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Photo-induced Hydrogen Evolution using Bipyridinium Salts as Electron Carriers

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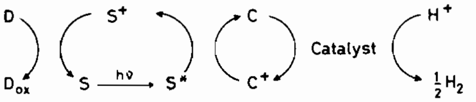
Photochemical redox systems have been proposed for solar energy utilization [1]. The system as shown in the following scheme, including a photosensitizer (S), an electron donor (D), and an electron carrier (C), has been able to evolve hydrogen from water when a suitable catalyst can be applied.



In the course of our studies [2], zinc meso-tetraphenylporphyrintrisulfonate (Zn–TPPS$_3$) exhibits particularly high activity as a photosensitizer for the reaction of the system. The electron carrier employed almost exclusively in these studies is methylviologen [3]. It is desirable to explore other suitable electron carriers. In this letter we describe some bipyridinium salts which are more suitable electron carriers than methylviologen.

Experimental

The bipyridinium compounds used as electron carriers are shown in Fig. 1. The compounds B, C, D and E were synthesized according to the literature [4]. The sample solution which consisted of Zn-TPPS$_3$, electron carrier, mercaptoethanol (RSH) as an electron donor and hydrogenase as a catalyst in phosphate buffer (pH 7.0) was deaerated by repeated freeze–pump–thaw cycles. A typical experiment was performed as follows under anaerobic reaction conditions. To 2.03×10^{-7} mol dm^{-3} of photosensitizer, 0.197 mol dm^{-3} of RSH and 1.27×10^{-4} mol dm^{-3} of electron carrier in water, excess hydrogenase was added. In these experiments excess amount of hydrogenase was used to make the photoreduction of electron carriers as the rate-determining step of the hydrogen evolution. The volume of the mixture was adjusted to 6.5 ml with 0.02 mol dm^{-3} phosphate 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. Light of wavelength less than 390 nm was cut off by a Toshiba L-39 filter.

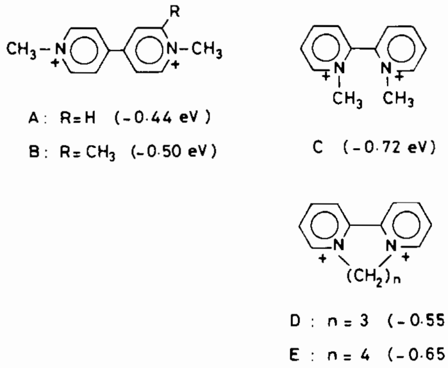


Fig. 1. Electron carriers (figures in parentheses indicate the redox potentials *vs.* NHE).

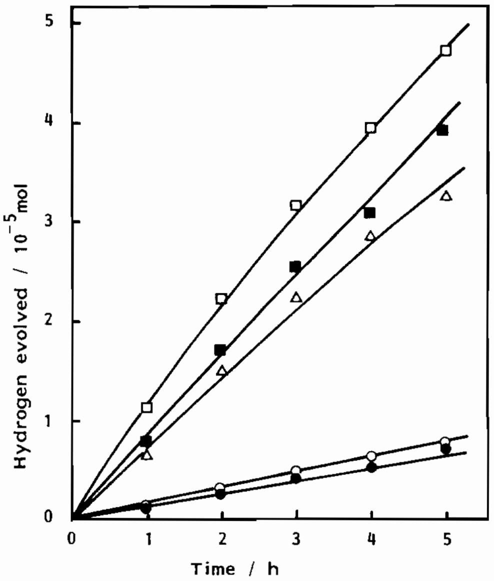


Fig. 2. Time dependence of photo-induced hydrogen evolution. ○: compound A; ●: B; △: C; □; D; ■: E; see text for reaction conditions.

Results and Discussion

When an aqueous solution containing Zn-TPPS$_3$, an electron carrier, RSH and hydrogenase was irradiated, hydrogen evolution with stationary rate was observed as shown in Fig. 2. It is evident that all the compounds shown in Fig. 1 can serve as electron carriers for photoinduced hydrogen evolution. Hydrogen evolution rates of the systems with compounds C, D and E were much greater than the one with methylviologen. Under the reaction conditions where the rate-determining step of hydrogen evolution is the step of the photoreduction of electron carriers,

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the electron carriers with low redox potentials will be favorably photoreduced. The rate order, however, does not always coincide with the order of the redox potentials of the compounds. The rate difference may depend on the efficiency of ion separation of electron transfer for the photoexcited Zn-TPPS3 to the compounds, or may depend on the difference of the association constants between Zn-TPPS$_3$ and bipyridinium salts. The complexes between Zn-TPPS$_3$ and viologens do not take part in the photoreduction of these compounds and only the uncomplexed Zn-TPPS$_3$ plays an important role in the reaction [5]. The study of electron transfer from Zn-TPPS$_3$ to viologen by laser flash photolysis is now in progress.

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