Photoinduced Hydrogen Evolution in Micellar System

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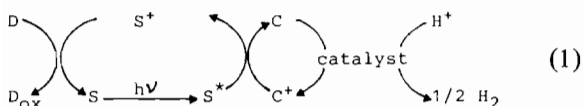*The Institute of Physical and Chemical Research, Hirosawa, Wako-shi 351, Japan*

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Abstract

Photoreduction of viologens by the irradiation of the system containing NADPH, zinc meso-tetraphenylporphyrintrisulfonate (Zn-TPPS$_3^{3-}$), viologen and colloidal platinum has been investigated in the presence of surfactant micelles. In the presence of either cationic micelles or anionic micelles, a remarkable increase in the accumulation of the reduced form of viologen was observed. The existence of the micelles depressed both the quenching rate of the photoexcited Zn-TPPS$_3^{3-}$ by viologen and the back reaction rate, recombination rate of the oxidized Zn-TPPS$_3^{3-}$ and reduced viologen. Compared with both reactions, it was clarified that the recombination rate strongly influenced the viologen reduction rate. The effect of the micelles was explained by the electrostatic effect among the charges of the micellar surface, Zn-TPPS$_3^{3-}$ and viologen. By the addition of colloidal platinum to the system, photoinduced hydrogen evolution was also studied.

Introduction

Various attempts have been made to develop suitable redox systems for photochemical utilization of solar energy. Recent works have shown that three component systems containing a photosensitizer (S), an electron donor (D), and an electron carrier (C) can be used to evolve hydrogen when a suitable catalyst is present [1, 2]. In the photoreduction of an electron carrier such as methylviologen with anionic porphyrins it is known that the reaction proceeds through the following oxidative quenching.

$$\text{(1)}$$

In the course of our studies, zinc tetraphenylporphyrintrisulfonate (Zn-TPPS$_3^{3-}$) exhibits particularly high activity as a photosensitizer for the reaction of the system [3]. As electron donors, triethanolamine and EDTA have been employed extensively in these studies. These materials, however, are sacrificed and are consumed when the photoreduction of water is carried out. Unlike these sacrificial reagents, NADPH (nicotinamide adenine dinucleotide phosphate) can be recycled by the combination of another suitable reaction. As shown in the following equation, the oxidized NADPH (NADP, or D$_{ox}$) is easily photoreduced in the presence of grana obtained from green plants.

$$\text{(2)}$$
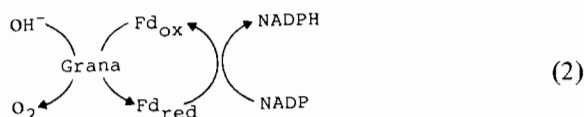
By the combination of reactions (1) and (2), the splitting of water into hydrogen and oxygen will be accomplished. Therefore, it is of importance to use NADPH as an electron donor. As we reported previously, NADPH could serve as an electron donor in the photoinduced hydrogen evolution systems [4].

To improve the rate of photoinduced hydrogen evolution as shown in reaction (1), effective charge separation between photoexcited sensitizer (S*) and electron carrier (C) is needed. The electrostatic field such as the micellar surface has been widely applied to separate charges effectively [5]. In few of the micellar systems, however, has hydrogen evolution been studied. In this paper we describe the effect of micelles on photoinduced hydrogen evolution in a system containing NADPH, Zn-TPPS$_3^{3-}$, bipyridinium salt and a catalyst.

Experimental

The hydrogenase from *Desulfovibrio vulgaris* was purified according to Yagi's method [6]. The con-

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centration of hydrogenase is not known but it has the ability to release 0.11 μmol of hydrogen by the reaction system: hydrogenase (0.5 ml) - methylviologen (2.10×10^{-6} mol) - $Na_2S_2O_4$ (2.30×10^{-5} mol) in 3.0 ml of 0.1 mol dm^{-3} Tris—HCl buffer (pH 7.0) at 30 °C for 10 min.

Colloidal platinum was prepared by the reduction of chloroplatinic acid with sodium citrate [7]. The platinum sol thus prepared has been found by electron microscopy to have particles with an average diameter of 34 Å with deviation from the mean of 25%.

The bipyridinium compounds used as electron carriers are shown in Fig. 1. The compounds A, B and C, were synthesized according to the literature [8].

The sample solution which consisted of Zn-TPPS$_3^{3-}$, electron carrier, NADPH, a catalyst (if included) and surfactant micelles were deaerated by repeated freeze-pump-thaw cycles.

In the photolysis with continuous irradiation the sample in a Pyrex cell with a magnetic stirrer was irradiated with light from a 200 W tungsten lamp. Light of wavelength less than 390 nm was cut off by a Toshiba L-39 filter.

Conventional laser flash photolysis was carried out by using a Nd-YAG Laser, Model HY-500 from JK Lasers Ltd., equipped with the second, third and fourth harmonic generators. The second harmonic (532 nm), *ca.* 100 mJ cm^{-2} and flash duration of 20 ns was used for excitation of the sample solutions throughout this study. Analyzing light beams from a Xenon lamp (Ushio UXL-150 D, 150 W) were intensified by a factor of *ca.* 20 during the detection of the transient spectrum. Transient spectra having the lifetime longer than 200 μs were measured without intensification of the analyzing light beams. The light beam, after passage through a sample cell entered to a monochromator (Model MC-20 N from Ritsu Appl. Opt. Co.). The output from Hamamatsu Photomultiplier (R 758) attached to the monochromator was displayed on a Tektronix oscilloscope, Model 7904.
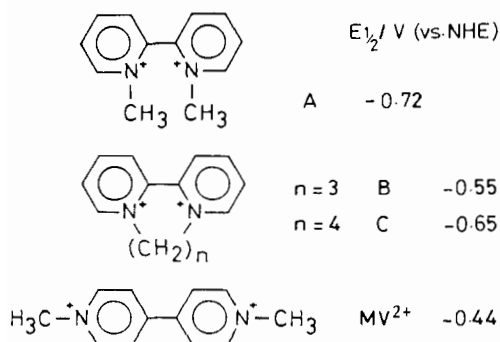

Fig. 1. Bipyridinium salts as electron carriers.

Results and Discussion

Photoreduction of Methylviologen by NADPH

When an aqueous solution containing Zn-TPPS$_3^{3-}$, methylviologen and NADPH was irradiated, the formation of the methylviologen cation radical was observed, as shown in Fig. 2, curve a. When a surfactant such as cetyl trimethyl ammonium bromide (CTAB, cationic surfactant) or sodium dodecyl sulfate (SDS, anionic surfactant) was added to the above three component system, remarkable increases in the accumulation of the methylviologen cation radical were observed in both cases. When triethanolamine was used instead of NADPH, increases in the accumulation of the methylviologen cation radical similar to those shown in Fig. 2, curve a were observed in both cases. The reason for the remarkable increase in the photoreduction rate of methylviologen will be discussed later.
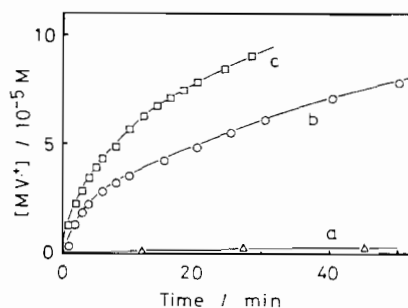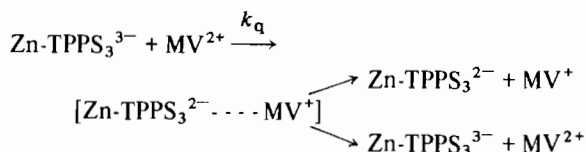

Fig. 2. Time dependence of MV$^+$ concentration. A sample solution containing NADPH (3.00×10^{-4} mol dm^{-3}), Zn-TPPS$_3^{3-}$ (2.60×10^{-7} mol dm^{-3}) and MV^{2+} (3.15×10^{-4} mol dm^{-3}) was irradiated at 30 °C. Surfactant: (a) none, (b) CTAB (3.60×10^{-3} mol dm^{-3}), (c) SDS (1.60×10^{-2} mol dm^{-3}).

Effect of SDS on Photoinduced Methylviologen Reduction

One of the most important steps of reaction (1) is the charge separation to form oxidized photosensitizer (S$^+$) and reduced electron carrier (C).

$$Zn\text{-}TPPS_3^{3-} + MV^{2+} \xrightarrow{k_q}$$

$$[Zn\text{-}TPPS_3^{2-} \cdots MV^+] \begin{array}{c} \nearrow Zn\text{-}TPPS_3^{2-} + MV^+ \\ \searrow Zn\text{-}TPPS_3^{3-} + MV^{2+} \end{array}$$

To get some information about the photoexcited photosensitizer, laser flash photolysis was carried out. The decay of the Zn-TPPS$_3^{3-}$ triplet state was monitored at 470 nm after the laser flash. In the presence of SDS, no distinguishable difference was observed and the lifetime of ^{3}Zn-TPPS$_3^{3-}$ in the presence of SDS was 1.4 ms which was similar to 1.6 ms in the absence of SDS.
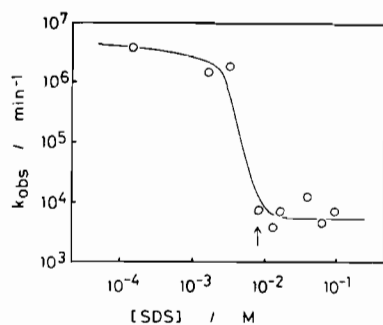
Fig. 3. Effect of SDS concentration on the decay of T-T absorption of $Zn\text{-TPPS}_3^{3-}$. Reaction conditions: $Zn\text{-TPPS}_3^{3-}$ (3.10×10^{-5} mol dm^{-3}) and MV^{2+} (3.35×10^{-4} mol dm^{-3}).

However, in the presence of methylviologen as a quencher, the quenching rate was strongly affected by SDS. As shown in Fig. 3, the quenching rate, k_{obs}, was fairly depressed with SDS concentration. In particular the rate was extremely depressed above critical micelle concentration (cmc). The arrow in Fig. 3 indicates cmc. For reaction (1) to proceed efficiently, it seems undesirable for the quenching reaction to be retarded. However, the efficiency of the quenching reaction, η, which is expressed as follows, is unity and is not influenced by k_q values, since k_o (the reverse of lifetime: 1.4 ms) is very small compared with the $k_q[MV^{2+}]$ term, e.g., $\eta = 0.85$ when $[MV^{2+}] = 3.35 \times 10^{-4}$ mol dm^{-3} and above cmc.

$$\eta = \frac{k_q[MV^{2+}]}{k_{obs}} = \frac{k_q[MV^{2+}]}{k_o + k_q[MV^{2+}]}$$

The back electron transfer, recombination of oxidized photosensitizer (S^+) and reduced electron carrier (C), was also followed by using laser flash photolysis.

$$Zn\text{-TPPS}_3^{2-} + MV^+ \longrightarrow Zn\text{-TPPS}_3^{3-} + MV^{2+}$$
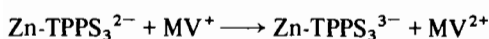
Figure 4A shows the oscilloscopic photograph monitored at 605 nm (the peak wavelength due to the methylviologen cation radical, MV^+) after a laser flash. In the presence of SDS, the decay of MV^+ was fairly depressed as shown in Fig. 4B. Figure 5 shows the lifetime of MV^+ against SDS concentration. The lifetime of MV^+ increased markedly above cmc.

As discussed above both reactions, the quenching reaction and the recombination reaction, are retarded by SDS. However, the efficiency of the quenching reaction is not influenced by k_q values. So, compared with the quenching reaction and the recombination reaction, the latter strongly influences the methylviologen reduction rate.

The above results are explained by the electrostatic effect among the charges of the micellar surface, $Zn\text{-TPPS}_3^{3-}$ and methylviologen. Since the
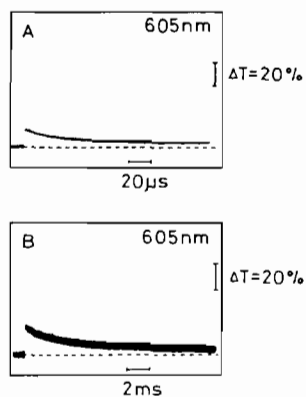

Fig. 4. Decay of MV^+ absorption. Reaction conditions: (A) $Zn\text{-TPPS}_3^{3-}$ (3.03×10^{-5} mol dm^{-3}), MV^{2+} (4.85×10^{-5} mol dm^{-3}); (B) $Zn\text{-TPPS}_3^{3-}$ (3.07×10^{-5} mol dm^{-3}), MV^{2+} (2.98×10^{-3} mol dm^{-3}), SDS (1.60×10^{-2} mol dm^{-3}).
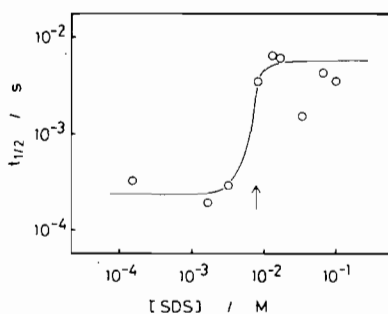

Fig. 5. Effect of SDS concentration on MV^+ lifetime. Reaction conditions: $Zn\text{-TPPS}_3^{3-}$ (3.10×10^{-5} mol dm^{-3}), MV^{2+} (3.35×10^{-4} mol dm^{-3}).

positively charged methylviologen (of both oxidized and reduced forms) is adsorbed on the micellar surface, the recombination of the reduced form of methylviologen and negatively charged $Zn\text{-TPPS}_3^{2-}$ formed after the charge separation, would be suppressed by strong electrostatic repulsion between the micellar surface and $Zn\text{-TPPS}_3^{2-}$. On the contrary, $Zn\text{-TPPS}_3^{3-}$ is adsorbed on the micellar surface when CTAB is used and the recombination would be suppressed by strong electrostatic repulsion between the micellar surface and reduced methylviologen.

The surface potential of the micelles can be controlled by the addition of sodium chloride. The surface potential of the SDS micelles is calculated by using the equation reported previously [9], in which the diameter of the SDS micelles is supposed to be 30 Å. Figure 6 shows that the methylviologen reduction rate strongly depends on the surface potential of the SDS micelles. The results also confirm that the rate increase in SDS is affected by electrostatic forces among the charges of the micellar surface, $Zn\text{-TPPS}_3$ and methylviologen.
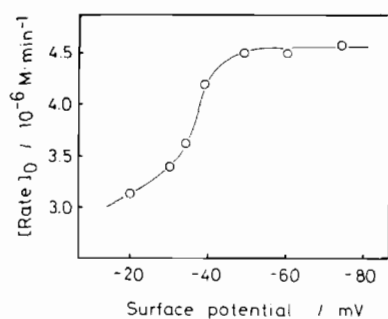
Fig. 6. Correlation between reduction rate and surface potential of SDS micelles. Reaction conditions: NADPH (3.01×10^{-4} mol dm^{-3}), Zn-TPPS$_3{}^{3-}$ (5.16×10^{-8} mol dm^{-3}), MV^{2+} (3.1×10^{-4} mol dm^{-3}), SDS (1.60×10^{-2} mol dm^{-3}), reaction temp., 30 °C.
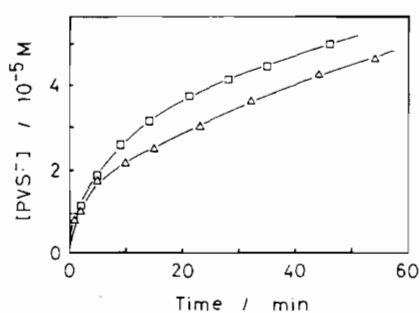

Fig. 7. Time dependence of PVS$^-$ concentration. A sample solution containing NADPH (3.03×10^{-4} mol dm^{-3}), Zn-TPPS$_3{}^{3-}$ (4.03×10^{-7} mol dm^{-3}) and PVS (3.13×10^{-4} mol dm^{-3}), was irradiated at 30 °C. Surfactant: △: none, □: SDS (1.60×10^{-2} mol dm^{-3}).

Effect of Charges of Electron Carriers

In the previous section methylviologen was used as an electron carrier. In this section, another viologen with a different charge is used. In contrast to methylviologen, propylsulfonate-viologen (PVS) is neutral in the oxidized form, and negatively charged when it is reduced. When an aqueous solution containing Zn-TPPS$_3{}^{3-}$, PVS and NADPH was irradiated, the formation of the PVS anion radical (PVS$^-$) was observed as shown in Fig. 7, curve a. This result is also explained by the electrostatic effect. As the SDS micellar surface is negatively charged, PVS and PVS$^-$ exist in the aqueous phase, and Zn-TPPS$_3{}^{3-}$ is also in the same phase since it is also negatively charged. As the reaction proceeds in the aqueous phase in the case of PVS, the micelles have no effect.

Photoinduced Hydrogen Evolution in the Presence of SDS

It is well-known that hydrogenase and colloidal platinum are suitable catalysts for hydrogen evolution. Before using them for photoinduced hydrogen evolution, the efficiency of the catalysts for hydrogen evolution in the presence of micelles was studied.
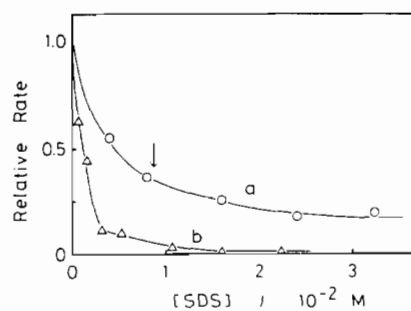

Fig. 8. Hydrogen evolution rate *vs.* SDS concentration. Hydrogen evolution rate was observed by the reduction of water in the presence of reduced methylviologen (1.68×10^{-4} mol dm^{-3}) and a catalyst at 30 °C. △: hydrogenase, ○: colloidal Pt.

Figure 8 shows the effect of added SDS against relative rate. It was found that these catalysts did not serve well in the presence of surfactant, SDS. The catalytic activity was determined by hydrogen evolution rate in these experiments. Methylviologen reduced by Na$_2$S$_2$O$_4$ was used as the reducing agent. It is apparent that both catalysts were inhibited by SDS. Hydrogenase was more strongly inhibited than colloidal platinum and was inactivated above cmc.

By using colloidal platinum, photoinduced hydrogen evolution was carried out. When the solution containing Zn-TPPS$_3{}^{3-}$, electron carrier, NADPH and colloidal platinum in the presence of SDS was irradiated, hydrogen evolution was observed as shown in Fig. 9. It is clear that the electron carriers with lower redox potentials are more effective for hydrogen evolution. Though methylviologen has been widely used as an electron carrier, methylviologen did not serve as a suitable electron carrier in the presence of SDS. As the redox potential of methylviologen in SDS shifts to the higher [10], methylviologen will
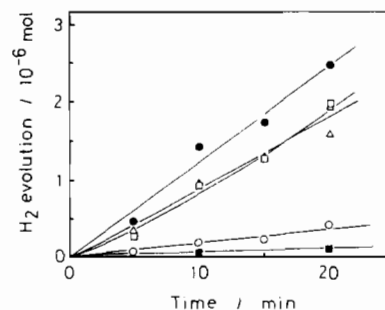

Fig. 9. Time dependence of hydrogen evolution with the system containing NADPH (6.02×10^{-4} mol dm^{-3}), Zn-TPPS$_3{}^{3-}$ (3.03×10^{-7} mol dm^{-3}), bipyridinium salt, catalyst and SDS at 30 °C. △: A (1.11×10^{-4} mol dm^{-3}) + colloidal Pt (2.05×10^{-3} mol dm^{-3}), □: B (1.12×10^{-4} mol dm^{-3}) + colloidal Pt (2.05×10^{-3} mol dm^{-3}), ●: C (1.11×10^{-4} mol dm^{-3}) + colloidal Pt (2.05×10^{-3} mol dm^{-3}), ○: MV (1.12×10^{-4} mol dm^{-3}) + colloidal Pt (2.05×10^{-3} mol dm^{-3}), ■: B (1.12×10^{-4} mol dm^{-3}) + hydrogenase.

not have a low enough redox potential for hydrogen evolution. So, it is apparent that the bipyridinium salts with lower redox potentials are favorable for photoinduced hydrogen evolution.

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