August, 1982] © *1982 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.,* ***55****, 2659—2660 (1982)* 2659

Efficient Photoreduction of Methylviologen Sensitized by Chlorophyll Derivatives and Hydrogen Evolution by Visible Light

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(Received December 22, 1981)

Synopsis. The photoreduction of methylviologen sensitized by chlorophyll derivatives and porphines was investigated using EDTA as a reducing agent. The quantum yield of the photoreduction depends greatly on the kind of central metal ion of chlorophyll derivatives and porphines. Zn–chlorophyll-a and Zn–tetraphyenylporphine show a high quantum efficiency amounting 0.4, which is higher than that of chlorophyll-a.

Redox reactions induced by photoexcitation of chlorophyll play an important role in the photosynthesis in green plants and some bacteria. Much work has been done to construct an artificial system having such a function by making use of photochemical reactions of chlorophyll, its derivatives and porphyrins.[1–9] Here we would like to report an efficient photoreduction of methylviologen (MV^{2+}) by chlorophyll derivatives.

Methylviologen was used as an electron acceptor and EDTA as an electron donor. Photochemical reactions were carried out in the mixture of dimethyl sulfoxide (DMSO) and water (9 : 1 in volume ratio) which dissolves chlorophylls and porphines. The solution of MV^{2+} and EDTA in a quartz cell was deaerated to remove oxygen before illumination. A Xe lamp (500 W, Ushio) and a monochromator (Nikon, p-250) were used for monochromatic illumination (≈1 mW) at the peak wavelength of the visible absorption band of each dye molecule. A strong absorption band at 610 nm of the reduced methylviologen, $MV^{+\cdot}$, was monitored by a spectrophotometer to follow the reaction. The quantum yield of the reaction (the number of $MV^{+\cdot}$ formed/the number of absorbed photons) was determined by using a thermopile (Eppley Lab. Inc.).

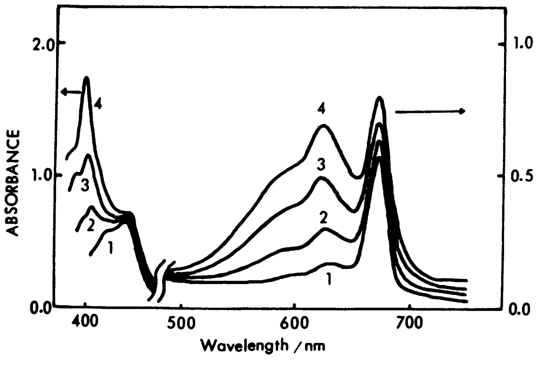

Fig. 1. Spectral changes of the solution (photocatalyst: Chl-a, electron donor: EDTA, electron acceptor: MV^{2+}) due to the reduction of MV^{2+} during illumination by a monochromatic light (≈ 1 mW) at 665 nm.
1) 0.0 min, 2) 2.0 min, 3) 12.0 min, 4) 37.0 min. [MgChl-a] = 9.4×10^{-6} M, [EDTA] = 1.0×10^{-2} M, [MV^{2+}] = 2.0×10^{-3} M. Solvent; DMSO: water = 1 : 1 (in volume ratio).

When chlorophyll-a was excited by visible light, it turned out to oxidize EDTA and reduce methylviologen. The net reaction is considered to be as follows.[9]

$$\mathrm{EDTA} + 2\mathrm{MV}^{2+} + \mathrm{H_2O} \longrightarrow \mathrm{C_2H_4N_2(CH_2COOH)_3H} + 2\,\mathrm{MV}^{+\cdot} + \mathrm{CH_2O} + \mathrm{CO_2} + 2\mathrm{H}^+$$
$$\Delta G^0 = 20\ \mathrm{kcal/mol}.$$

Due to the formation of reduced methylviologen the deaerated solution colored blue by illumination. Besides (Chl-a, its derivatives such as ZnChl and CuChl were found to work well as a photocatalyst for the reduction of methylviologen (MV^{2+}). Figure 1 shows the spectral change of the solution (photocatalyst: Chl-a, electron donor: EDTA, electron acceptor: MV^{2+}) during illumination with a monochromatic light at 665 nm. The introduction of air into the solution after illumination extinguished the blue color of the reduced methylviologen ($MV^{+\cdot}$) but did not cause any change of the absorption intensity of photocatalysts such as Chl-a and its derivatives, which indicates that they work reversibly as photocatalysts. Table 1 shows the quantum yield of the photoreduction for chlorophyll derivatives and porphines determined spectrophotometrically. One interesting thing is that the quantum yield depends remarkably on the kind of the central metal and is comparatively high, as seen in this table. Another interesting thing is that the quantum yield of an artificial compound such as ZnChl and ZnTPP is higher than that of MgChl, Chlorophyll-a (a natural compound). This suggests a possibility of constructing an artificial photosysnthetic device which is superior to the photosysnthetic system in the nature.

As is shown in Table 1, TPP derivatives have a similar tendency with Chl derivatives in the dependence of the quantum yield on the kind of central metal ion. Since the fluorescence intensity of Chl-a and ZnTPP is hardly influenced by adding EDTA and MV^{2+}, the triplet

Table 1. Quantum yield of phoreduction of methylviologen by chlorophyll derivatives, porphines, and dyes. They were excited by a monochromatic light at the peak wavelength of the visible absorption band
[MV^{2+}] = 2.0×10^{-3} M, [EDTA] = 1.0×10^{-2} M, Solvent; DMSO: Water = 9 : 1.
The concentration of each dye is about 1×10^{-5} M.

	Dye	Quantum yield/%
a	MgChl-a (Chl-a)	23
	ZnChl-a	40
	CuChl-a	13
b	MgTPP	10
	ZnTPP	40
	CuTPP	1

state is considered to be responsible for the above reaction. MgTPP has the longest lifetime (46 ms[11]). ZnTPP the next one (25 ms[11]) and CuTPP the shortest one (0.6 ms[11]) at liq. N_2 temperature. Although the life-time was measured at liq. N_2 temperature, the order of their magnitude would be the same at room temperature. Therefore, it seems reasonable to attribute the lowest quantum yield of photoreduction for CuTPP to the shortest triplet life-time. However, it can not be explained in terms of the triplet life-time (τ_T) that the quantum yield for MgTPP is smaller than that for ZnTPP. Another factor to be taken into consideration would be the rate of triplet population (γ_T: the quantum yield of intersystem crossing). It is 0.97 for ZnTPP,[11] 0.84 for MgTPP[11] and 1.0 for CuTPP.[12] Since the reactivity would depend on the product, $\tau_T\gamma_T$, we compared its value for ZnTPP with that for MgTPP. The value for MgTPP (39 ms) is still larger than that for ZnTPP (24 ms). Therefore these factors could not explain the fact that ZnTPP is better than MgTPP for photoreduction of MV^{2+}. Another important factor to be taken into consideration is the energetical relation. Since the oxidation potential of ZnTPP (0.95 V *vs.* NHE) is more positive than that of MgTPP (0.78 V *vs.* NHE),[13] the cation radical of ZnTPP would oxidize EDTA more efficiently than that of MgTPP would if the reaction rate of the recombination between the dye cation and $MV^{+\cdot}$ is assumed not to depend on the kind of the central metal ions.

We tried hydrogen evolution by adding Pt or Pt/TiO_2 catalyst which is already a popular method.[9,14–16] After Pt catalyst was added to the solution of EDTA, MV^{2+}, and Chl-a (or ZnTPP) either in DMSO–water (1 : 1) mixture or in MeOH–water (8 : 2) mixture, it was irradiated by visible light (λ>440 nm) for 3 h. The hydrogen evolution was confirmed by a quadrupole mass spectrometer. The hydrogen evolution rate was about 5 μmol/h in MeOH–water mixture for ZnTPP.

This work was supported by the Joint Studies Program (1979) of the Institute for Molecular Science.

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