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METHYL VIOLOGEN REDUCTION WITH WATER SOLUBLE METALLO-PORPHYRINS BY VISIBLE LIGHT IRRADIATION AND HYDROGEN EVOLUTION FROM WATER BY HYDROGENASE

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The formation of the cation radical of methyl viologen was established when an aqueous metallo-porphyrin, methyl viologen and reducing agent was irradiated by visible light, and the activities of photosensitizers were compared. When hydrogenase was added to the system, hydrogen evolution was observed.

Zinc(II)-tetraphenylporphyrin (Zn-TPP) is one of the well-known photosensitizers, since the photoexcited state of Zn-TPP serves as a good reducing agent and is liable to be oxidized in the presence of a suitable oxidizing agent such as methyl viologen (1,1'-dimethyl-4,4'-bipyridinium chloride).

As Zn-TPP is insoluble in water, Zn-TPP has been used[1,2] as a micellar solution in an aqueous system by the use of surfactant. We prepared some water soluble metallo-porphyrins and their activities for the reduction of methyl viologen were compared with other porphyrins and ruthenium complex. As reduced form of methyl viologen (MV^+) is known to produce hydrogen in the presence of a suitable catalyst, an attempt was made to reduce water to hydrogen by the system containing a photosensitizer, methyl viologen and an enzyme hydrogenase.

All reagents, obtained from Wako Pure Chemicals Co., were of the highest available purity. Zinc-meso-tetraphenylporphyrinetrisulfonic acid (Zn-$TPPS_3$) was synthesized by refluxing equimolar $TPPS_3$ and zinc acetate in methanol for 30 min. Desulfovibrio vulgaris cells were grown according to the literature[3] and the hydrogenase from D. vulgaris was purified by Yagi's method[4].

A typical experiment was performed as follows under anaerobic conditions. To 1.57×10^{-7} M of photosensitizer, 1.30×10^{-4} M of methyl viologen and 1.20×10^{-1} M of mercaptoethanol as a reducing agent in water, if necessary, 0.5 ml of hydrogenase was added. The volume of the mixture was adjusted to 6 ml with 0.1 M Tris-HCl buffer (pH 7.0; this value is suitable for hydrogenase). This solution was then irradiated in a Pyrex reactor at 30°C with a 200 W tungsten lamp for slide projector. The concentration of the hydrogenase was not known, but it had the ability to release 7.51×10^{-7} mol of hydrogen in the following reaction system: hydrogenase (0.5 ml) - methyl viologen (2.10×10^{-6} mol) - $Na_2S_2O_4$ (2.30×10^{-5} mol) in 3 ml of 1.20×10^{-2} M phosphate buffer (pH 7.0) at 30°C for 10 min.

Light of wavelength less than 390 nm was cut off with a Toshiba L-39 filter. A portion of the evolved hydrogen was collected via sampling valve and analyzed by g.l.c.

Table Activities of Photosensitizers for Reduction of Methyl Viologen

Photosensitizer	Solvent	Reaction time (min)	Activity $\left(\frac{\text{mol-MV}^+}{\text{mol-photosensitizer}}\right)$
Zn-$TPPS_3$	H_2O	10	138
$TPPS_3$	H_2O	10	2.4
Zn-TPP	Triton X-100/H_2O (v/v: 3/7)	10	2.2
Hematoporphyrin	CDBAH/H_2O (v/v: 1/57)	10	0.98
Zn-protoporphyrin	H_2O	20	0
Protoporphyrin	H_2O	10	0
Mn-protoporphyrin	H_2O	30	0
$Ru(bpy)_3^{2+}$	H_2O	10	0.87

The activities of photosensitizers for the reduction of methyl viologen were compared as shown in the Table. It is apparent that Zn-$TPPS_3$ is far better than the other porphyrins and $Ru(bpy)_3^{2+}$ as photosensitizers. When protoporphyrin was used as a ligand instead of $TPPS_3$, no catalytic activity was observed. Though zinc free $TPPS_3$ also serves as a photosensitizer, the spectrum of $TPPS_3$ changed gradually by the irradiation and $TPPS_3$ became inactive after 10 min irradiation.

In the case of Zn-$TPPS_3$ system, MV^+ increased with time and about 30 % of methyl viologen was reduced at 1 h irradiation. When the light was off, MV^+ decreased gradually and disappeared after 5 h. When irradiated again methyl viologen was reduced with the same rate as the initial rate. During the reaction, no spectrum change of Zn-$TPPS_3$ was observed.

When hydrogenase was added to the system containing Zn-$TPPS_3$, methyl viologen and mercaptoethanol, hydrogen evolution was observed at constant rate with reaction time. The amount of hydrogen evolved per hour (turnover numbers) for Zn-$TPPS_3$ was 614.

Hydrogen evolution was also observed by the irradiation of sunlight instead of the tungsten lamp.

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