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The Complexation of Zinc Tetraphenylporphyrintrisulfonate by Viologen and Its Role in Photoredox Processes

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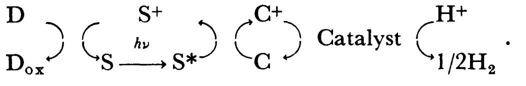
The formation of the cation radicals of viologen dyes was established when an aqueous solution containing zinc tetraphenylporphyrintrisulfonate (Zn–TPPS$_3$), viologen dye, and 2-mercaptoethanol was irradiated by visible light. The reduction of viologen has been studied kinetically; its reduction rate may be expressed as follows:

$$v = \frac{d[V^+]}{dt} = \left(\frac{k_3[\text{Zn-TPPS}_3]_0}{1+K_1[V^{2+}]+K_2[V^+]}\right)\left(\frac{k_4[V^{2+}]}{k_{-3}+k_4[V^{2+}]}\right)\left(\frac{k_6[\text{RSH}]}{k_5[V^+]+k_6[\text{RSH}]}\right),$$

where [V^{2+}], [V$^+$], and [RSH] are the concentrations of the oxidized form and the reduced form of viologen, and 2-mercaptoethanol respectively. On the basis of the rate expression, a reaction mechanism containing the complexation of Zn–TPPS$_3$ by viologen was proposed. On the addition of hydrogenase to the above photoirradiation system, hydrogen evolution was observed by the irradiation of visible light.

Photochemical redox systems have been developed for the purpose of solar-energy utilization.[1] The systems, containing, as shown in the following scheme, a photosensitizer (S), an electron donor (D), and an electron carrier (C), have been used to evolve hydrogen from water when a suitable catalyst is present:



(1)

As photosensitizers, metallo-porphyrins have been employed extensively in these studies.[2] As catalysts, hydrogenase and colloidal platinum are predominant. Methylviologen has been used almost exclusively as an electron carrier.

As both the photosensitizer and the electron carrier serve as redox catalysts in the above reaction, the overall reaction may be expressed as follows:

$$\text{D} + \text{H}^+ \xrightarrow{h\nu} \text{D}_{\text{ox}} + 1/2\text{H}_2. \tag{2}$$

When EDTA, triethanolamine, or 2-mercaptoethanol (RSH) is used as an electron donor, the following reactions occur:

$$(\text{HOOCCH}_2)_2\text{N}(\text{CH}_2)_2\text{N}(\text{CH}_2\text{COOH})_2 + \text{H}_2\text{O} \longrightarrow (\text{HOOCCH}_2)_2\text{N}(\text{CH}_2)_2\text{NHCH}_2\text{COOH} + \text{CO}_2 + \text{HCHO} + \text{H}_2, \tag{3}$$

$$\text{N}(\text{CH}_2\text{CH}_2\text{OH})_3 + \text{H}_2\text{O} \longrightarrow \text{NH}(\text{CH}_2\text{CH}_2\text{OH})_2 + \text{CHOCH}_2\text{OH} + \text{H}_2, \tag{4}$$

$$2\text{RSH} \longrightarrow \text{RSSR} + \text{H}_2. \tag{5}$$

The overall reaction shown above, the light-induced oxidation of the electron donor, involves a net solar energy storage, and part of the light energy is also stored. If back reaction proceeds upon the addition of a suitable catalyst and the stored light energy is taken out as heat, the stored solar energy can be used when needed. In the cases of Reactions (3) and (4), complex products with three or four components are formed, and it may not be easy to get the starting materials by means of the back reaction. In the case of Reaction (5), however, the back reaction proceeded easily. When cystine was used as the disulfide (RSSR), the starting material, cysteine, was produced with the palladium catalyst by the hydrogenation of RSSR under mild reaction conditions (at 30 °C; hydrogen pressure: 1 atm). By the conversion of cysteine to cystine and hydrogen, about 30 kJ mol^{-1} of light energy is stored. Therefore, the hydrogen production reaction expressed by Reaction (5) seems to be suitable for a solar-energy-storage system.

The photoreduction of electron carriers should proceed nicely to get an efficient hydrogen evolution, provided the hydrogen evolution rate is determined by the photoreduction of the electron carrier as is shown in Eq. (1). For this purpose, suitable combinations of the components and the optimum reaction conditions are discussed in this study.

Experimental

Materials. All the chemicals, obtained from the Tokyo Kasei Kogyo Co., were of the highest available purity. The ethyl-, propyl-, and butylviologens were synthesized according to the literature.[3] The zinc *meso*-tetraphenylporphyrintrisulfonate (Zn–TPPS$_3$) was synthesized by refluxing TPPS$_3$ and zinc acetate (molar ratio; 1 : 10) in methanol for 2 h.

Desulfovibrio vulgaris cells (Miyazaki type, which has kindly been provided by Prof. T. Yagi of Shizuoka Univ.) were cultured according to the literature.[4] The hydrogenase [H$_2$: ferricytochrome C$_3$ oxidoreductase, EC 1.12.2.1] from *Desulfovibrio vulgaris* was purified according to Yagi's method.[5] The concentration of hydrogenase is not known, but it has the ability to produce 4.88 μmol of hydrogen when this reaction system is used: hydrogenase (0.5 ml)–methylviologen (4.15×10^{-6} mol)–Na$_2$S$_2$O$_4$ (2.87×10^{-5} mol) in 6.0 ml of 0.02 mol dm^{-3} of Tris–HCl buffer (pH 7.0) at 30 °C for 10 min.

Measurement Procedure. The sample solution, which consisted of the photosensitizer, the viologen dye, 2-mercaptoethanol, and hydrogenase (if included) in 0.02 mol dm^{-3} of the 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 8.33×10^{-8} mol dm^{-3} of the photosensitizer, 1.26×10^{-4} mol dm^{-3} of the viologen dye and 0.21 mol dm^{-3} of RSH as a reducing agent in water, 0.5 ml of hydrogenase (if included) was added. The volume of the mixture was then adjusted to 6.0 ml with 0.02 mol dm^{-3} of the Tris–HCl buffer (pH 7.0). In the photolysis with continuous irradiation, the sample, in a Pyrex cell equipped with a magnetic stirrer, was irradiated with light from a 200-W tungsten lamp. Light at wavelengths less than 390 nm was cut off by a Toshiba L-39 filter. A portion of the evolved hydrogen was collected *via* a sampling valve and analyzed by means of gas chromatography.

Results and Discussion

Photoreduction of Viologen Dyes by RSH. When an aqueous solution containing Zn–TPPS3, viologen dye, and RSH was irradiated, the formation of the viologen cation radical was observed. As is shown in Fig. 1, the concentration of the viologen radical increased rapidly at the beginning of the reaction, and then reached a constant value. When the light was then cut off, the concentration of the cation radical decreased gradually. The difference in the constant values may depend on the difference in the photoinduced viologen-reduction rates and the backward reaction rates in the absence of light.

As is shown in Figs. 2, 3, and 4, the initial rate of cation-radical formation (the slopes of the curves at the beginning of the reaction in Fig. 1) increases at any viologen-dye concentration, and then decreases after a maximum point. To clarify this abnormal phenomenon, the rate decrease at a higher viologen concentration, the following experiments were carried out.

Complexation of Zn–TPPS3 by Viologen Dyes. When Zn–TPPS3 was mixed with ethylviologen, the characteristic Soret absorption band (418 nm) decreased with the increase in the ethylviologen concentration, and a new spectrum appeared which has a characteristic absorption band at 425 nm through the isosbestic point at 422 nm (Fig. 5). Similar complex formations between metalloporphyrins and methylviologen have recently been reported.[6]

When the complex is formed by the following reaction:

$$\text{Zn–TPPS}_3 + \text{EtV}^{2+} \overset{K_1}{\rightleftharpoons} \text{complex} \tag{6}$$

EtV^{2+}: ethyl viologen,

the equilibrium constant, K_1, is expressed by:

$$K_1 = \frac{[\text{complex}]}{[\text{Zn–TPPS}_3][\text{EtV}^{2+}]}. \tag{7}$$

This equation can be rewritten as follows by using the initial Zn–TPPS3 concentration, $[\text{Zn–TPPS}_3]_0$:

$$\frac{[\text{Zn–TPPS}_3]_0}{[\text{complex}]} = 1 + \frac{1}{K_1[\text{EtV}^{2+}]}. \tag{8}$$

As the complex concentration is calculated from the absorbance of the complex, the relation between

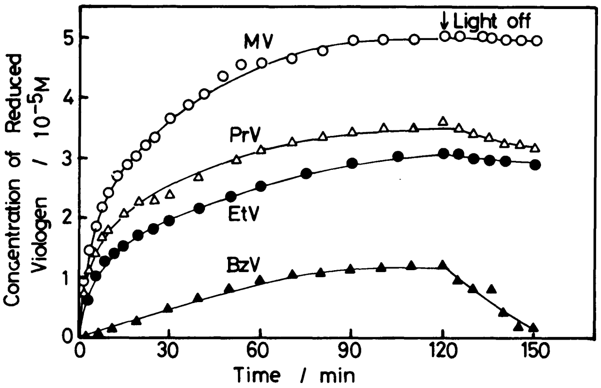


Fig. 1. Time dependence of reduced viologen concentration. (1 M = 1 mol dm^{-3})
Reaction conditions; Zn–TPPS$_3$, 8.33 × 10^{-8} mol dm^{-3}; RSH, 0.21 mol dm^{-3}; methylviologen (MV), 1.26 × 10^{-4} mol dm^{-3}; ethylviologen (EtV), 1.22 × 10^{-4} mol dm^{-3}; propylviologen (PrV), 9.50 × 10^{-5} mol dm^{-3}; benzylviologen (BzV), 1.42 × 10^{-4} mol dm^{-3}; reaction temp, 30°C.

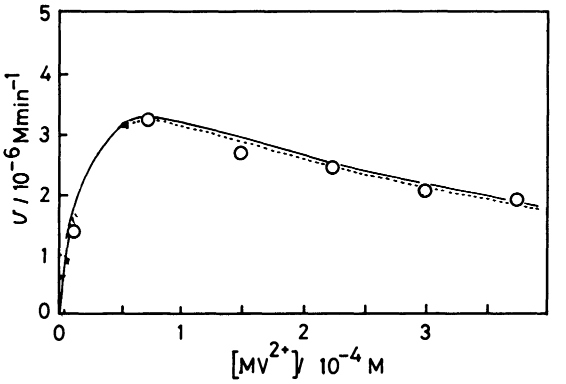


Fig. 2. Relation between photo-induced reduction rate of methylviologen and its concentration.

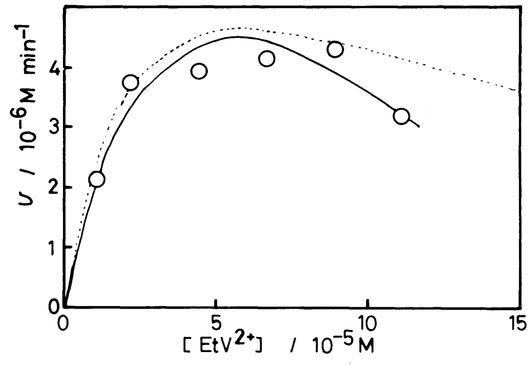


Fig. 3. Relation between photo-induced reduction rate of ethylviologen and its concentration.

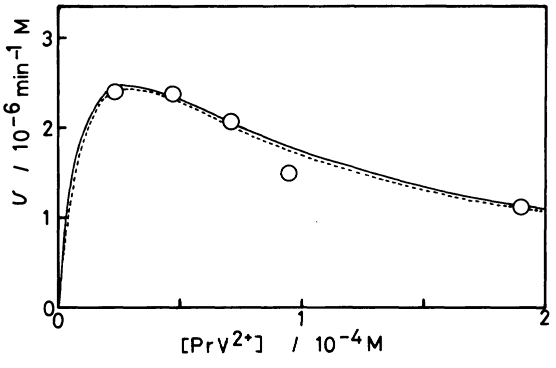


Fig. 4. Relation between photo-induced reduction rate of propylviologen and its concentration.

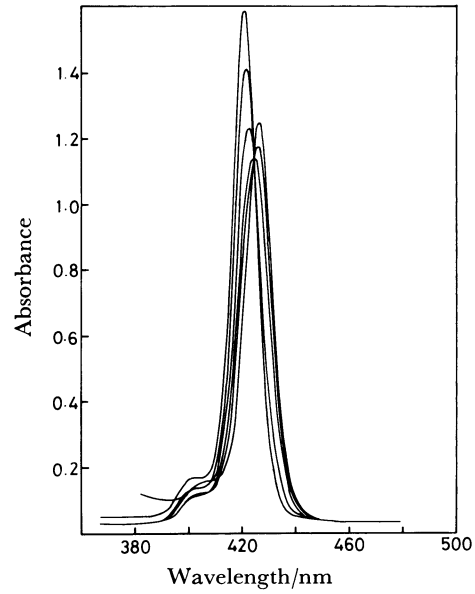


Fig. 5. Spectrum change of Zn–TPPS$_3$ by the addition of ethylviologen.

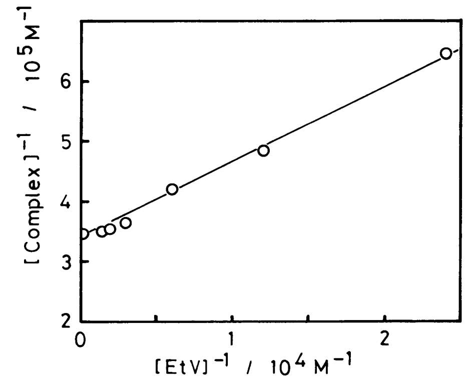


Fig. 6. Relation between [complex]$^{-1}$ and [EtV^{2+}]$^{-1}$.

[complex]$^{-1}$ and [EtV^{2+}]$^{-1}$ can be plotted to as shown in Fig. 6. The good linear relation between [complex]$^{-1}$ and [EtV^{2+}]$^{-1}$ shows the formation of a 1 : 1 complex of Zn–TPPS$_3$ and ethylviologen.

When other viologen dyes were used, the respective complex formation was observed, as is shown in Fig. 7. The equilibrium constants obtained by Eq. (8) are listed in Table 1.

The reduced form of viologen dye also produced a complex with Zn–TPPS$_3$. When the benzylviologen reduced by $Na_2S_2O_4$, for example, was added to Zn–TPPS$_3$, a new spectrum (Fig. 8 Spectrum c) was observed, which shows that Zn–TPPS$_3$ forms a complex with reduced benzylviologen.

Complex formation was also observed when metal-free porphyrin, TPPS$_3$, was used (the data is not shown); this shows that the central metal of the metalloporphyrin does not play an important role in the complex formation, but that the porphyrin ring combines with viologen dye.

Kinetics and Mechanism of Photo-induced Reduction of Viologen Dyes. As has been mentioned above, Zn–TPPS$_3$ forms complexes with both oxidized and reduced forms of viologen dyes. After comparing the reaction mechanisms reported for similar systems[7] and the above results, the following scheme containing complex-formation processes may be proposed:

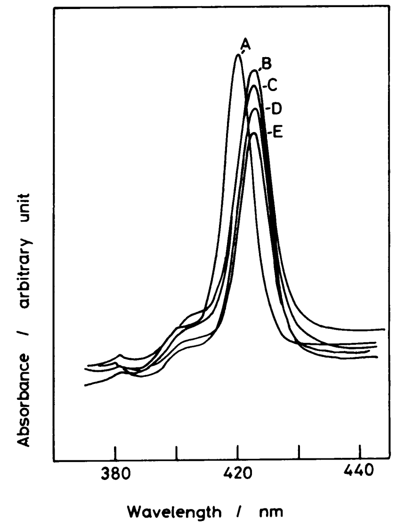


Fig. 7. Spectrum change of Zn–TPPS$_3$ by the addition of viologens.
A: Zn–TPPS$_3$, B: Zn–TPPS$_3$+methylviologen, C: Zn–TPPS$_3$+propylviologen, D: Zn–TPPS$_3$+ethylviologen, E: Zn–TPPS$_3$+butylviologen.

TABLE 1. LIST OF K_1 AND k_4/k_{-3} VALUES

	K_1/dm^3 mol^{-1}	(k_4/k_{-3})/dm^3 mol^{-1}
Methylviologen	$(2.1\pm0.1)\times10^4$	$(8.2\pm0.8)\times10^3$
Ethylviologen	$(2.9\pm0.1)\times10^4$	$(1.0\pm0.1)\times10^4$
Propylviologen	$(3.0\pm0.1)\times10^4$	$(2.9\pm0.2)\times10^4$

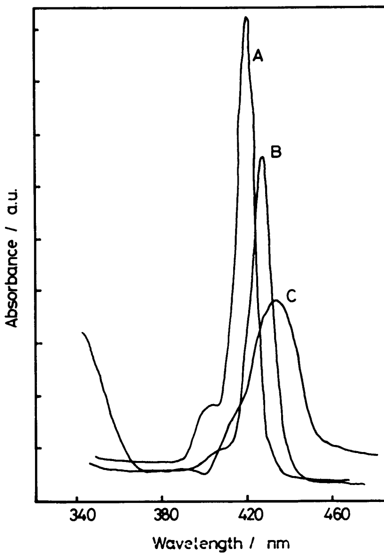


Fig. 8. Spectrum change of Zn–TPPS$_3$ by the addition of benzylviologen and reduced benzylviologen.
A: Zn–TPPS$_3$, B: Zn–TPPS$_3$+benzylviologen, C: Zn–TPPS$_3$+reduced benzylviologen.

$$\text{Zn-TPPS}_3 + V^{2+} \overset{K_1}{\rightleftharpoons} [\text{Zn-TPPS}_3\ V^{2+}]_{\text{complex}},$$

$$\text{Zn–TPPS}_3 + \text{V}^+ \overset{K_2}{\rightleftharpoons} [\text{Zn–TPPS}_3\ \text{V}^+]_{\text{complex}},$$

$$\text{Zn–TPPS}_3 \underset{k_{-3}}{\overset{h\nu, k_3}{\rightleftharpoons}} \text{Zn–TPPS}_3^*,$$

$$\text{Zn–TPPS}_3^* + \text{V}^{2+} \xrightarrow{k_4} \text{Zn–TPPS}_3^+ + \text{V}^+,$$

$$\text{Zn–TPPS}_3^+ + \text{V}^+ \xrightarrow{k_5} \text{Zn–TPPS}_3 + \text{V}^{2+},$$

$$\text{Zn–TPPS}_3^+ + \text{RSH} \xrightarrow{k_6} \text{Zn–TPPS}_3 + 1/2\,\text{RSSR},$$

where V^{2+} and V^+ are oxidized and reduced forms of viologen dyes respectively. K_1 and K_2 are equilibrium constants. k_{-3}, k_4, k_5, and k_6 are rate constants, but k_3 is not, for it is a function of light flux. As the fraction of light absorption is small under these experimental conditions, *i.e.*, as the εCl value is small enough, ΦI_0 can be replaced by $k_3[\text{Zn–TPPS}_3]_0$.

If the complexes are not effective for viologen photoreduction, and if only free Zn–TPPS3 is effective for this reaction, as Rougee *et al.* have previously established by a similar system,[6a)] the following rate expression can be derived on the basis of the above reaction mechanism by the use of the steady-state approximation for $[\text{Zn–TPPS}_3^*]$ and $[\text{Zn–TPPS}_3^+]$:

$$v = \frac{d[\text{V}^+]}{dt} = \left(\frac{k_3[\text{Zn–TPPS}_3]_0}{1+K_1[\text{V}^{2+}]+K_2[\text{V}^+]}\right)\left(\frac{k_4[\text{V}^{2+}]}{k_{-3}+k_4[\text{V}^{2+}]}\right) \times \left(\frac{k_6[\text{RSH}]}{k_5[\text{V}^+]+k_6[\text{RSH}]}\right). \tag{9}$$

At the initial state of the reaction, V^+ grows linearly with the reaction time, for the rate of the back reaction, Zn–TPPS_3^+ reduction by V^+, is negligibly small at this stage. Equation (9) is rewritten as follows:

$$v = \left(\frac{k_3[\text{Zn–TPPS}_3]_0}{1+K_1[\text{V}^{2+}]}\right)\left(\frac{k_4[\text{V}^{2+}]}{k_{-3}+k_4[\text{V}^{2+}]}\right), \tag{10}$$

or

$$\frac{1}{v(1+K_1[\text{V}^{2+}])} = \left(\frac{1}{k_3[\text{Zn–TPPS}_3]_0}\right)\left(1+\frac{k_{-3}}{k_4[\text{V}^{2+}]}\right). \tag{11}$$

According to Eq. (11), $1/v(1+K_1[\text{V}^{2+}])$ should be linearly related to $1/[\text{V}^{2+}]$, and the intercept, $1/k_3[\text{Zn–TPPS}_3]_0$, should not depend on the type of viologen dye. The good linear relations and the same intercept in the cases of methylviologen and ethylviologen, as shown in Fig. 9, indicate that Eq. (9) is adequate. From the slopes and the intercept of the straight lines, the ratios of such rate constants as k_4/k_{-3} (as shown in Table 1) and k_3 were obtained. By using the values listed in Table 1 and k_3, the relations between v and $[\text{V}^{2+}]$ are obtained from Eq. (9); they are shown by the dotted lines in Figs. 2, 3, and 4. The experimental values agree well with the theoretial results except for some deviations in the case of ethylviologen. The good fittings of the curves show that the above-mentioned scheme explains the experimental results satisfactorily.

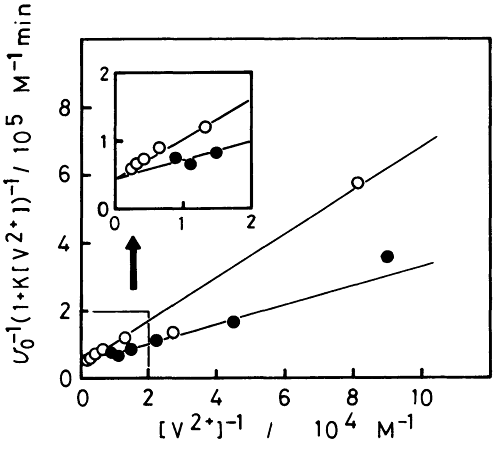


Fig. 9. Relation between $V_0^{-1}(1+K_1[\text{V}^{2+}])^{-1}$ and $[\text{V}^{2+}]^{-1}$.

A typical time dependence of the viologen-radical concentration is shown in Fig. 10. The time course can be obtained by integrating Eq. (9). As $[\text{V}^{2+}]_0 \ll [\text{RSH}] \simeq \text{constant}$ under these experimental conditions, and if $K_1 \simeq K_2$, Eq. (9) can be rewritten as follows:

$$\left(\frac{k_4[\text{V}^{2+}]}{k_{-3}+k_4[\text{V}^{2+}]}\right)\frac{1}{v} = \left(\frac{k_3[\text{Zn–TPPS}_3]_0}{1+K_1[\text{V}^{2+}]_0}\right)^{-1}\left(1+\frac{k_5[\text{V}^+]}{k_6[\text{RSH}]}\right). \tag{12}$$

This relation is confirmed by the good linearity of the $\left(\frac{k_4[\text{V}^{2+}]}{k_{-3}+k_4[\text{V}^{2+}]}\right)\frac{1}{v}$ *vs.* $[\text{V}^+]$ plot, as is shown in Fig. 11. From the slope and the intercept of the straight line, the ratio of the rate constants, k_5/k_6, is obtained. By

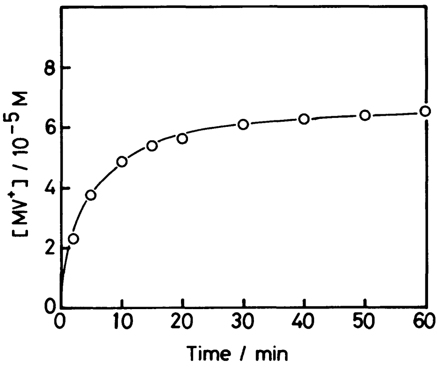


Fig. 10. Time dependence of reduced methylviologen concentration.
Reaction conditions: Zn–TPPS$_3$, 1.31×10^{-7} mol dm^{-3}; RSH, 0.85 mol dm^{-3}; methylviologen, 6.92×10^{-5} mol dm^{-3}, —: calculated; ○: observed.

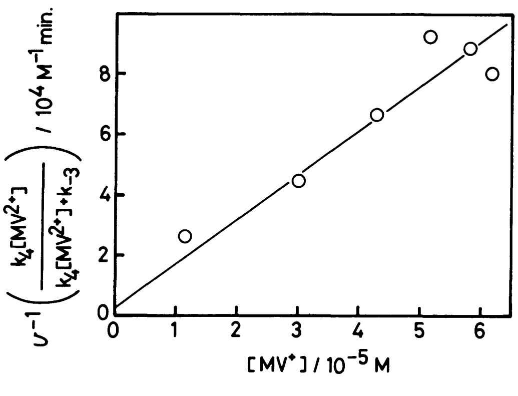


Fig. 11. Relation between $v^{-1}\left(\frac{k_4[\text{MV}^{2+}]}{k_4[\text{MV}^{2+}]+k_{-3}}\right)$ and $[\text{MV}^{2+}]$.

integrating Eq. (11), Eq. (13) can be obtained:

$$\frac{k_5[\mathrm{V}^+]^2}{2k_6[\mathrm{RSH}]} - \frac{k_{-3}}{k_4}[\mathrm{V}^+]\left(1-\frac{k_5}{k_6[\mathrm{RSH}]}\right) - \frac{k_4}{k_{-3}}\left(1+\frac{k_5}{k_6[\mathrm{RSH}]}\right)\ln\left(\frac{[\mathrm{V}^{2+}]_0-[\mathrm{V}^+]}{[\mathrm{V}^{2+}]_0}\right) = \frac{k_3[\mathrm{Zn\text{-}TPPS_3}]_0}{1+K_1[\mathrm{V}^{2+}]_0}t. \quad (13)$$

By using the constant values obtained from Figs. 9, 11, and Table 1, the time dependence of $[\mathrm{V}^+]$ can be plotted on the basis of Eq. (13), as is shown by the solid line in Fig. 10. The good fit of the observed data (open circles) and the calculated data (solid line) indicates that Eq. (9) is adequate for expressing the kinetic data; it also supports the proposed reaction mechanism.

Photo-induced Hydrogen Evolution with Hydrogenase. As the reduced forms of methy-, ethyl-, propyl-, and benzylviologens have been known to produce hydrogen in the presence of a suitable catalyst, an attempt was made to produce hydrogen by the use of an electron-transfer system conbinning Zn–TPPS3 and viologen dyes.[8]

By the addition of hydrogenase to the system containing RSH, Zn–TPPS3, and viologen dye, photo-induced hydrogen evolution was carried out. Experiments were preformed by using higher initial concentrations of viologen dye in order to minimize the free Zn–TPPS3, where more than 70% of the porphyrin is complexed, and also by using the optimum concentration, where the maximum reduction rate of viologen dye is given as is shown in Figs. 2, 3, and 4. In these experiments, an excess amount of hydrogenase was used to make the rate-determining step of the hydrogen-evolution reaction to the photoreduction of viologen dyes. As is shown in Figs. 12 and 13, a continuous hydrogen evolution was observed in both cases. The higher hydrogen evolution rate was obtained by using the optimum concentration of the viologen dyes.

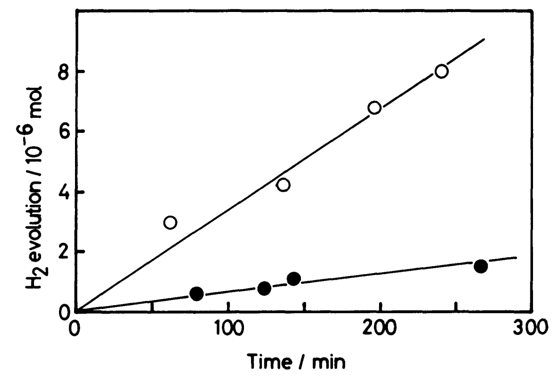


Fig. 12. Time dependence of hydrogen evolution. Reaction conditions; Zn–$TPPS_3$, 1.31×10^{-7} mol dm^{-3}; RSH, 0.21 mol dm^{-3}; ethylviologen, 5.53×10^{-4} mol dm^{-3} (●), 2.22×10^{-5} mol dm^{-3} (○); hydrogenase, 1.0 ml; reaction temp, 30°C.

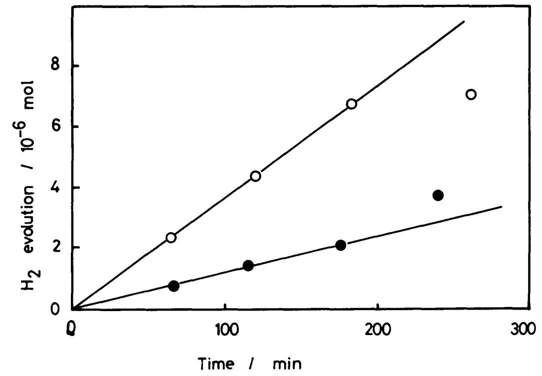


Fig. 13. Time dependence of hydrogen evolution. Reaction conditions; Zn–$TPPS_3$, 1.31×10^{-7} mol dm^{-3}; RSH, 0.21 mol dm^{-3}; methylviologen, 3.46×10^{-4} mol dm^{-3} (●), 7.40×10^{-5} mol dm^{-3} (○); hydrogenase, 1.0 ml; reaction temp, 30°C.

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