SIMULTANEOUS EVOLUTION OF HYDROGEN AND OXYGEN BY WATER PHOTOLYSIS WITH PRUSSIAN BLUE AND TRIS(2,2'-BIPYRIDYL)RUTHENIUM(II) COMPLEX

Masao KANEKO*, Naoki TAKABAYASHI, and Akira YAMADA

The Institute of Physical and Chemical Research, Hirosawa, Wako-shi   351

Simultaneous evolution of hydrogen and oxygen gases was achieved by visible light irradiation of water containig prussian blue and tris(2,2'-bipyridyl)ruthenium(II) complex.   The gases evolved were analyzed by gas chromatography and mass spectroscopy. The mechanism for the water photolysis was also discussed.

Water photolysis to give simultaneous evolution of hydrogen and oxygen gases is one of the most attracting and important subjects of solar energy conversion. Most photochemical systems of water photolysis are utilizing semiconductors   such as titanium dioxide[1-3] and cadmium   sulfide.[4]   The only one system containing no semiconductor for simultaneous H_2 and O_2 evolution was reported by Grätzel   et al., who used tris(2,2'-bipyridyl)ruthenium(II) complex (abbreviated to $Ru(bpy)_3^{2+}$), methylviologen (MV^{2+}), platinum colloid, and ruthenium dioxide sol protected by poly(styrene-co-maleic anhydride).[5]   This photolysis system is complicated and sensitive to the preparative techniques of the reagents, which often makes the conversion not reproducible.   The O_2 analysis data of that paper would be insufficient.   It might occur that the poly(styrene-co-maleic anhydride), instead of water, works as a reducing agent for H_2 production, because the copolymer can reduce MV^{2+} under visible light irradiation to give its cation radical[6]   which can reduce protons to H_2 on Pt catalyst.   The present authors have found a simple system of water photolysis composed of prussian blue (ferrous potassium hexacyano-ferrate(III); $KFe[Fe(CN)_6]$, abbreviated to PB) and $Ru(bpy)_3^{2+}$ to evolve hydrogen and oxygen gases simultaneously, and the results are described.

PB has a polynuclear structure with mixed valent iron ions, and forms a colloidal solution.[7]   A solution of PB was prepared by mixing a 40 mM aqueous solu-

tion of potassium ferricyanide, $K_3[Fe(CN)_6]$, and an equimolar aqueous solution of ferrous chloride while stirring, and used within one day after preparation. The irradiation of a 10 ml aqueous solution containing 10 μM Ru(bpy)$_3^{2+}$, 5 mM PB, and 0.5 M KCl at pH 2 (HCl-KCl buffer) under argon at room temperature with visible light (cutoff filters; Toshiba VY-42 and IRQ-80, light intensity; 78 mW/cm^2) from a 500 W xenon lamp gave simultaneous H_2 and O_2 evolution. The gas chromatogram (Fig. 1) of the gas evolved after 15 h's irradiation showed the presence of both H_2 and O_2. The O_2 content evolved by the photochemical reaction was calculated by subtracting the content of O_2 coming from the air. The H_2 and O_2 evolved were 0.27 ± 0.01 and 0.14 ± 0.02 μl, respectively. Fig. 2 shows the mass spectrum of the gas evolved by the irradiation of the solution of 90 % D_2O containing 2.0 % $H_2^{18}O$, 10 μM Ru(bpy)$_3^{2+}$, 5 mM PB and 0.5 M KCl under the same condition as the above. The peaks at m/e = 3 and 4 are due to DH$^+$ and D$_2^+$, respectively, and that at m/e = 34 to $^{18}O^{16}O^+$. The ratio of the peak intensity of D$_2^+$/DH$^+$ was 4.3 (theoretical; 4.5), and that of $^{18}O^{16}O^+$/$^{16}O_2^+$ was 0.039 (theoretical; 0.040). These results indicate that water was decomposed to give hydrogen and oxygen. The irradiation of a 10 ml aqueous solution containing 1 μM Ru(bpy)$_3^{2+}$, 500 μM PB, and 0.5 M KCl at pH 2 for 90 h gave 1.3 μl H_2 and 0.7 μl O_2, showing that the turnover number of the Ru complex is 11 under this condition. After this reaction the Ru complex and the PB suffered no change.

The addition of KCl caused the increase in the yield of the photochemical reaction probably by stabilizing PB. The optimum concentration of the KCl added
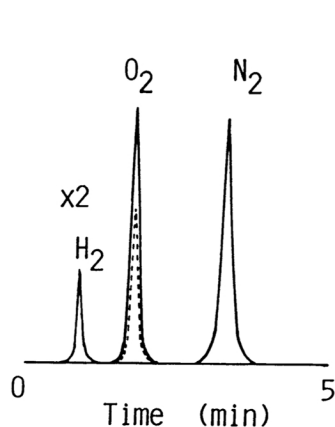

Fig. 1 Gas chromatogram of H_2 and O_2 evolved by irradiation of aqueous solution containing Ru(bpy)$_3^{2+}$, PB, and KCl at pH 2 under Ar. for 15 h. ----; O_2 from the air.
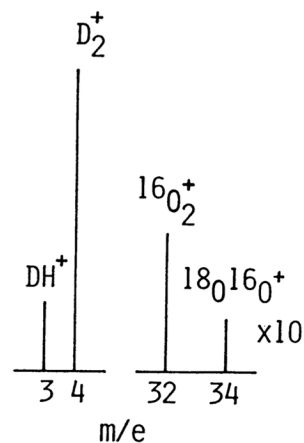

Fig. 2 Mass spectrum of the gas evolved by irradiation of 90 % D_2O solution containing 2.0 % $H_2^{18}O$, Ru(bpy)$_3^{2+}$, PB and KCl at pH 2 under Ar. for 15 h.

was around 0.5 M. The addition of   more   KCl retarded the   reaction, which would be due to the partial aggregation of PB. Continueous stirring of the reaction mixture was required for the water photolysis, since the aggregation of PB leads to the inactivation of the   water photolysis system.

Table 1.   Effect of wavelength of the incident light on the photolysis of water containing 10 μM $Ru(bpy)_3^{2+}$, 5 mM PB and 0.5 M KCl at pH 2 (HCl-KCl buffer) under argon at room temperature.   Solution; 10 ml.

Wavelength (nm) of the incident light	Reaction time (h)	Gas evolved (μl)	
		H_2	O_2
>400	15	0.27	0.14
>550	15	0	0
450*[a]	70	0	0
700*[a]	70	0	0
450 + 700*[a,b]	70	0.09	0.05

*a) Interference filter was used: Light intensities; 1.8 mW/cm^2 (450 nm) and 3.8 mW/cm^2 (700 nm). Solution; 2 ml.
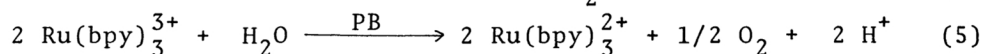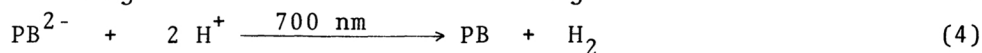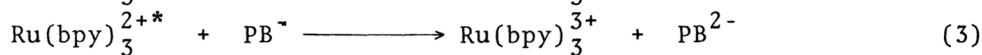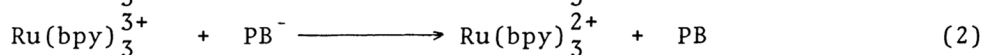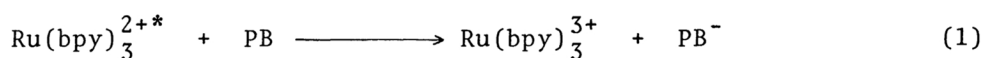
*b) Two light sources were used.

The effect of the wavelength of the incident light on the water photolysis was shown in Table 1.   The excitation of the Ru complex (λ_{max} = 452 nm) was essential for the photolysis.   The irradiation either by 450 or 700 nm monochromatic light did not induce water photolysis, and both the excitation of the Ru complex and the PB (λ_{max} = 700 nm) were required.   The quenching of the excited state of the $Ru(bpy)_2^{2+}$ by PB was very efficient.   The rate constant of the quenching at 30 °C was measured to be 3.50 x 10^{10} (M^{-1} s^{-1}) from the emission quenching and the lifetime of $Ru(bpy)_3^{2+*}$.   The Stern-Volmer constant (k_{sv}) obtained from the lifetime measurement was about one third of that obtained from emission quenching,indicating that a static quenching of the $Ru(bpy)_3^{2+*}$ by PB occurs.   There must be some interaction between the two species, which might play an importnat role for the photochemical process.   The details will be reported elsewhere.

One of the interesting features of the present water photolysis system is that PB provides more than two kinds of functions, i.e., electron mediator and catalysts for H_2 and O_2 evolution.   The photochemical reaction of a 10 ml aqueous solution of 10 mM EDTA, 20 μM $Ru(bpy)_3^{2+}$, and 5 mM PB at pH 6 (KH_2PO_4-NaOH buffer) for 1 h gave 0.09 μl H_2.   The same reaction of a blank solution without PB gave no H_2. In that H_2 evolving system, the PB must work as a mediator to accept electron from $Ru(bpy)_3^{2+*}$ and also as a H_2 evolving site.   In order to study the effect of the excitation of PB, the following experiments were carried out.   L-ascorbic acid reduces PB, but the reaction of both the reagents in the dark does not give H_2.   How

ever, the irradiation of a solution containing 5 mM PB, 10 μM L-ascorbic acid, and 0.5 M KCl at pH 2 gave a small amount of H_2 (ca. 0.03 μl) in 2 h , while no H_2 was formed in the dark.   These results suggest that a partially reduced PB can give H_2 under irradiation.   Reaction of 100 μM $Ru(bpy)_3^{3+}(ClO_4^-)_3$ with 5 mM PB in water at pH 2 gave 4.5 μl O_2 (yield; 74 %) in 1 h by water oxidation, while a blank   solution without PB did not give O_2, indicating that PB acts as O_2 evolving site with the trivalent Ru complex as oxidant.

The reaction scheme can be considered as follows.   The quenching of $Ru(bpy)_3^{2+*}$ by PB would be oxidative, because the irradiation of the mixed solution of the Ru complex, PB and EDTA gave H_2 as described above (Eq.(1)).   Since PB has a poly-

$$Ru(bpy)_3^{2+*} + PB \longrightarrow Ru(bpy)_3^{3+} + PB^- \qquad (1)$$

$$Ru(bpy)_3^{3+} + PB^- \longrightarrow Ru(bpy)_3^{2+} + PB \qquad (2)$$

$$Ru(bpy)_3^{2+*} + PB^- \longrightarrow Ru(bpy)_3^{3+} + PB^{2-} \qquad (3)$$

$$PB^{2-} + 2 H^+ \xrightarrow{\text{700 nm}} PB + H_2 \qquad (4)$$

$$2 Ru(bpy)_3^{3+} + H_2O \xrightarrow{\text{PB}} 2 Ru(bpy)_3^{2+} + 1/2 O_2 + 2 H^+ \qquad (5)$$

nuclear structure[7], it could behave as a kind of electron pool to give PB^{2-} (Eq. (3)).   Two protons would be reduced by the PB^{2-} under excitation to give H_2 (Eq. (4)).   On the other hand, the function of PB as a kind of charge pool must be im- portant in the O_2 evolving reaction (Eq.(5)).

The quantum yield for the H_2 and O_2 evolution with both 450 and 700 nm mono- chromatic light irradiation was the order of 0,01 % based on the 450 nm light ab- sorbed.   Although the quantum yield is not high so far, the simultaneous H_2 and O_2 evolution by such the simple two components system would be surprising in it- self.   The roles of PB both as electron and charge pool would be the crucial point, which must be due to its polynuclear structure and to its mixed valence state.

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