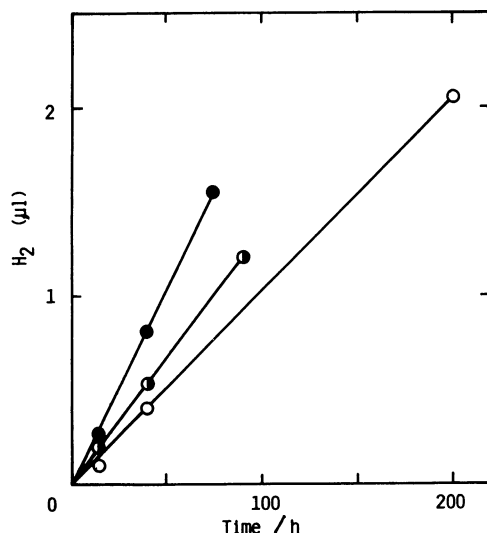


Fig. 1. Time dependencies of H_2 evolved by irradiation of the photolysis system composed of PB and $[Ru(bpy)_3]^{2+}$ in the presence of 0.5M KCl at pH 2. Under argon at room temperature. Solution; 10ml.

	PB (μM)	$[Ru(bpy)_3]^{2+}$ (μM)
●	500	1
○	500	10
○	5000	100

ous solution containing EDTA, $[Ru(bpy)_3]^{2+}$, and PB gave H_2 ⁶⁾, suggesting that PB works as the H_2 -evolving catalyst. The irradiation of an aqueous solution containing 10 μM ascorbic acid and 5 mM PB gave a small amount of H_2 (0.03 μl), while no H_2 was formed in the dark. An excess ascorbic acid brought about the formation of Prussian White, which is a Fe^{2+} - Fe^{2+} -type polynuclear cyanide complex, but H_2 was not formed even under irradiation. These results lead to the conclusion that H_2 is formed only by the irradiation of partially reduced PB. As will be shown later (Fig. 7), the ground state of Prussian White (entirely reduced PB) can not reduce protons because of its redox potential, but the excited state of a partially reduced PB must induce proton reduction to give H_2 . The excitation of PB at the λ_{max} of 700 nm is known to be due to an intervalent charge transfer (ICT) between the adjacent Fe^{2+} and Fe^{3+} ions through the antibonding π orbitals of the bridging CN ligand.⁸⁾ Since the Fe^{2+} ion itself can not reduce protons, the reduction of the protons must occur through the antibonding π orbitals of CN groups under excited conditions. The partially reduced PB would bring about the excitation of the adjacent CN ligands under ICT conditions, and such activated states of the adjacent CN groups would reduce two near-by protons to give H_2 .

It has been shown that the $[Ru(bpy)_3]^{3+}$ complex alone can not oxidize water in the absence of a catalyst.⁹⁾ The oxidation of water to give O_2 by $[Ru(bpy)_3]^{3+}$ in the presence of PB has led to the conclusion that PB works also as a catalyst for water oxidation.⁶⁾ Table 1 shows that a small amount of $[Ru(bpy)_3]^{3+}$ with respect to PB produces a high yield of O_2 when PB is used as the catalyst. The use of a higher concentration of

TABLE 1. OXYGEN EVOLUTION BY $[Ru(bpy)_3]^{3+}(ClO_4^-)_3$ WITH PB AS THE CATALYST

$[Ru(bpy)_3]^{3+}/M$	(μl)	O_2 evolved Yield/% ^{a)}
10^{-4}	4.5	74
10^{-3}	5.3	8.8
10^{-2}	11.5	1.9

PB: 5 mM, pH 2 (HCl-KCl buffer); solution: 10 ml; reaction for 1 h at 21 °C. a) Based on $[Ru(bpy)_3]^{3+}$.

$[Ru(bpy)_3]^{3+}$ increased the amount of O_2 evolved; however, its yield rather decreased. This is due to the oxidative degradation of PB, *i.e.*, the formation of a Fe^{3+} - Fe^{3+} -type complex (so-called Berlin Green), which was observed to form upon adding an excess of $[Ru(bpy)_3]^{3+}$ to PB. When a small amount of $[Ru(bpy)_3]^{3+}$ is used PB works as a good catalyst for O_2 formation by means of water oxidation. Considering the redox potential of $[Ru(bpy)_3]^{3+/2+}$ (1.27 V at pH 7), it can oxidize water to give O_2 only in the presence of a 4-electron oxidation catalyst.¹⁰⁾ Therefore, PB would work as a 4-electron oxidation catalyst to oxidize two molecules of water to form one molecule of O_2 through its polynuclear structure. The 4-electron catalytic reduction of O_2 by means of electrode reaction with PB-coated glassy carbon¹¹⁾ supports the occurrence of a multi-electron process in the polynuclear PB lattice.

For the water photolysis, an excess of PB with respect to $[Ru(bpy)_3]^{2+}$ is required. Table 2 shows that at least a

TABLE 2. DEPENDENCIES OF WATER PHOTOLYSIS ON THE PB AND $[Ru(bpy)_3]^{2+}$ CONCENTRATIONS

$[Ru(bpy)_3]^{2+}/M$	[PB]/M	$H_2(\mu l)$
10^{-4}	5×10^{-3}	0.36
10^{-4}	5×10^{-4}	0
10^{-4}	5×10^{-5}	0
10^{-5}	5×10^{-3}	0.27
10^{-5}	5×10^{-4}	0.21
10^{-5}	5×10^{-5}	0

KCl: 0.5 M, pH 2 (HCl-KCl buffer); solution: 10 ml; reaction for 15 h at 21 °C.

50-fold excess of PB is needed. As will be shown later (Fig. 5), a low concentration of PB can efficiently quench the excited state of the Ru complex. It can, therefore, be concluded that a large excess of PB is necessary not for the quenching process, but for the catalytic redox reactions.

Colloidal particles of PB were studied by means of an electron micrograph. The average diameter of the particles was about 23 nm. Studies by means of optical and electron microscopes showed that the particles aggregate to *ca.* 1 μm in the presence of KCl, even when stirred. The standing of the colloidal solution in the presence of KCl induced the growth of the aggregates to tens of μm , and at last caused the sedimentation of almost 90% of the PB. The rates of aggregation and sedimentation depend on the KCl concentration. The aggregation and sedimentation of PB lower its activity markedly. The presence of KCl in the solution hinders the study by means of microscope; however, since PB

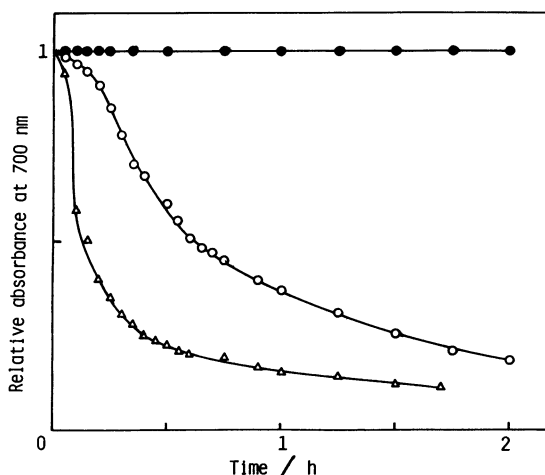


Fig. 2. Decrease of absorbance at 700 nm induced by aggregation and sedimentation of PB at pH 2. PB; 0.5 mM, $[\text{Ru}(\text{bpy})_3]^{2+}$; 10 μM . KCl concentration (M): ●; 0, ○; 0.5, Δ; 0.9.

aggregation brings about a decrease of its absorbance at 700 nm, the aggregation can be followed by means of visible spectroscopy. The decrease in the absorbance at 700 nm on standing is shown in Fig. 2. No absorbance change was observed in the absence of KCl, while the addition of KCl remarkably enhanced the absorbance decrease; *i.e.*, the aggregation becomes very rapid on the addition of KCl when there is no stirring. During a photochemical reaction, no spectrum change is observed, since the reaction mixture is stirred vigorously. However, the results of Fig. 2 reflect at least the effect of KCl on the aggregation of PB, which is not observed as a spectrum change under stirring.

The pH dependency of the H_2 formation is shown in Fig. 3. No photochemical reaction was observed below pH 1.5 or above 3.5. Since H_2 is formed by the reduction of protons, a lower pH should give a higher H_2 yield. However, the O_2 evolution by the $[\text{Ru}(\text{bpy})_3]^{3+}$ oxidation of water showed its optimum point at pH values from 2 to 3, and no O_2 was formed at pH 1.⁹⁾ If O_2 is not evolved efficiently, the back-electron transfer shown

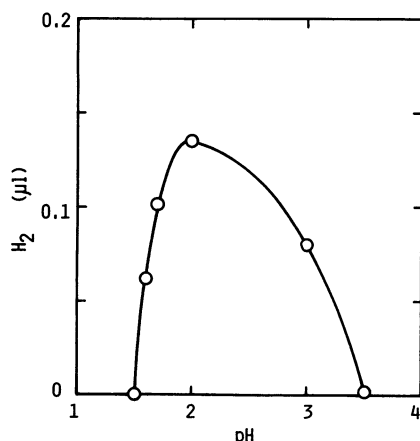


Fig. 3. pH dependency of H_2 formation. PB; 1 mM, $[\text{Ru}(\text{bpy})_3]^{2+}$; 10 μM , KCl; 0.5 M, Buffer solution: pH 1.5–2 (HCl–KCl), pH 2.5–3 (CH_3COONa –HCl), pH 3.5 (CH_3COONa – CH_3COOH). Irradiated under argon for 15 h. Solution; 4 ml.

later as Eq. 4 lowers the efficiency of the photolysis. Thus, the low efficiency of O_2 evolution would be one of the reasons for the low activity below pH 2 in Fig. 3. Since the redox potential of PB^+/PB is only slightly more positive than that of $\text{H}_2\text{O}/\text{O}_2$ at pH 2 as shown later in Fig. 7, the shift of the latter potential to more positive value at lower pH than 2 (*e.g.*, 1.17 V for $\text{H}_2\text{O}/\text{O}_2$ at pH 1) might be the reason for the lower activity at the pH lower than 2.

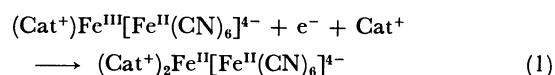
In the present water–photolysis system, the addition of KCl enhances the reaction rate. The effect of a neutral salt on the photolysis is shown in Table 3. RbCl

TABLE 3. EFFECT OF NEUTRAL SALT ON WATER PHOTOLYSIS WITH PB AND $[\text{Ru}(\text{bpy})_3]^{2+}$

Neutral salt	Diameter (nm) of hydrated cation	$\text{H}_2(\mu\text{l})$
RbCl	0.24	0.2
KCl	0.25	0.2
NaCl	0.37	0
LiCl	0.47	0
BaCl ₂	0.58	0

PB: 5 mM, $[\text{Ru}(\text{bpy})_3]^{2+}$; 10 μM ; salt: 0.4 M, pH 2; solution: 10 ml; reaction for 15 h at 21 °C.

and KCl were effective, but NaCl, LiCl, and BaCl₂ did not induce photolysis. For the reduction of PB, a cation (Cat^+) must enter into the PB lattice in order to compensate the negative charge of the electron (Eq. 1):



Itaya *et al.* recently studied the electrochemical reduction of PB coated on a platinum electrode in the presence of various neutral salts.¹²⁾ They found that neutral salts composed of cations whose hydrated ions are smaller than the pore size of the PB lattice (0.35 nm) can induce PB reduction, but neutral salts composed of larger cations are entirely ineffective. The results in Table 3 also shows that only the cations whose hydrated ions are smaller than the PB pore size are effective for the water photolysis.

The dependence of the photochemical reaction on the concentration of KCl is shown in Fig. 4. It has an optimum point at about 0.5 M. As has been described above, the present photolysis system demands the presence of a neutral salt such as KCl. On the other hand, neutral salt makes colloidal dispersions aggregate (see Fig. 2), because colloids are stabilized by an electrostatic repulsion of the charged particles. The decrease in photolysis at the higher concentration of KCl in Fig. 4 is thus explained by the easy aggregation of PB.

The excited state of the $[\text{Ru}(\text{bpy})_3]^{2+}$ is efficiently quenched by PB. The formation of H_2 by the irradiation of the mixture of EDTA, $[\text{Ru}(\text{bpy})_3]^{2+}$, and PB in water⁶⁾ indicated that the oxidative quenching of $[\text{Ru}(\text{bpy})_3]^{2+*}$ by PB is involved. The Stern–Volmer plots of the $[\text{Ru}(\text{bpy})_3]^{2+*}$ quenching by PB in the presence of 0.5 M KCl are shown in Fig. 5 (a). The quenching-rate constant is calculated to be $1.99 \times 10^{10} \text{ (M}^{-1} \text{ s}^{-1})$, using the lifetime (528 ns) of the $[\text{Ru}(\text{bpy})_3]^{2+*}$ under these conditions. If the quenching is entirely due

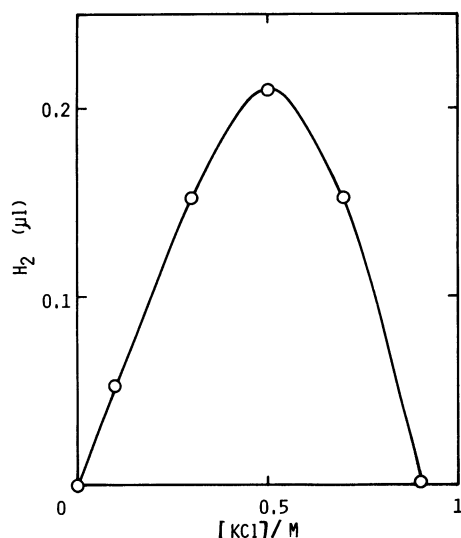


Fig. 4. Dependency of H_2 formation on KCl concentration. PB; 5 μ M, $[Ru(bpy)_3]^{2+}$; 10 μ M, pH 2. Irradiated under argon for 15 h. Solution; 10 ml.

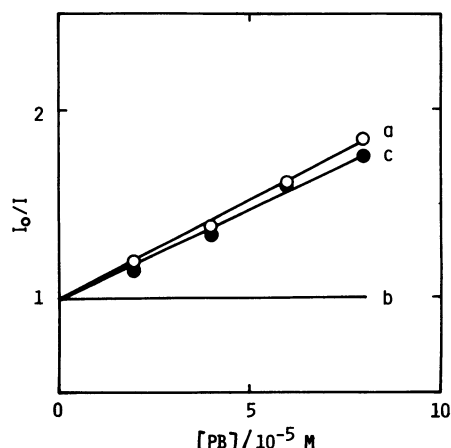


Fig. 5. Stern-Volmer plots for the quenching of $[Ru(bpy)_3]^{2+}$ by PB measured by emission intensity at 600 nm. $[Ru(bpy)_3]^{2+}$; 20 μ M, pH 2, under argon, excited at 450 nm. (a) KCl; 0.5 M, (b) Theoretical line when no quenching occurs, (c) NaCl; 0.5 M.

to electron transfer from $[Ru(bpy)_3]^{2+*}$ to PB, it would not occur in the presence of NaCl instead of KCl, because PB can not be reduced in the presence of NaCl.¹²⁾ The plots must fall on the (b) line of Fig. 5 in this case. If the quenching is only partly due to the electron transfer, the Stern-Volmer plots measured in the presence of NaCl would fall between (a) and (b) lines. The quenching of $[Ru(bpy)_3]^{2+*}$ in the presence of NaCl without KCl was measured; it is shown in Fig. 5(c). The (c) line lies between (a) and (b), indicating that the quenching is partly due to electron transfer. The ratio of the electron-transfer quenching is estimated to be 8.5% from the ratio of the difference in the (a) and (c) slopes to the slope of (a), assuming that the other quenching process of the $[Ru(bpy)_3]^{2+*}$ by PB is not affected by the cation species of the neutral salt present.

The Stern-Volmer plots, as measured by means of emission quenching and the lifetime, are shown in Fig. 6. The two plots fall on quite different lines,

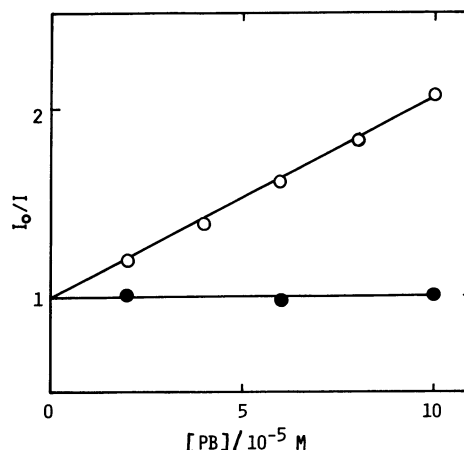
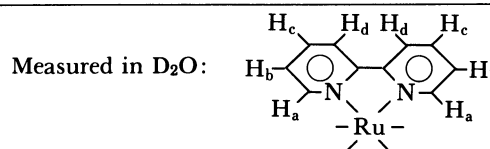


Fig. 6. Stern-Volmer plots measured by emission quenching (O) and lifetime (●) of $[Ru(bpy)_3]^{2+}$ with PB as a quencher. $[Ru(bpy)_3]^{2+}$; 20 μ M, KCl; 0.5 M, pH 2, under argon, at 25°C, excited at 450 nm.

indicating that static quenching occurs. It is suggested that there is an interaction between PB and $[Ru(bpy)_3]^{2+}$. No such interaction was observed in the visible spectrum, but the 1H NMR spectrum showed an evidence of it. The proton signals of the bpy rings of the Ru complex shown in Table 4, that were observed at the δ values of 7–9, did not appear in the presence of PB at $\delta=0-15$. It was observed that the proton signals of benzoic acid, which does not form any complex with PB, are not affected by the presence of PB. These results indicate some strong interaction, probably complex formation, between $[Ru(bpy)_3]^{2+}$ and PB. Such an interaction must cause the static quenching of $[Ru(bpy)_3]^{2+*}$ by PB.

TABLE 4. 1H NMR OF $[Ru(bpy)_3]^{2+}$ IN THE ABSENCE AND PRESENCE OF PB

Proton	δ in the absence of PB	δ in the presence of PB
H_a	9.04 (Doublet)	Not observed between $\delta=0-15$
H_c	8.56 (Triplet)	
H_d	8.34 (Triplet)	
H_b	7.88 (Doublet)	



In a photochemical conversion system using MV^{2+} as an electron mediator, the presence of even a trace of oxygen inhibits the photochemical reaction, because O_2 very rapidly oxidizes the cation radical of MV^{2+} formed as an intermediate. For the same reason, MV^{2+} is not suited as an electron mediator for a system that aims at simultaneous O_2 and H_2 evolution. The effect of O_2 on the water photolysis by PB and $[Ru(bpy)_3]^{2+}$ is shown in Table 5. It is interesting that H_2 was evolved even in the presence of O_2 , although the efficiency decreased to one-third that of the system containing no O_2 . The shape of the O_2 molecule can be approximated as a cylinder which has a diameter of about 0.28 nm and a length of 0.4 nm. The O_2 molecule can, therefore,

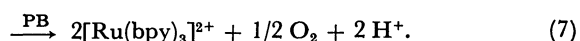
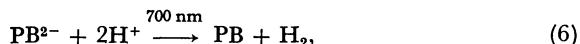
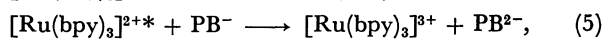
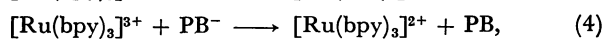
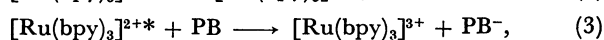
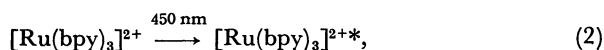
TABLE 5. EFFECT OF O₂ ON THE WATER PHOTOLYSIS WITH PB AND [Ru(bpy)₃]²⁺

Atmosphere	H ₂ (μl)
Argon	0.27
Air	0.09

PB: 5 mM, [Ru(bpy)₃]²⁺: 10 μM; KCl: 0.5 M, pH 2 (HCl-KCl buffer); reaction: 15 h.

enter into the PB lattice only from the direction of its axis, the inside of the lattice being fairly protected against O₂ attack. From a thermodynamic point of view, the active site of H₂ evolution must be sensitive to O₂ oxidation, leading to inactivation. The fact of H₂ evolution in spite of the presence of O₂ shown in Table 5 suggests, then, that the active reduction sites are located inside the PB lattice, allowing the water photolysis even under air.

The mechanism of the present water-photolysis system can be summarized as follows:



The excited state of [Ru(bpy)₃]²⁺ is quenched by PB by means of a static process. A part of the quenching occurs by means of electron transfer from [Ru(bpy)₃]^{2+*} to PB in the presence of cation such as K⁺ or Rb⁺, thus giving [Ru(bpy)₃]³⁺ and PB⁻ (Eq. 3). Although back-electron transfer (Eq. 4) might prevail, the electron-transfer quenching of [Ru(bpy)₃]^{2+*} by PB⁻ would also occur to form [Ru(bpy)₃]³⁺ and PB²⁻ (Eq. 5). The PB²⁻ thus formed would reduce two protons under excited ICT-conditions to give H₂ (Eq. 6). The active site for this reduction process would be located inside the lattice, protected against O₂ attack. When four molecules of [Ru(bpy)₃]³⁺ are accumulated, they oxidize water with the PB catalyst to give O₂ (Eq. 7).

As has been shown before (Fig. 6), strong static quenching occurs in the present photolysis system. In addition, the entire shift of the [Ru(bpy)₃]²⁺ proton peaks of the NMR spectrum in the presence of PB (shown in Table 3), and the almost complete quenching of the excited state of [Ru(bpy)₃]²⁺ by PB under usual reaction conditions, show that almost all the Ru complexes are interacting with PB. Assuming that PB has a spherical form, one particle 23 nm in diameter contains about 6 × 10³ unit cells. One PB particle then interacts with 2.4 × 10² [Ru(bpy)₃]²⁺ molecules under the usual conditions of a 10 μM Ru complex and 1 mM PB. Since [Ru(bpy)₃]^{2+*} is entirely quenched by PB under these conditions, the occurrence of the multi-electron reduction of PB shown in Eq. 5 is possible. The mixing of [Ru(bpy)₃]²⁺ with PB before or after the formation of the latter complex did not affect

the catalysis. Considering this result and the fact that the Ru Complex is too large to be included in the PB lattice, the Ru complex must be present on the surface of the PB particle. The location of the oxidation sites has not been elucidated by the experiments so far; however, it might be located on or near the PB surface, considering that the oxidation and reduction sites must be located separately.

The presence of Pt colloids and/or RuO₂ (powders or sol) in the reaction mixture did not increase the rate of water photolysis. These results would support the above-mentioned mechanism, the idea that the inner or surface structure of PB colloids plays an important role in the H₂ and O₂ evolution.

The potential diagram of the present photolysis system (at pH 2) is shown in Fig. 7. The redox

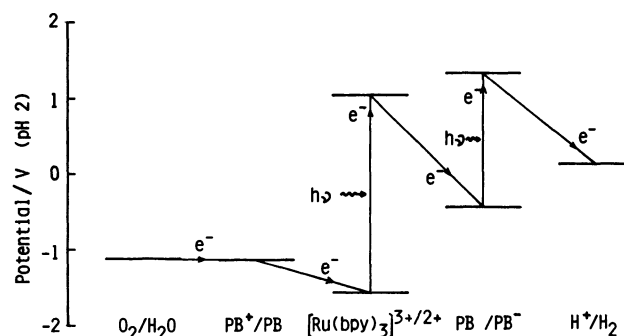


Fig. 7. Potential diagram of the water photolysis system with PB and [Ru(bpy)₃]²⁺.

potentials of PB are the values at pH 4 reported by Itaya *et al.*¹²⁾ It could be assumed that the potentials of PB are almost pH-independent. Since the ground state of PB⁻ can not reduce protons potentially, the excitation of the partially reduced PB is necessary in order to reduce H⁺ to give H₂. Such a diagram is regarded as a model for the photoinduced electron flow of the photosynthesis, where two steps of excitation brings about an endoergic electron transfer from water to CO₂.

PB thus works as a kind of electron mediator and also as a catalyst for both H₂ and O₂ evolution. These multifunctionalities of PB are due to its polynuclear and mixed-valent structure.

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