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Letter

Effect of cationic surfactant on photoinduced hydrogen evolution with hydrogenase

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Abstract

Photoinduced hydrogen evolution with hydrogenase by use of a three component system consisting of triethanolamine, zinc-tetraphenylporphyrin tetrasulfonate ($ZnTPPS_4$) and methyl viologen was investigated in cationic surfactant, cetyltrimethylammonium bromide (CTAB). In the presence of CTAB, the lifetime of reduced methyl viologen and $ZnTPPS_4$ cation radical increased and effective hydrogen evolution from reduced methyl viologen with hydrogenase was accomplished.

Keywords: Hydrogenase; Cetyltrimethylammonium bromide; Photoinduced hydrogen evolution

1. Introduction

Photochemical redox reactions have been studied extensively by means of converting solar energy to chemical energy [1,2]. Three component systems consisting of an electron donor, a photosensitizer and an electron carrier has been used to photoinduced hydrogen evolution from water in the presence of a suitable catalyst, such as hydrogenase [3,4]. One of the important processes of the reaction is charge separation to form oxidized photosensitizer and reduced electron carrier. As we reported previously, the effective charge separation has been accomplished in sodium dodecyl sulfate (SDS) micellar system. However, little hydrogen evolution with hydrogenase in SDS was observed because of the denaturation of hydrogenase by SDS [5,6].

When cationic surfactant, cetyltrimethylammonium bromide (CTAB) was used, photoinduced hydrogen evolution with hydrogenase was observed and effective charge separation between reduced methyl viologen and $ZnTPPS_4$ cation radical was accomplished.

2. Experimental

The sample solution containing $ZnTPPS_4$, methyl viologen, triethanolamine, hydrogenase and CTAB was deaerated by repeated freeze–pump–thaw cycles. For the photolysis under steady state irradiation, 200 W tungsten lamp was used at 30°C. The light of the wavelength less than 390 nm was removed by Toshiba L-39 cut-off filter. Laser flash photolysis was carried out by using Nd-YAG laser with second harmonic light with 532 nm (pulse width 10 ns). The amount of hydrogen evolved was detected by gas chroma-

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tography (detector:TCD, column: active carbon). Hydrogenase was obtained from *Desulfovibrio vulgaris* (Miyazaki) and purified according to Yagi's method [7]. The hydrogenase concentration is not known, but it has the ability to release 0.7 μmol of hydrogen in the reaction system of 10 μl hydrogenase, 1.2×10^{-5} mol of methyl viologen and 7.7×10^{-5} mol of dithionite in 5.0 ml of 50 mmol dm^{-3} Tris–HCl buffer (pH = 7.4) at 30°C for 10 min.

3. Results and discussion

When the sample solution containing $ZnTPPS_4$, methyl viologen, triethanolamine and CTAB was irradiated, accumulation of reduced methyl viologen was observed as shown in Fig. 1. The rate of photoreduction of methyl viologen in the presence of CTAB was five times faster than that in the absence of CTAB. In the case of CTAB, the effective photoreduction was established as well as in case of SDS micellar system [5,6].

By using laser flash photolysis, the rates of elementary processes of the photo-reaction were measured. The rate constant of quenching of the photoexcited triplet state of $ZnTPPS_4$ by methyl viologen in the presence of 2.5×10^{-2} mol dm^{-3} CTAB was estimated to be 3.1×10^{6} mol^{-1} dm^3 s^{-1}. Though the value is pretty low, the quenching efficiency of the triplet state of $ZnTPPS_4$ by

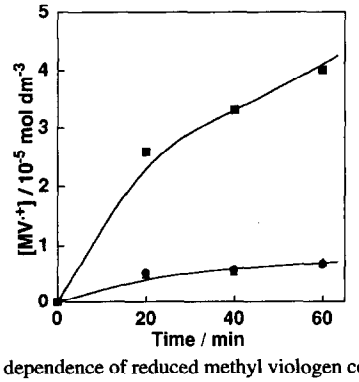

Fig. 1. Time dependence of reduced methyl viologen concentration. The sample solution containing triethanolamine (0.25 mol dm^{-3}), $ZnTPPS_4$ (0.13 μmol dm^{-3}) and methyl viologen (0.22 mmol dm^{-3}) in 4.0 ml of 25 mmol dm^{-3} Tris–HCl buffer (pH = 7.4) was irradiated at 30°C. ■: CTAB (25 mmol dm^{-3}) ▲: CTAB (25 μmol dm^{-3}) ●: without CTAB.

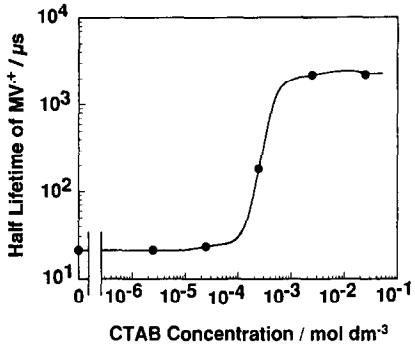

Fig. 2. Concentration dependence of CTAB on lifetime of $MV^{\cdot +}$. The sample contains $ZnTPPS_4$ (30 μmol dm^{-3}) and methyl viologen (0.75 mmol dm^{-3}) in 4.0 ml of 25 mmol dm^{-3} Tris–HCl buffer (pH = 7.4).

methyl viologen in the presence of CTAB was estimated to be 0.85. Fig. 2 shows CTAB concentration dependence on the lifetime of reduced methyl viologen monitored at 605 nm after laser flash. The lifetime of reduced methyl viologen in the presence of 2.5×10^{-2} mol dm^{-3} CTAB was about 100 times as long as that in the absence of CTAB, showing that the back electron transfer from reduced methyl viologen to $ZnTPPS_4$ radical cation in the presence of CTAB was strongly suppressed. The retardation of back electron transfer reaction is explained by an electrostatic effect among the surface charge of CTAB micelles, $ZnTPPS_4$, and methyl viologen. The charge recombination of the reduced methyl viologen and $ZnTPPS_4$ cation radical after the charge separation may be suppressed by strong electrostatic repulsion induced by the adsorption of negatively charged $ZnTPPS_4$ on the cationic micellar surface.

As the long-lived charge separation was attained by the addition of CTAB, the photoinduced hydrogen evolution with hydrogenase was attempted in CTAB micellar system. When the sample solution containing $ZnTPPS_4$, methyl viologen, triethanolamine, hydrogenase and CTAB was irradiated, hydrogen evolution was observed as shown in Fig. 3. The rate of hydrogen evolution in the presence of CTAB was about seven times that in the absence of CTAB. Though the effective photoreduction of methyl viologen was attained in the case of SDS, little hydrogen evolution was observed by denaturation of

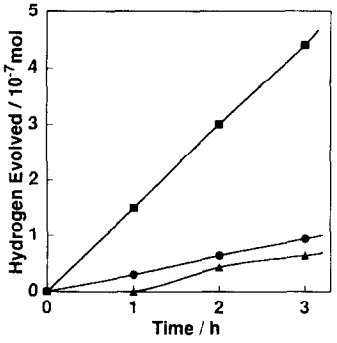

Fig. 3. Time dependence of hydrogen evolution. The sample solution containing triethanolamine (0.25 mol dm^{-3}), $ZnTPPS_4$ (0.13 μmol dm^{-3}), methyl viologen (0.22 mmol dm^{-3}) and hydrogenase (10 μl) in 4.0 ml of 25 mmol dm^{-3} Tris–HCl buffer (pH = 7.4) was irradiated at 30°C. ■: CTAB (25 mmol dm^{-3}) ●: CTAB (25 μmol dm^{-3}) ▲: without CTAB.

hydrogenase [6]. In the case of CTAB, effective hydrogen evolution was observed without denaturation of hydrogenase.

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