

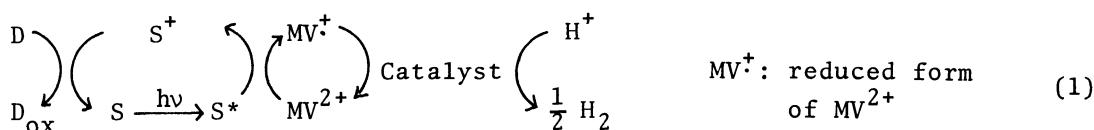
PHOTO-INDUCED HYDROGEN EVOLUTION IN THE PRESENCE OF NADPH
AS AN ELECTRON DONATING AGENT

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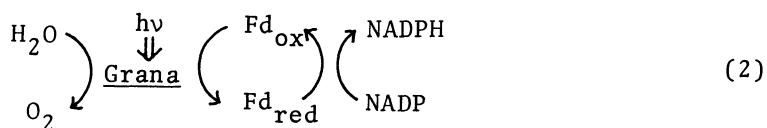
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The cation radical of methylviologen was formed when an aqueous solution containing photosensitizer, methylviologen (MV^{2+}), and NADPH was irradiated by visible light. On the addition of hydrogenase to the photo-irradiation system hydrogen evolution was observed.

Various attempts have been made to develop suitable redox systems for photochemical utilization of solar energy. Recent works¹⁾ have shown that three component systems containing a photosensitizer (S), an electron donor (D), and an electron acceptor can be used to evolve hydrogen when a suitable catalyst is present as shown by the following equation.



Triethanolamine and EDTA, as electron donors, have been employed extensively in these studies. These materials, however, are sacrifice and are consumed when the photoreduction of water is carried out. Unlike these sacrificial reagents, NADPH²⁾ can be a reproducible electron donor. As shown in the following equation, the oxidized NADPH (NADP²⁺ or D_{ox}) is easily photoreduced in the presence of grana obtained from green plants.



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 know whether NADPH can serve as an electron donor in the photo-induced hydrogen evolution system as shown in Eq.1. In this letter we hope to describe the photoreduction of MV^{2+} in the presence of NADPH and hydrogen evolution by the addition of hydrogenase.

The hydrogenase from D. vulgaris was purified according to Yagi's method.³⁾ The concentration of hydrogenase is not known but it has the ability to release $0.11 \mu\text{mol}$ of hydrogen by the reaction system: hydrogenase (0.5 ml) - MV^{2+} (2.10×10^{-6} mol) - $\text{Na}_2\text{S}_2\text{O}_4$ (2.30×10^{-5} mol) in 3.0 ml of $0.1 \text{ mol} \cdot \text{l}^{-1}$ Tris-HCl buffer (pH 7.0) at 30°C for 10 min. A typical experiment was performed under anaerobic reaction conditions at 30°C . A reaction mixture (6.0 ml) containing photosensitizer, MV^{2+} , NADPH and hydrogenase (if included) in Tris-HCl buffer (pH 7.0) was

deaerated by repeated freeze-pump-thaw cycles, and irradiated continuously with light from a 200 W tungsten lamp. The reaction vessel ($l = 0.15$ dm) was settled at 7.0 cm's distance from the light source. Light of wavelength less than 350 nm was removed by a Toshiba UV-35 filter.

When an aqueous solution containing photosensitizer, MV^{2+} , and NADPH was irradiated, the growth of the cation radical of MV^{2+} was observed. As shown in the figure hematoporphyrin (Hm) dissolved in water using cetyltrimethylammonium bromide (CTAB) was far better than zinc meso-tetraphenylporphyrin trisulfonate ($Zn\text{-TPPS}_3$), which was the most active photosensitizer when mercaptoethanol was used as an electron donor.⁴⁾ The figure also shows the nature of the surfactant which has a notable effect on the reaction rate. When anionic surfactant, sodiumdodecyl sulfate (SDS), was used, activity was very low. These effects of the surfactants may be explained by the reaction mechanism where the reductive quenching of the photo-excited Hm by NADPH is predominant. As the micellar surface is positively charged in the case of cationic micelles, the recombination of oxidized NADPH and Hm anion radical may be suppressed.

When hydrogenase was added to the system containing Hm, MV^{2+} , and NADPH, hydrogen evolution was observed. The amount of hydrogen evolved for 1.5, 3.0, and 6.0 h irradiation was 0.19, 0.34, and 0.45 μmol , respectively.

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References

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- 2) NADP and NADPH are oxidized and reduced forms of nicotinamide adenine dinucleotide phosphate, respectively.
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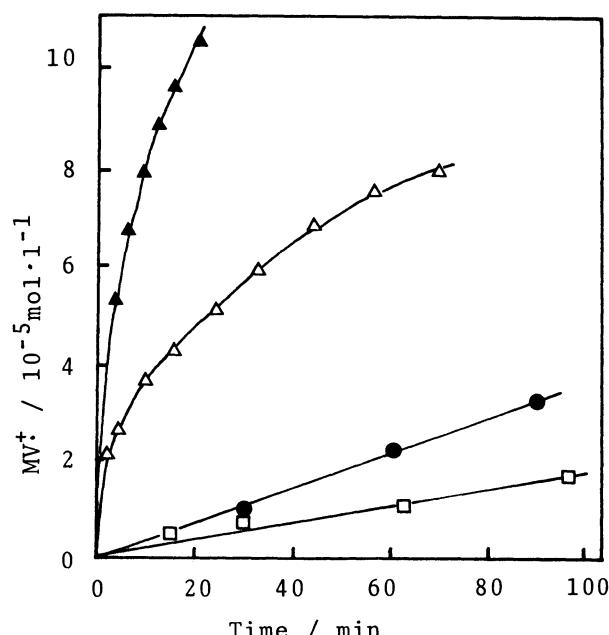


Fig. 1. Time dependence of MV^+ upon steady-state irradiation of aqueous solution (6.0 ml) containing MV^{2+} (2.44×10^{-5} mol), NADPH (2.16×10^{-5} mol), and Hm (CTAB, 4.28×10^{-7} mol: ▲), Hm (Triton X-100, 5.04×10^{-7} mol: △), Hm (SDS, 4.26×10^{-7} mol: ●), or $Zn\text{-TPPS}_3$ (3.63×10^{-7} mol: □)

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