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

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

In this study, we describe the methyl viologen (1,1′-dimethyl-4,4′-bipyridinium chloride) reduction, in the absence of the above reducing agent, with tris-(2,2′-bipyridine)ruthenium dication ($Ru(bpy)_3^{2+}$) by the irradiation of visible light.

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 Chemical 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 (0.30 *M*), $Ru(bpy)_3^{2+}$ (6.27×10^{-5} *M*) and methyl viologen (1.3×10^{-3} *M*) in a Pyrex reactor was irradiated with the light of wavelength 460 nm by using a Toshiba KL-46 filter at 30 °C. As a light source a 200 W tungsten lamp for slide projector was used.

For hydrogen evolution, 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.

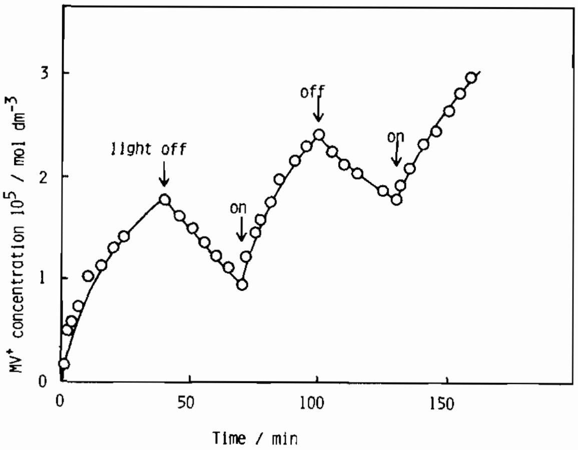

Fig. 1. Time dependence of MV^+ concentration by irradiation of visible light (λ = 460 nm). Reaction conditions: $Ru(bpy)_2^{3+}$, 6.27×10^{-5} *M*; MV, 1.3×10^{-3} *M*; NaOH, 0.3 *M*; NaCl, 0.03 *M*; at 30 °C.

Results and Discussion

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 time dependence of MV^+ concentration is shown in Fig. 1. The concentration of MV^+ increased rapidly and decreased when irradiation was stopped. The growth of MV^+ was also observed when the system was irradiated again. 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. So, the light absorbing species was continuously regenerated and served as a photosensitizer or a true catalyst. No MV^+ formation was observed in the absence of light in this pH range. As any suitable reducing agent was not added in this system, hydroxyl ion may be responsible for the reducing agent, for the oxidized state of $Ru(bpy)_3^{3+}$ is available to oxidize hydroxyl ions [4].

Though the reduced form of methyl viologen has an 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 7 h irradiation, 1.21 μmol of hydrogen evolution was observed. No hydrogen evolution in alkaline solution may be caused by the low rate of proton reduction because of the low proton concentration.

Methyl viologen reduction and hydrogen evolution was also observed by the irradiation of sunlight instead of the tungsten lamp.

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