Photoinduced Hydrogen Evolution from Water Using Bipyridinium Salts as Electron Carriers

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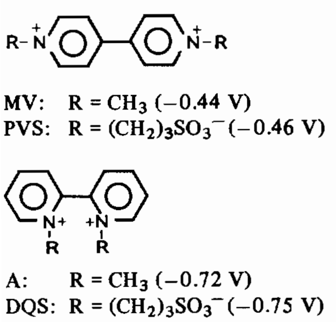
Photoinduced redox systems have been proposed to increase the utilization of solar energy. In the course of our studies, it was found that zinc meso-tetraphenylporphyrintrisulfonate (Zn–TPPS$_3$) exhibited particularly high activity as a photo-sensitizer for photoinduced hydrogen evolution [1, 2]. The electron carrier employed almost exclusively in these studies is methylviologen [3, 4]. It is desirable to explore other suitable electron carriers. In this letter we hope to describe that some bipyridinium salts are more suitable electron carriers than is methylviologen.

Experimental

The compounds used as electron carriers are listed in Fig. 1. The compounds A, PVS and DQS were synthesized according to the literature [5]. A typical experiment was performed as follows under anaerobic reaction conditions at 30 ℃. To 1.02×10^{-8} mol dm^{-3} of Zn–TPPS$_3$, 1.27×10^{-4} mol dm^{-3} of methylviologen and 0.19 mol dm^{-3} of mercaptoethanol, 0.5 ml of hydrogenase was added. The mixture was adjusted to 6.5 ml with 0.02 mol dm^{-3} of phosphate buffer (pH 7.0). In the photolysis the sample was irradiated with light from a 200 W tungsten lamp at 30 ℃. Light of wavelength less than 390 nm was cut off using a Toshiba L-39 filter.



MV: R = CH_3 (–0.44 V)
PVS: R = $(CH_2)_3SO_3^-$ (–0.46 V)

A: R = CH_3 (–0.72 V)
DQS: R = $(CH_2)_3SO_3^-$ (–0.75 V)

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

Results and Discussion

When an aqueous solution containing Zn–TPPS$_3$, an electron carrier, mercaptoethanol and hydrogenase was irradiated, hydrogen evolution was observed (Fig. 2). In every case, the hydrogen evolved almost linearly with irradiation time. It is apparent that compound A is the most suitable electron carrier among the bipyridinium salts used and is about four times more active than is methylviologen. In these experiments an excess amount of hydrogenase was used, not to make the rate-determining step of the reaction to be the step of hydrogen evolution, but the step of the photoreduction of electron carriers, *i.e.*, the rates of photoreduction of electron carriers are equal to the rates of hydrogen evolution. In these reaction conditions the electron carriers with high redox potential are expected to be suitable electron carriers. However, the order of hydrogen evolution rate (DQS > PVS, A > MV) does not coincide with the order of the redox potentials (MV > A, PVS > DQS). It has been clarified that Zn–TPPS$_3$ forms the complexes with bipyridinium salts, which do not take part in the photoreduction of the bipyridinium salts, but that only Zn–TPPS$_3$ serves as a photosensitizer in the reaction [6–8]. The measured association constants between Zn–TPPS$_3$ and electron carriers are listed in Table I. The above results are explained as follows. The low hydrogen evolution rate (V_{H_2}) with methylviologen is caused by the large association constant. Though DQS has a small asso-

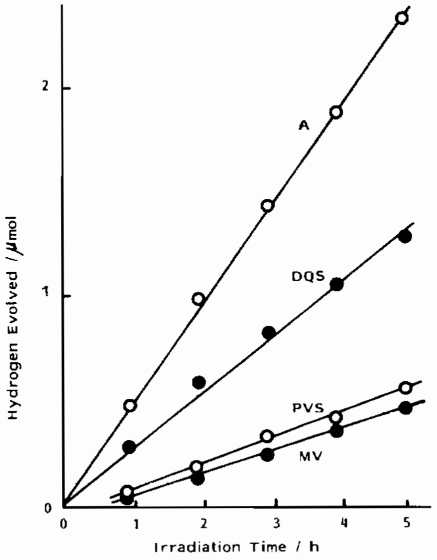


Fig. 2. Time dependence of hydrogen evolution. Zn–TPPS$_3$/mercaptoethanol/bipyridinium salt/hydrogenase system. See the reaction conditions in the text.

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TABLE I. Association Constant of the Complex Formation and Hydrogen Evolution Rate.

	MV	PVS	A	DQS
Association constant (mol^{-1} dm^{-3})	17000	730	1000	540
Hydrogen evolution rate (mol h^{-1})	0.107	0.127	0.457	0.257

ciation constant, the rate is not so high because of the low redox potential. The high evolution rate is observed in the case of compound A on account of the low redox potential and the relatively small association constant. From the above results it is concluded that the electron carrier used in this system needs not only the high enough redox potential but also the low association constant of the complex formation.

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