Photo-induced Cleavage of Water with Tris(2,2'-bipyridine) Ruthenium Dication or Hematoporphyrin in Alkaline Solution

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The formation of the cation radical of methyl viologen was established when an alkaline solution containing hematoporphyrin (Hm) or tris(2,2'-bipyridine) ruthenium dication (Ru(bpy)$_3^{2+}$) was irradiated by visible light. Hydroxyl ion served as reducing agent in these systems. The reduction of methyl viologen has been studied kinetically and the reaction mechanism is discussed.

On addition of colloidal platinum to the above photo-irradiation system, hydrogen evolution was observed by water reduction.

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Introduction

Photochemical cleavage of water into its elements with light absorbing species is a goal in the field of solar energy conversion. Hydrogen evolution has been studied extensively by the photoreduction of water in the presence of a suitable reducing agent such as EDTA, triethanolamine, mercaptoethanol or cysteine [1].

In the absence of these reducing agents, the reduction of methyl viologen (1,1'-dimethyl-4,4'-bipyridinium chloride) was found in this study with Ru(bpy)$_3^{2+}$ or Hm by irradiation of visible light in alkaline media.

As the reduced form (MV$^+$) of methyl viologen has a sufficient redox potential for the reduction of water and is known to produce hydrogen in the presence of a suitable catalyst, an attempt was made to decompose water to hydrogen.

Experimental

Methyl viologen was purchased from Tokyo Kasei Kogyo Co. and the other chemicals were of the highest available purity (Wako Pure Chemicals Co.). Ru(bpy)$_3^{2+}$ was synthesized according to ref. 2. Colloidal platinum was prepared according to ref. 3.

A typical experiment was performed as follows, under anaerobic conditions. Six milliliters of alkaline solution containing NaOH (0.3 M), Ru(bpy)$_3^{2+}$ (6.27 × 10^{-5} M) and methyl viologen (1.30 × 10^{-3} M) in a Pyrex reactor were irradiated with the light of wavelength 460 nm using a Toshiba KL-46 filter at 30 °C. As a light source a 200 W tungsten lamp from a slide projector was used. In the case of Hm a micellar surfactant, cetyldimethylbenzylammonium-hydroxide (CDBAH), was used to dissolve Hm in water, and a Toshiba VY-50 filter was used to cut off the wavelength below 500 nm in the photolysis.

For the hydrogen evolution reaction, after the photoreduction of methyl viologen, 1.22 ml of 4 N hydrochloric acid with colloidal platinum was added from the side arm of the reactor to neutralize the solution. A portion of the evolved hydrogen was collected *via* a sampling valve and analyzed by gas chromatography.

Results and Discussion

Photoreduction of Methyl Viologen with Ru(bpy)$_3^{2+}$

When alkaline solution containing Ru(bpy)$_3^{2+}$ and methyl viologen was irradiated, the growth of the cation radical of methyl viologen, which has characteristic absorption bands at 400 and 620 nm, was observed. The concentration of MV$^+$ increased rapidly, and decreased when irradiation was stopped. Though the concentration of MV$^+$ increased with time, Ru(bpy)$_3^{2+}$, which has a characteristic absorption band at 450 nm, remained unchanged throughout the irradiation period. The amount of MV$^+$ formed was more than that of Ru(bpy)$_3^{2+}$ introduced, that is, the turnover numbers of MV$^+$ formation against Ru(bpy)$_3^{2+}$ was more than unity. The light absorbing species was thus continuously regenerated and served as a photosensitizer or a true catalyst.

As no suitable reducing agent was added in this system, hydroxyl ion may have been responsible for
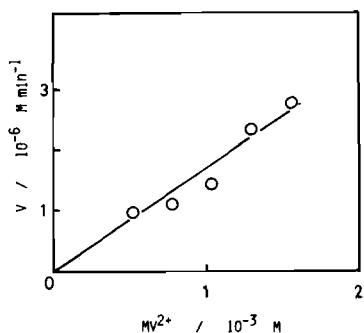
Fig. 1. Dependence of Methyl Viologen Reduction Rate on Concentration of Methyl Viologen. Solution containing $Ru(bpy)_3^{2+}$ (6.27 × 10^{-5} *M*), NaOH (0.33 *M*) and Methyl Viologen was irradiated at 30 °C.
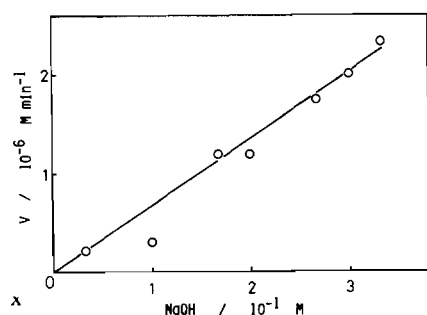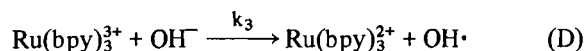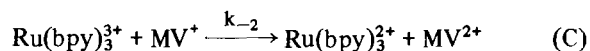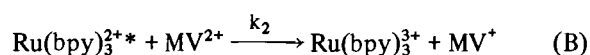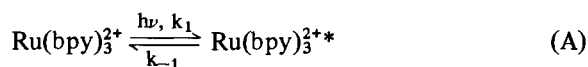

Fig. 2. Dependence of Methyl Viologen Reduction Rate on Concentration of NaOH. Solution containing $Ru(bpy)_3^{2+}$ (6.27 × 10^{-5} *M*), Methyl Viologen (1.30 × 10^{-3} *M*) and NaOH was irradiated at 30 °C.

the reducing agent, since the oxidized state of Ru-$(bpy)_3^{2+}$ is available to oxidize hydroxyl ions [4].

The initial rate of methyl viologen reduction, V, (which was expressed by the slope of time course of MV^+ where 2 × 10^{-6} *M* of methyl viologen was reduced) was proportional to the concentration of $Ru(bpy)_3^{2+}$ as well as that of methyl viologen (Fig. 1). A linear relation was also obtained between V and NaOH concentration under constant ionic strength, which was kept constant by adding sodium chloride (Fig. 2).

From the above results, the following mechanism is proposed analogously to that of the system containing $Ru(bpy)_3^{2+}$, methyl viologen and triethanolamine.

$$Ru(bpy)_3^{2+} \underset{k_{-1}}{\overset{h\nu,\ k_1}{\rightleftharpoons}} Ru(bpy)_3^{2+}* \qquad (A)$$

$$Ru(bpy)_3^{2+}* + MV^{2+} \xrightarrow{k_2} Ru(bpy)_3^{3+} + MV^+ \qquad (B)$$

$$Ru(bpy)_3^{3+} + MV^+ \xrightarrow{k_{-2}} Ru(bpy)_3^{2+} + MV^{2+} \qquad (C)$$

$$Ru(bpy)_3^{3+} + OH^- \xrightarrow{k_3} Ru(bpy)_3^{2+} + OH\cdot \qquad (D)$$

where k_{-1}, k_2, k_{-2} and k_3 are rate constants and k_1 is a function of light flux.

As the fractional light absorption is small under these experimental conditions, the rate of the reaction (A), $\phi_a I_a$, can be replaced by $k_1[Ru(bpy)_3^{2+}]_0$. The following rate expression is derived from the use of the steady state approximation for [Ru-$(bpy)_3^{2+}*$] and [$Ru(bpy)_3^{3+}$].

$$V = \frac{d[MV^+]}{dt}$$

$$= k_1 k_2 k_3 [Ru(bpy)_3^{2+}]_0 \times$$

$$\times \left(\frac{[MV^{2+}]}{k_{-1} + k_2[MV^{2+}]} \right) \left(\frac{[OH^-]}{k_{-2}[MV^+] + k_3[OH^-]} \right)$$

Even at the initial stage of the reaction, MV^+ does not increase linearly with reaction time, since the rate of back reaction of $Ru(bpy)_3^{2+}$ and MV^+ expressed by the term $k_{-2}[MV^+]$ is not sufficiently small to be neglected.

If the terms of k_{-1} and $k_{-2}[MV^+]$ are large enough compared to the term of $k_2[MV^{2+}]$ and $k_3[OH^-]$, respectively, eqn. (1) can be approximated by

$$V = \frac{k_1 k_2 k_3}{k_{-1} k_{-2}[MV^+]} [Ru(bpy)_3^{2+}]_0 [MV^{2+}][OH^-] \qquad (2)$$

In other words, the reaction rate should be proportional to the concentration of the individual component used. The agreement of the eqn. (2) with the experimental results shows that the proposed mechanism is adequate.

Photoreduction of Methyl Viologen with Hm

When alkaline solution containing Hm and methyl viologen was irradiated with light of wavelength > 500 nm, the reduction of methyl viologen was also observed. As shown in Fig. 3, the concentration of the cation radical MV^+ increased rapidly at the initial stage of the reaction and reached a constant value. When the solution was re-irradiated in anaerobic conditions after reoxidizing MV^+ by introducing air into the system, MV^+ was produced with a lower rate than the first irradiation. As the absorption spectrum of the Hm was changed after the irradiation, the cessation of the reaction at low conversion may be caused by the photodecomposition of Hm.

The initial rate of methyl viologen reduction, V, (evaluated by the slope of time course at the low concentration of MV^+, 3.0 × 10^{-6} *M*) was proportional to the concentration of Hm, as well as that of methyl
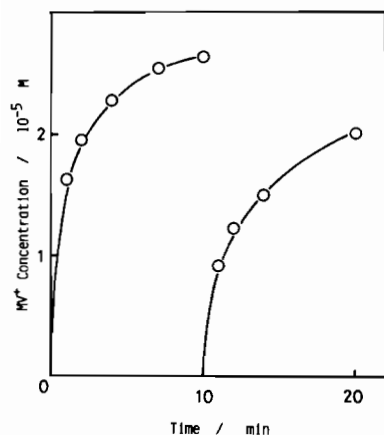
Fig. 3. Time Dependence of MV$^+$ Concentration. Solution containing Hm (1.05 × 10^{-5} *M*), Methyl Viologen (1.30 × 10^{-3} *M*), NaOH (0.33 *M*) and CDBAH (2.29 × 10^{-5} *M*) was irradiated at 30 °C.

Fig. 5. Dependence of Methyl Viologen Reduction Rate on NaOH Concentration. Solution containing Hm (1.05 × 10^{-5} *M*), CDBAH (2.29 × 10^{-5} *M*), Methyl Viologen (1.30 × 10^{-3} *M*) and NaOH was irradiated at 30 °C.

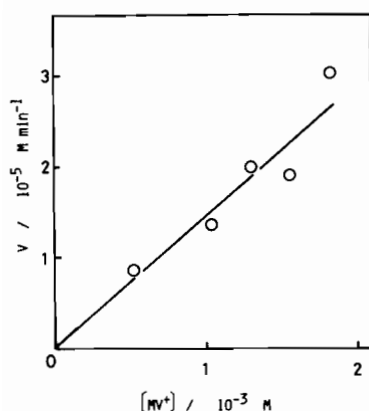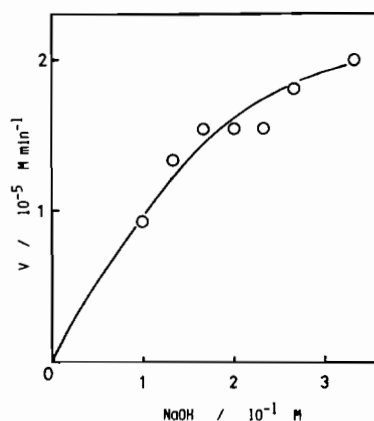
Fig. 4. Depencence of Methyl Viologen Reduction Rate on Methyl Viologen Concentration. Solution containing Hm (1.05 × 10^{-5} *M*), NaOH (0.33 *M*), CDBAH (2.29 × 10^{-5} *M*) and Methyl Viologen was irradiated at 30 °C.

viologen (Fig. 4); it showed Langmuir-adsorption type dependence on the concentration of NaOH (Fig. 5).

To investigate the effect of ionic strength on the reaction, either NaCl, KCl, or NaOCl$_4$ was added or Na$_2$HPO$_4$–NaOH buffer was used instead of NaOH. The solution became turbid upon adding the salt and no photoreduction of methyl viologen was observed in any case. Though the reason of these phenomena is not known at this stage, the inactivation may be caused by the interaction of added salts with the micellar surfactant used to solubilize Hm in water.

In the case of Hm the following reaction mechanism may be proposed, containing the reductive quenching reaction of Hm by hydroxyl ion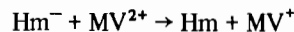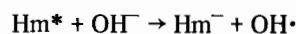. In this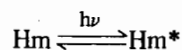 mechanism Hm is reduced first and then oxidized by methyl viologen in contrast to the reaction mechanism proposed in the case of Ru(bpy)$_3^{2+}$, since it has been reported that Hm tends to be reduced in contrast to the Ru(bpy)$_3^{2+}$ [5].

$$Hm \xrightleftharpoons{h\nu} Hm^*$$

$$Hm^* + OH^- \rightarrow Hm^- + OH\cdot$$

$$Hm^- + MV^{2+} \rightarrow Hm + MV^+$$

Hydrogen Evolution by Adding Colloidal Platinum

Though the reduced form of methyl viologen has enough redox potential for the reduction of water to produce hydrogen, hydrogen evolution was not observed even in the presence of colloidal platinum.

When the system was neutralized by adding hydrochloric acid in the presence of colloidal platinum after 5 h and 7 h irradiation, 0.61 μmol and 1.21 μmol of hydrogen evolution respectively was observed by the Hm and Ru(bpy)$_3^{2+}$ systems. No hydrogen evolution in alkaline solution may be caused by the low rate of proton reduction because of the low proton concentration. In both systems methyl viologen reduction and hydrogen evolution was also observed using sunlight instead of the tungsten lamp.

Acknowledgement

References

1 For example, M. Kirch, J.-M. Lehn and J.-P. Sauvage, *Helv. Chim. Acta, 62*, 1345 (1979);
I. Okura, M. Takeuchi and N. Kim-Thuan, *Chem. Lett.,* 765 (1980);
I. Okura and N. Kim-Thuan, *J. Chem. Res. (S),* 344 (1979); *J. Chem. Soc., Chem. Comm., 84* (1980);
I. Okura, S. Nakamura, N. Kim-Thuan and K. Nakamura, *J. Mol. Catal., 6,* 261 (1979);
I. Okura and N. Kim-Thuan, *J. Mol. Catal., 6,* 277 (1979);
I. Okura and N. Kim-Thuan, *J. Mol. Catal., 5,* 311 (1979).
2 S. Anderson and K. R. Seddon, *J. Chem. Res. (S),* 74 (1979).
3 K. Aika, L. L. Ban, I. Okura, S. Namba and J. Turkevich, *J. Res. Inst. Catal., Hokkaido Univ., 24,* 54 (1976).
4 C. Creutz and N. Sutin, *Proc. Nat. Acad. Sci. U.S.A., 72,* 2858 (1975).
5 I. Okura and N. Kim-Thuan, *J. Chem. Soc., Faraday I, 76,* 2209 (1980).