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Photoinduced Hydrogen Evolution with Hydrogenase Using Bipyridinium Salts as Electron Carriers

Ichiro OKURA,* Hiroki FUJIE, Shigetoshi AONO, Tatsuya KITA,
and Naruhiko KAJI
Department of Chemical Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo 152

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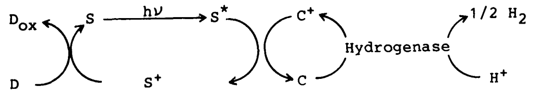
Synopsis. Photoinduced hydrogen evolution was carried out by using bipyridinium salts as electron carriers. Hydrogen evolution rate strongly depends on the type of bipyridinium salt. The order of the rate values undergoes a change by the change in the rate-determining step.

Photochemical redox systems have been proposed for solar-energy utilization.[1,2] The systems illustrated in Scheme 1, consisting of a photosensitizer (S), an electron donor (D), and an electron carrier (C), have been able to evolve hydrogen from water in the presence of hydrogenase.

The electron carrier employed almost exclusively in these studies is methylviologen, except for a few cases.[3,4] In this paper we hope to describe that some bipyridinium salts are more suitable electron carriers than methylviologen when the rate-determining step for this reaction is the photoreduction of bipyridinium salts.

Experimental

The hydrogenase from *Desulfovibrio vulgaris* (Miyazaki type) was purified according to Yagi's method.[5] The bipyridinium salts used in this experiment are listed in Fig. 1. Compounds A, B, and C were synthesized according to the literature.[6,7] The concentration of hydrogenase is not known, but it has the ability to release 19.8×10^{-6} mol of hydrogen in the following system: hydrogenase (0.5 ml)–methylviologen (1.7×10^{-4} mol dm^{-3})–$Na_2S_2O_4$ (3.8×10^{-3} mol dm^{-3}) in 6.0 ml of a 0.02 mol dm^{-3} phosphate buffer (pH 7.0) at 30 °C for 30 min. The sample solution, which consisted of zinc meso-tetraphenylporphyrintrisulfonate (Zn-$TPPS_3$), an electron carrier, 2-mercaptoethanol (RSH) as an electron donor, and hydrogenase in a phosphate buffer (pH 7.0), was deaerated by repeated freeze-pump-thaw cycles. 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 of wavelengths shorter than 390 nm was cut off by a Toshiba L-39 filter.

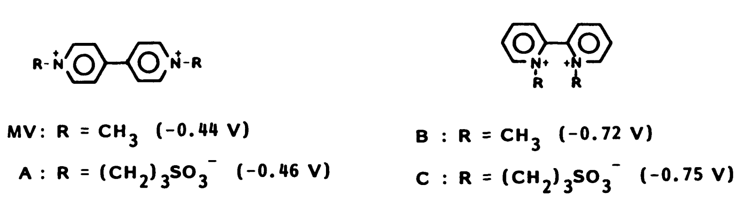


Scheme 1.

Results and Discussion

When an aqueous solution containing RSH, Zn-$TPPS_3$, bipyridinium salt, and hydrogenase was irradiated, hydrogen evolution at a stationary rate was observed, as is shown in Fig. 2. In these experiments an excess amount of hydrogenase was used to make the photoreduction of electron carriers the rate-determining step of the hydrogen evolution. It is evident that all the compounds shown in Fig. 1 can serve as electron carriers for photoinduced hydrogen evolution. The hydrogen-evolution rate of the system for the B electron carrier was much greater than that for methyl viologen. Under the reaction conditions where the rate-determing step of hydrogen evolution is the step of the photoreduction of electron carriers, the bipyridinium salts with low redox potentials will be favorably photoreduced. The order of the rate values, however, does not always coincide with the order of the redox potentials of the bipyridinium salts. The above results are not explained by the electrostatic effect. MV and B are positively charged, and A and C are neutral in the oxidized form. Positively charged bipyridinium salts do not always have high activity, as is shown in the case of MV. As we reported previously,[8] the back reaction (recombination of the oxidized Zn-$TPPS_3$ and reduced bipyridinium salt) may play a part in the photoinduced hydrogen evolution reaction in these systems.

By the increase in the Zn-$TPPS_3$ concentration, the rate-determining step of photoinduced hydrogen evolution is changed from the photoreduction of



MV: R = CH_3 (−0.44 V)
A : R = $(CH_2)_3SO_3^-$ (−0.46 V)
B : R = CH_3 (−0.72 V)
C : R = $(CH_2)_3SO_3^-$ (−0.75 V)

Fig. 1. Electron carriers. (Values in parenthese indicate the redox potentials vs. NHE).

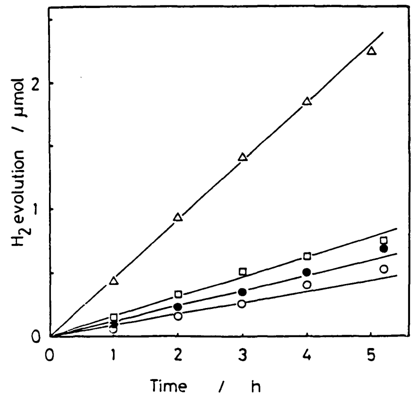


Fig. 2. Time dependence of hydrogen evolution by irradiation at 30 °C. To the solution containing RSH (2.26×10^{-1} mol dm^{-3}), Zn-TPPS$_3$ (1.00×10^{-8} mol dm^{-3}), and bipyridinum salt (8.3×10^{-5} mol dm^{-3}) 0.5 ml of hydrogenase was added and adjusted to 6.5 ml with 0.02 mol dm^{-3} phosphate buffer (pH 7.0). Bipyridinium salts are labelled in Fig. 1; ●: MV, ○: A, △: B, □: C.

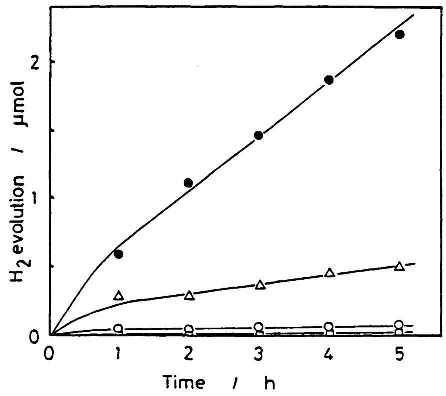


Fig. 3. Time dependence of hydrogen evolution by irradiation at 30 °C. To the solution containing RSH (2.27×10^{-1} mol dm^{-3}), Zn-TPPS$_3$ (1.00×10^{-6} mol dm^{-3}), and bipyridinium salt (8.3×10^{-5} mol dm^{-3}) 0.5 ml of hydrogenase was adjusted to 6.5 ml with 0.02 mol dm^{-3} phosphate buffer (pH 7.0). Bipyridinium salts are labelled in Fig. 1; ●: MV, ○: A, △: B, □: C.

bipyridinium salts to hydrogen evolution by reduced bipyridinium salts. Figure 3 shows the photoinduced hydrogen evolution in the region of higher concentrations of Zn-TPPS3 compared with Fig. 2. In the experimental conditions of Fig. 3, it was confirmed that the rate-determining step of hydrogen evolution was the step of water reduction by reduced bipyridinium salt, for the hydrogen-evolution rate was proportional to the amount of hydrogenase used. Methylviologen shows a remarkably high activity for photoinduced hydrogen evolution. The high activity of methylviologen may be caused by the fact that methylviologen is a better substrate of the hydrogenase than are other bipyridinium salts.

From the above results, it is apparent that the photoinduced hydrogen evolution rate with the systems shown in Scheme 1 depends greatly on the type of bipyridinium salt and that the order of the rate values undergoes a change with a change in the rate-determining step.

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