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BIS(η^5-INDENYL)IRON(II)-CATALYZED PHOTOREDUCTION OF METHYLVIOLOGEN[+]

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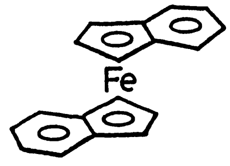
Bis(η^5-indenyl)iron(II) catalyzes the photoreduction of methylviologen in methanol solutions under irradiation with near ultraviolet light. The quantum yields for the formation of the cation radical of methylviologen ($MV^{\overset{+}{\cdot}}$) with 400-480 nm light are 0.04-0.05. But under light of wavelength shorter than 400 nm bis(η^5-indenyl)iron(II) acts as a triplet quencher for the excited methylviologen in the triplet state and lowers the yield of $MV^{\overset{+}{\cdot}}$. A reaction mechanism in which the excited singlet state of bis(η^5-indenyl)iron(II) is involved is proposed for the sensitized reduction of methylviologen.

The photochemical production of hydrogen from water is one of the important targets for the storage of solar energy and its conversion into various types of chemical energy. Since the discovery of the photoredox system consisting of $[Ru(bpy)_3]^{2+}$ and methylviologen by Lehn and Sauvage,1) most of work dealing with the photochemical decomposition of water to hydrogen have been done using $[Ru(bpy)_3]^{2+}$ as a sensitizer.2) Recently, zinc tetraphenylporphyrin derivatives have been used as an alternative,3) because they are water-soluble and have redox potentials suitable for water splitting.4)

Although ferrocene has been found to be an electron donor in its excited state,5) little has been reported about its photocatalytic nature. Only a few reports have appeared concerning the photoelectrochemical nature of ferrocene derivatives which can modify semiconductor electrodes.6) It is noteworthy that electron donating and light-harvesting abilities of ferrocene can be improved by introducing a substituent in the cyclopentadienyl ring of ferrocene. From this point of view, we have examined the photocatalytic nature of ferrocene derivatives using methylviologen as an electron acceptor.

In this paper we wish to report that one of the ferrocene derivatives, bis(η^5-indenyl)iron(II) (**1**), acts as a photocatalyst for the reduction of methylviologen (MV^{2+}) in methanol solutions under the irradiation with near ultraviolet light.



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[+] Dedicated to Professor Schulte-Frohlinde on the occasion of his 60th birthday.

A sample solution (5 cm^3) containing **1**[7] (1.45-3.87×10^{-4} mol dm^{-3}), methylviologen (MV^{2+})(1.29×10^{-2} mol dm^{-3}), and triethanolamine (TEOA)(5.9×10^{-2} mol dm^{-3}) in methanol was prepared in a quartz cell (1 cm x 1 cm, with a stopcock for the introduction of Ar gas) under a stream of Ar. The sample solution was irradiated for 2-30 min with monochromatic light (lamp, Osram HBO 200 W; monochromator, Shimadzu-Bausch & Lomb grating monochromator; dispersion, 7.4 nm mm^{-1}; slit width, 1.5 mm). The photoreduction of methylviologen was monitored by the growth of the absorption at 603 nm, which is ascribed to the cation radical ($MV^{\cdot+}$). The determination of the light intensity was carried out by chemical actinometry.[8]

In Figs. 1a and 1b are shown the UV-spectra of **1** and the wavelength dependence of **1**-catalyzed photoreduction of MV^{2+}. Here we discuss the photocatalytic activity of **1** in terms of a modified quantum yield, $Q_{MV^{\cdot+}}$,[9] which is calculated on the basis of the light quanta absorbed by **1**.

$$Q_{MV^{\cdot+}} = \frac{\text{Amount of } MV^{\cdot+} \text{ formed by the contribution of excited } \mathbf{1}}{\text{Amount of light quanta absorbed by } \mathbf{1}}$$

As shown in Fig. 1a, **1** has diffused absorptions in near ultraviolet region: **1** absorbs the near ultraviolet light much more effectively than ferrocene, the parent compound.

Figure 1b shows that : 1) **1** catalyzes the photoreduction of MV^{2+} in the longer wavelength region where **1** is solely excited; 2) with the light of 400-480 nm, **1** catalyzes more effectively ($Q_{MV^{\cdot+}}$, 0.04-0.05) than with the light of $\lambda > 546$ nm ($Q_{MV^{\cdot+}}$, 0.008).

The **1**-catalyzed photoreduction of MV^{2+} at 480 nm is not inhibited by 1,3-pentadiene (Fig. 2, △). This indicates that the excited singlet state of **1** gives an electron to the ground-state MV^{2+} under the irradiation with near ultraviolet light.

In contrast with the promotion of photoreduction of MV^{2+} by **1** in longer wavelength region, **1** inhibits the photoreduction which is brought about by an excited MV^{2+}: $Q_{MV^{\cdot+}}$ decreases as the wavelength becomes shorter (in the region of $\lambda < 400$ nm where MV^{2+} and **1** absorbs light competitively).

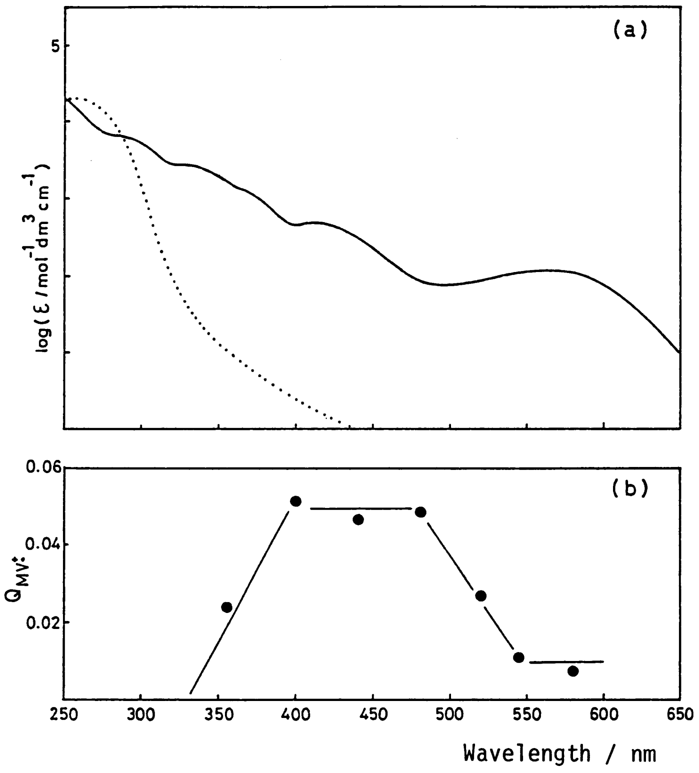


Fig. 1a. UV-Vis Spectra of bis(η^5-indenyl)-iron(II) (——) and methylviologen (········) in methanol solutions.

Fig. 1b. Wavelength dependence of the quantum yield ($Q_{MV^{\cdot+}}$) for the formation of methylviologen cation radical ($MV^{\cdot+}$).

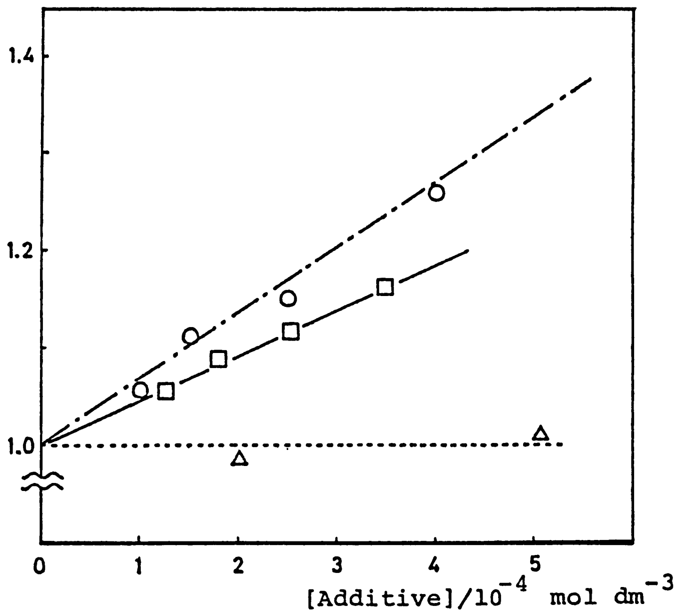
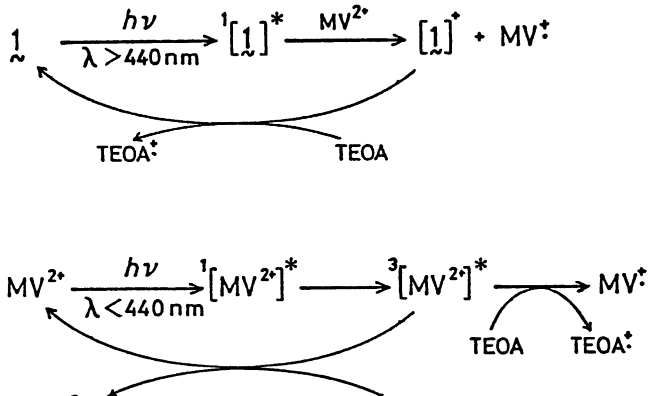


Fig. 2. Stern-Volmer plots.
For the effects of 1,3-pentadiene (○) and 1 (□) on the photoreduction of MV^{2+} in methanol solutions (313 nm).
For the effects of 1,3-pentadiene (△) on the photoreduction of MV^{2+} in methanol solutions in the presence of 1 (480 nm).

a) $\frac{\Phi_o}{\Phi} = \frac{\text{Quantum yield in the absence of additive}}{\text{Quantum yield in the presence of additive}}$



Scheme 1.

The inhibition of photoreduction of MV^{2+} by 1 in this shorter wavelength region can be explained by the quenching of the triplet state of MV^{2+}. A Stern-Volmer plot in terms of a corrected quantum yield, which is calculated on the basis of the light absorbed by MV^{2+} (Fig. 2, □) indicates that 1 quenches the excited MV^{2+}. The photoreduction of MV^{2+} at 313 nm in the absence of 1 is also inhibited by a triplet quencher, 1,3-pentadiene, in a similar manner to the inhibition by 1 (Fig. 2, ○). These facts suggest that triplet excited MV^{2+} itself undergoes photoreduction and that 1 quenches the triplet excited MV^{2+}.

The photoreduction of the 1-MV^{2+}-TEOA system are summarized in Scheme 1.

In the course of the photoreduction, 1 should be effectively regenerated: When air is introduced into the 1-MV^{2+}-TEOA system (1, 3.49×10^{-5} mol dm^{-3}; MV^{2+}, 1.29×10^{-2} mol dm^{-3}; TEOA, 5.90×10^{-2} mol dm^{-3}) after the irradiation with 480 nm light in order to destroy $MV^{+\cdot}$, the UV-spectra of the system are identical with those of the system before the irradiation. These facts indicate that 1 acts as a photocatalyst for the reduction of MV^{2+}.

The irradiation of the 1-MV^{2+}-TEOA system with solar light brings about the formation of $MV^{+\cdot}$ and the amount of $MV^{+\cdot}$ is about 1/3 of that of the $[Ru(bpy)_3]^{2+}$-MV^{2+}-TEOA system under the same reaction conditions.

Based on these results, 1 can be expected to be one of the candidates for a photocatalyst which can produce hydrogen from water.

Further investigation of this system is now under way in our laboratory.

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9) In the case that most of the incident light is absorbed by the system ($\lambda < 440$ nm), the quantum yield for the formation of $\mathrm{MV}^{\dot{+}}$ can be defined as the following equation:

$$Q_{\mathrm{MV}^{\dot{+}}} = \frac{[\mathrm{MV}^{\dot{+}}]_{\mathbf{1}+\mathrm{MV}^{2+}} - [\mathrm{MV}^{\dot{+}}]_{\mathrm{MV}^{2+}} \times L}{1 - L} \times \frac{1}{I_0\, t}$$

, where $[\mathrm{MV}^{\dot{+}}]_{\mathbf{1}+\mathrm{MV}^{2+}}$ and $[\mathrm{MV}^{\dot{+}}]_{\mathrm{MV}^{2+}}$ are the amounts of $\mathrm{MV}^{\dot{+}}$ (mol) in the system consisting of **1** and MV^{2+}, and of MV^{2+} only, respectively; L is the fraction of light absorbed by MV^{2+} and is defined as:

$$L = \frac{C_{\mathrm{MV}^{2+}}\, \varepsilon_{\mathrm{MV}^{2+}}}{C_{\mathbf{1}}\varepsilon_{\mathbf{1}} + C_{\mathrm{MV}^{2+}}\, \varepsilon_{\mathrm{MV}^{2+}}}$$

, where $C_{\mathrm{MV}^{2+}}$ and $C_{\mathbf{1}}$ are the concentrations of MV^{2+} and **1**, respectively; $\varepsilon_{\mathrm{MV}^{2+}}$ and $\varepsilon_{\mathbf{1}}$ are the molar absorption coefficients of MV^{2+} and **1**, respectively; I_0 is the amount of light quanta (mol) absorbed by the system at wavelength λ per second; t is the irradiation time (s).

In the case that most of the incident light is passed through the system ($\lambda > 440$ nm), $Q_{\mathrm{MV}^{2+}}$ is defined as the following equation:

$$Q_{\mathrm{MV}^{\dot{+}}} = \frac{[\mathrm{MV}^{\dot{+}}]_{\mathbf{1}+\mathrm{MV}^{2+}} - [\mathrm{MV}^{\dot{+}}]_{\mathrm{MV}^{2+}}}{I \times t}$$

, where $[\mathrm{MV}^{\dot{+}}]_{\mathbf{1}+\mathrm{MV}^{2+}}$, $[\mathrm{MV}^{\dot{+}}]_{\mathrm{MV}^{2+}}$, and t are the same as the case described above; I is the amount of light quanta (mol) absorbed solely by **1** per second.

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