Kinetics and Mechanism of Photo-induced Methyl Viologen Reduction with an Organic Dye 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 solution containing an organic dye, methyl viologen, and mercaptoethanol was irradiated by visible light. The reduction of methyl viologen has been studied kinetically and the reduction rate was expressed as follows.

$$V = \frac{d[MV^+]}{dt} = k_1 k_2 k_3 [S]_o \left(\frac{[MV^{2+}]}{k_{-1} + k_2[MV^{2+}]}\right) \times \left(\frac{[RSH]}{k_{-2}[MV^+] + k_3[RSH]}\right)$$

where [S], [MV^{2+}], [MV^+], and [RSH] are the respective concentrations of the dye photosensitizer, oxidized and reduced forms of methyl viologen, and mercaptoethanol. On the basis of the rate expression, the reaction mechanism is discussed.

On the addition of hydrogenase to the above photoirradiation system, hydrogen evolution was observed by the irradiation of visible light.

Introduction

Various attempts have been made to develop suitable redox systems for the photochemical utilization of solar energy. Recent works have shown that a three component system containing a photosensitizer, an electron donor, and an electron acceptor can be used to evolve hydrogen from water when a suitable catalyst is present [1]. The photosensitizers employed are almost exclusively ruthenium complexes and metallo-porphyrins, since most organic compounds are hardly dissolved in water and the photo-excited states of these compounds do not have enough redox potentials for water cleavage.

In this study an organic dye, 3,3′-sulfonic-propyl-5,5′-dichloro-9-ethylcarbocyanine (abbreviated as SE, Fig. 1), was found to be an effective photosensitizer for photo-reduction of methyl viologen, and kinetic studies of methyl viologen cation radical (MV^+) growth with SE were carried out and the mechanism of methyl viologen reduction was discussed.

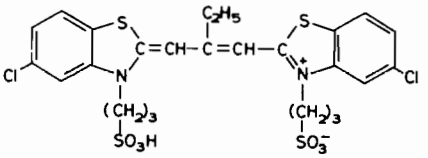

Fig. 1. The dye SE.

As MV^+ has been known to produce hydrogen in the presence of a suitable catalyst, an attempt was made to reduce water to hydrogen by the use of the modified electron transfer system which combines SE and methyl viologen photo-irradiation system and a catalyst for hydrogen production. Hydrogenase extracted from *Desulfovibrio vulgaris* should serve as a suitable catalyst for this process, for it is known as a specific enzyme for methyl viologen.

Experimental

Materials

Methyl viologen was purchased from Tokyo Kasei Kogyo Co.; SE was kindly provided by Konishiroku Co. The other chemicals, obtained from Wako Pure Chemical Co., were of the highest available purity.

Desulfovibrio vulgaris (Miyazaki type) cells (kindly provided by Professor T. Yagi of Shizuoka Univ.) were cultured according to the literature [2]. The enzyme hydrogenase was purified according to Yagi's method [3]. The concentration of hydrogenase is not known but it has the ability to release 1.12×10^{-5} mol of hydrogen in the following reaction system: hydrogenase (0.5 ml)- methyl viologen (1.78×10^{-6} mol)–$Na_2S_2O_4$ (2.30×10^{-5} mol) in 3.0 ml of 0.1 *M* Tris-HCl buffer (pH 7.0) at 30 °C for 10 min.

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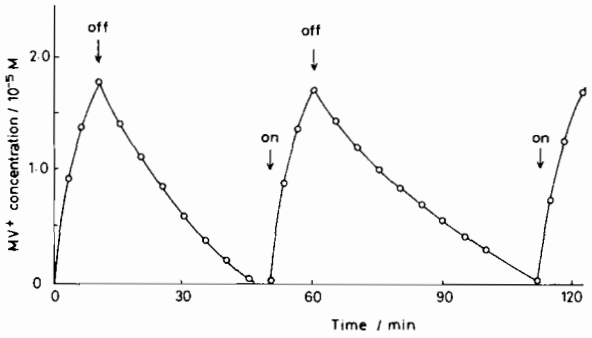

Fig. 2. Time dependence of MV^+ radical concentration. Reaction conditions: SE, 3.33×10^{-6} *M*; methyl viologen, 1.20×10^{-4} *M*; RSH, 1.07×10^{-1} *M*; reaction temp., 30° C.

Measurement Procedure

The sample solution which consisted of SE, mercaptoethanol (RSH), methyl viologen and hydrogenase (if included) in 6.0 ml of 0.1 *M* Tris-HCl buffer (pH 7.0; this value is suitable for hydrogenase), was deaerated by repeated freeze–pump–thaw cycles. A typical experiment was performed as follows under anaerobic conditions: to 3.33×10^{-6} *M* of SE, 1.20×10^{-4} *M* of methyl viologen and 1.07×10^{-1} *M* of RSH as a reducing agent in 0.1 *M* of Tris-HCl buffer, 0.5 ml of hydrogenase (if included) was added. The volume of the mixture was adjusted to 6.0 ml with 0.1 *M* Tris-HCl buffer (pH 7.0). 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 (from a slide projector). Light of wavelength less than 350 nm was cut off by a Toshiba UV-35 filter. A portion of the evolved hydrogen was collected via a sampling valve and analyzed by g.l.c.

Results and Discussion

When an aqueous solution containing photosensitizer, methyl viologen and RSH was irradiated, the growth of the cation radical of methyl viologen, which has characteristic absorption bands at 395 and 605 nm, was observed. Though the bands at 515 and 553 nm (which correspond to SE) decreased rapidly by the irradiation in the absence of RSH, the bands were kept almost unchanged in the presence of RSH. As shown in Fig. 2, the time dependence of methyl viologen increased rapidly at the beginning of the reaction and reached a constant value. After 10 min irradiation, about 16% of the methyl viologen was reduced and existed in the MV^+ form. When irradiation ceased after 10 min, the concentration of MV^+ decreased gradually and reached zero. MV^+ was reformed by re-irradiating the system, and the MV^+ formation rate was almost the same as the initial rate, for MV^+ returns to the original (oxidized) form in the absence of light.

Kinetics of Methyl Viologen Reduction

The reduction rate of methyl viologen (V), obtained from the slope of the tangent of the time course at the low concentration of MV^+ (5.1×10^{-6} *M*), was used in view of the considerable percentage error in the initial rate obtained from the slope of the curve at the beginning of the reaction. V was proportional to the concentration of SE, but showed Langmuir adsorption type dependence on the concentration of methyl viologen, as well as on the concentration of RSH, *i.e.* V increases and reaches a constant value with the increase of the concentration of methyl viologen and RSH. By comparing the reaction mechanisms reported on similar systems [4] and the above results, the following scheme for the reduction of methyl viologen is proposed:

$$SE \underset{k_{-1}}{\overset{h\nu,\, k_1}{\rightleftharpoons}} SE^*$$

$$SE^* + MV^{2+} \xrightarrow{k_2} SE^+ + MV^+$$

$$SE^+ + MV^+ \xrightarrow{k_{-2}} SE + MV^{2+}$$

$$SE^+ + RSH \xrightarrow{k_3} SE + RSH_{oxidized}$$

where k_{-1}, k_2, k_{-2} and k_3 are rate constants, but k_1 is not, for it is a function of the light flux. As the fractional light absorption is small in this experimental condition, *i.e.* the value ϵCl is small enough, ϕI_o can be replaced by $k_1[SE]_o$. $[SE]_o$ is the total amount of SE in the system. On the basis of the above reaction mechanism, the following rate expression is derived by the use of the steady state approximation for $[SE^*]$ and $[SE^+]$:

$$V = \frac{d[MV^+]}{dt} = k_1 k_2 k_3 [SE]_o \left(\frac{[MV^{2+}]}{k_{-1} + k_2[MV^{2+}]}\right) \times \left(\frac{[RSH]}{k_{-2}[MV^+] + k_3[RSH]}\right) \quad (1)$$

Even at the initial stage of the reaction, MV^+ does not grow linearly with reaction time, for the rate of the back reaction, SE^+ reduction by MV^+, is not negligibly small even at this stage. Equation (1) is rewritten as follows.

$$1/V = \frac{1}{k_1 k_2 k_3 [SE]_o}\left(k_2 + \frac{k_{-1}}{[MV^{2+}]}\right)\left(k_3 + \frac{k_{-2}[MV^+]}{[RSH]}\right) \quad (2)$$

According to eqn. (2) 1/V should be linearly related to $1/[MV^{2+}]$ and $1/[RSH]$, for $k_{-2}[MV^+]$ is constant. The good linear relations as shown in Figs. 3 and

4 indicate that eqn. (1) is adequate. From the slopes and the intercepts of the straight lines a ratio of rate constants such as $k_2/k_{-1} = 2.0 \times 10^4\ M^{-1}$ was obtained. This ratio is a parameter to express the activity of a photosensitizer. When zinc-tetraphenylporphyrintrisulfonic acid (Zn-$TPPS_3$) and zinc-tetraphenylporphyrin (Zn-TPP) were used as photosensitizers instead of SE, the kinetic data obeyed the same equation (1) and the rate constant ratios were $5.2 \times 10^4\ M^{-1}$ and $7.0 \times 10^2\ M^{-1}$, respectively. As reported previously, Zn-$TPPS_3$ was much more active than other porphyrins and ruthenium complexes [5]. In the case of SE, the same order of the ratio as Zn-$TPPS_3$ was obtained.

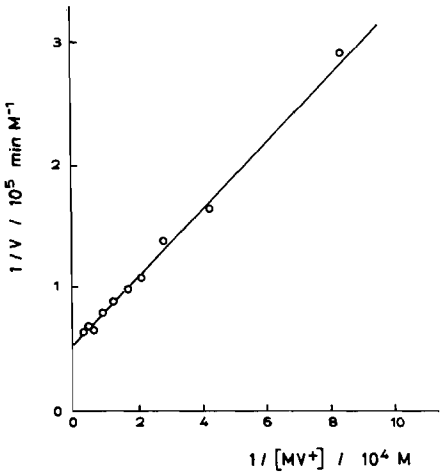

Fig. 3. Relation between 1/V and $1/[MV^{2+}]$. Reaction conditions: SE, 3.33×10^{-6} *M*; RSH, 1.07×10^{-1} *M*; reaction temp., 30° C.

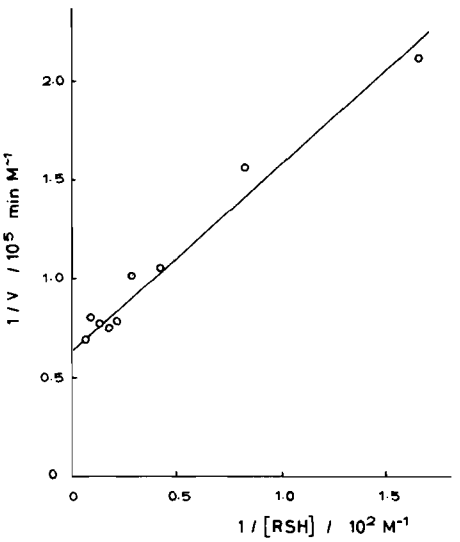

Fig. 4. Relation between 1/V and 1/[RSH]. Reaction conditions: SE, 3.33×10^{-6} *M*; MV^{2+}, 1.20×10^{-4} *M*; reaction temp., 30° C.

Hydrogen Evolution by Adding Hydrogenase to the System

When hydrogenase was added to the system containing SE, methyl viologen and RSH, hydrogen evolution was observed as follows:

Time/h	1	2	4
Evolved H_2/μmol	12.6	28.2	40.0

The amount of hydrogen evolved per hour (turnover numbers) for SE was 70. No hydrogen evolution was observed when any component of the system was omitted.

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