Photoreduction of Viologens and Hydrogen Evolution with Hydrogenase

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Ethyl-, propyl-, and n-butyl-viologens are found to be electron carriers for photoinduced hydrogen production and also can be cofactors of hydrogenase. As these viologens are photoexcited by visible light irradiation or sunlight, simpler systems without another photosensitizer can be developed for the photochemical utilization of solar energy.

Introduction

Photochemical redox systems have been developed for the purpose of utilization of solar energy. Recent works have shown that three component systems containing a photosensitizer, an electron donor and an electron carrier can be used to evolve hydrogen from water when a suitable catalyst is present [1]. Hydrogenase is available as a catalyst for this process. The electron carrier employed almost exclusively in these studies is methyl viologen (1,1′-dimethyl-4,4′-bipyridinium chloride): the reduced form of methyl viologen has not only a sufficient redox potential to reduce water into hydrogen, but it also serves as a cofactor of hydrogenase. It is desirable to explore other suitable electron carriers. The aim of the present investigation was to determine whether materials such as ethyl-, propyl-, and n-butyl-viologens can serve as electron carriers for hydrogen production and also can be cofactors of hydrogenase.

Though methyl viologen is not photoexcited by visible light irradiation or sunlight, ethyl-, propyl, n-butyl-viologens are photoexcited by sunlight radiation. We report here a system where these viologens are photoreduced by visible light in the presence of an irreversible electron donor. In this system viologens serve not only as an electron carrier but also as a photosensitizer. We attempted to reduce water to hydrogen by the use of the modified electron transfer system which combines an electron donor and viologen photo-irradiation system and a catalyst for hydrogen production.

Experimental

Materials

All chemicals were obtained from Tokyo Kasei Kogyo Co. and were of the highest available purity. Ethyl-, propyl-, and n-butyl-viologens were synthesized according to the literature [2]. Hydrogenase from *Desulfovibrio vulgaris* (Miyazaki type) was purified according to Yagi's method [3].. The concentration of hydrogenase is not known, but it has the ability to produce 1.9 μmol of hydrogen by the reaction system: hydrogenase (0.5 ml) – methyl viologen (1.78×10^{-6} mol) – $Na_2S_2O_4$ (2.87×10^{-5} mol) in 6.0 ml of 0.1 *M* Tris-HCl buffer (pH 7.0) at 30 °C for 10 min.

Measurement Procedure

The sample solution consisted of zinc-tetraphenylporphyrintrisulfonic acid (Zn-$TPPS_3$, if included) as a photosensitizer, viologen dye, 2-mercaptoethanol (RSH) as an electron donor, and hydrogenase (if included) in Tris-HCl buffer (pH 7.0). It was deaerated by repeated freeze-pump-thaw cycles, and irradiated continuously with light from a 200 W tungsten lamp. Light of wavelength less than 350 nm was removed by a Toshiba UV-35 filter. A portion of the evolved hydrogen was collected via a sampling valve and analyzed by g.l.c.

Results and Discussion

Hydrogen Evolution from Reduced Viologens with Hydrogenase

The investigation was carried out to determine whether ethyl-, propyl-, and n-butyl-viologens can be cofactors of hydrogenase. A typical hydrogen evolution experiment was performed as follows under anaerobic conditions at 30 °C. To viologen dye (*ca.* 1.8×10^{-7} mol) and $Na_2S_2O_4$ (2.87×10^{-5} mol), 0.5 ml of hydrogenase was added. The mixture was adjusted to 6.0 ml with 0.1 *M* of Tris-HCl buffer

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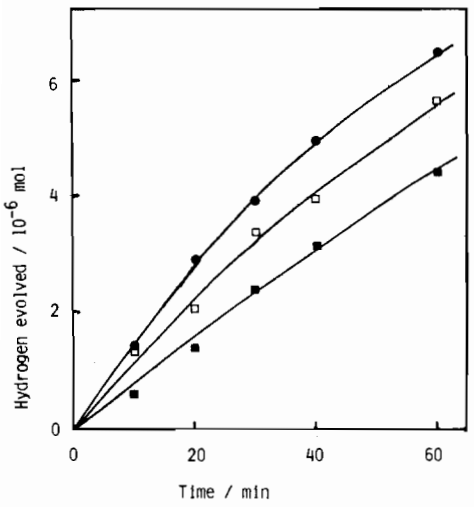

Fig. 1. Time dependence of hydrogen evolution with viologen – $Na_2S_2O_4$ (4.79 × 10^{-3} *M*) – hydrogenase (0.5 ml) system. ■: ethyl viologen (3.41 × 10^{-5} *M*); ●; propyl viologen (3.45 × 10^{-5} *M*); □: n-butyl viologen (3.31 × 10^{-5} *M*).

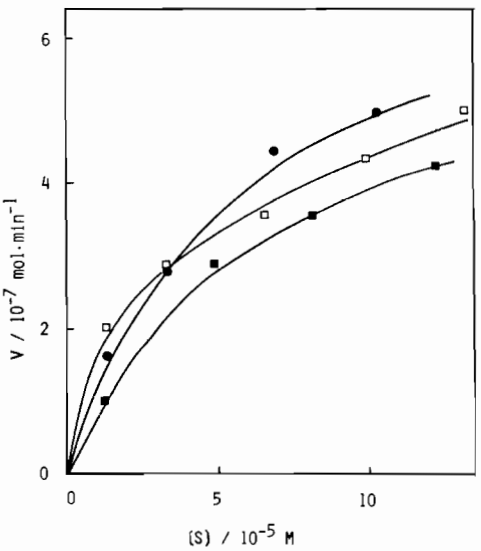

Fig. 2. Dependence of hydrogen evolution rate on viologen concentration. ■: ethyl viologen; ●: propyl viologen; □: n-butyl viologen; reaction conditions are the same as in Fig. 1.

(pH 7.0; this value is suitable for hydrogenase). Time dependence of hydrogen evolution is shown in Fig. 1, from which it is evident that all the viologens used in this experiment can be cofactors of hydrogenase. The amount of hydrogen evolved increases gradually and reaches a constant value.

As shown in Fig. 2 the initial rate increases with any viologen dye concentration. As viologen

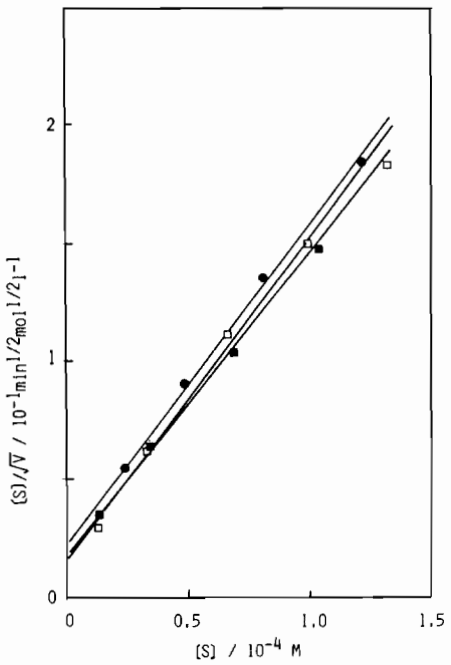

Fig. 3. Relation between $[S]/\sqrt{V}$ and [S]. ●: ethyl viologen; ■: propyl viologen; □: n-butyl viologen.

dye is a one electron transfer agent, two molecules of viologen are needed for the production of one molecule of hydrogen. Consequently, the following hydrogen evolution mechanism is considered.

$$E + S \underset{}{\overset{K}{\rightleftharpoons}} ES$$

$$ES + S \overset{K}{\rightleftharpoons} ES_2$$

$$ES_2 + 2H^+ \xrightarrow{k} E + 2S_{ox} + H_2$$

where E is an enzyme, and S and S_{ox} are the reduced and oxidized form of the substrate, respectively. K is the equilibrium constant and k the rate constant.

At the first step, the substrate combines with the enzyme and an ES complex is formed, another substrate combines with ES to form ES_2. It is assumed that the equilibrium constants in these two steps are the same. The ES_2 complex can give two electrons to protons to form hydrogen, and the complex itself returns to its original form.

On the basis of the above mechanism the rate, V, is expressed as follows:

$$V = \frac{kK^2[S]^2}{(1 + K[S])^2}$$

or

TABLE I. Kinetic Parameters Calculated from the Slopes and the Intercepts in Fig. 3.

	methyl viologen	ethyl viologen	propyl viologen	n-butyl viologen
$K/10^4\ M^{-1}$	1.6 ± 0.3	6.9 ± 2.2	7.7 ± 2.4	5.0 ± 1.6
$k/10^{-7}\ min^{-1}\ mol$	6.3 ± 1.0	5.6 ± 0.8	6.3 ± 0.9	5.9 ± 0.4

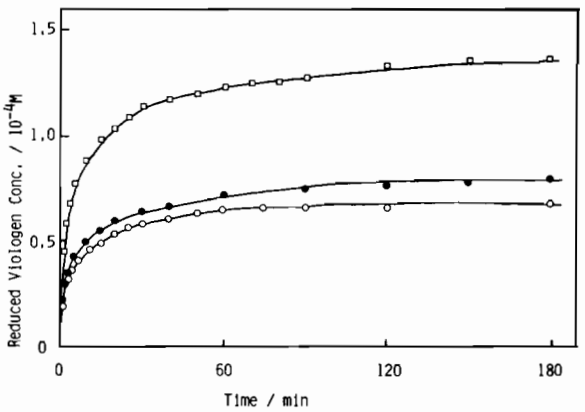

Fig. 4. Time dependence of reduced viologen concentration by the irradiation of viologen–Zn–$TPPS_3$ (1.08×10^{-6} *M*)–RSH (2.0×10^{-1} *M*) system. □: ethyl viologen (1.50×10^{-4} *M*); ●: propyl viologen (1.27×10^{-4} *M*); □: n-butyl viologen (1.22×10^{-4} *M*).

$$\frac{[S]}{\sqrt{V}} = \frac{[S]}{\sqrt{k}} + \frac{1}{\sqrt{kK}}$$

An $[S]/\sqrt{V}$ *vs.* [S] plot is shown in Fig. 3. Good linear relations were obtained, which supports the above mentioned mechanism. Although the [S]/V *vs.* [S] plot on the basis of the first order kinetic equation,

$$V = \frac{kK[S]}{1 + K[S]}$$

was also tried, there were some deviations. From the slopes and the intercepts, k (turnover number) and K for hydrogen evolution are calculated as shown in Table I. Though k values do not depend on the types of viologens, K values of ethyl-, propyl-, and n-butyl-viologens are larger than that of methyl viologen. Consequently, ethyl-, propyl-, and n-butyl-viologens are apt to form enzyme-substrate complexes (ES).

Photoreduction of Viologens and Hydrogen Evolution with Hydrogenase

When an aqueous solution containing Zn-$TPPS_3$, viologen dye and 2-mercaptoethanol (RSH), was irradiated, the growth of the cation radical of viologen was observed. As shown in Fig. 4, the concentration of viologen radical increased rapidly at the beginning of the reaction and reached a constant value. The conversions at constant values are 90%, 60% and 56% for ethyl-, propyl-, and n-butyl-viologens respectively. The difference of the constant values with the type of viologens may depend on the difference of photoinduced-viologen reduction rates and the backward reaction rates.

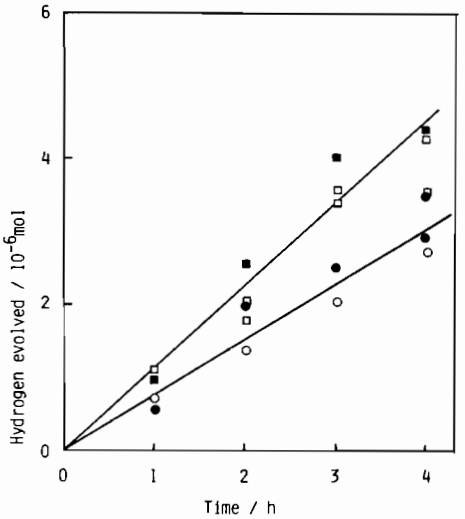

Fig. 5. Hydrogen evolution by the irradiation of viologen–Zn–$TPPS_3$ (1.08×10^{-6} *M*)–RSH (2.0×10^{-1} *M*)–hydrogenase (0.5 ml) system. ■: methyl viologen (4.37×10^{-4} *M*); □: ethyl viologen (4.49×10^{-4} *M*); ●: propyl viologen (4.45×10^{-4} *M*); □: n-butyl viologen (4.89×10^{-4} *M*).

As these viologens are photoinduced and can be cofactors of hydrogenase, they will serve as electron carriers of hydrogen evolution. When hydrogenase was added to the solution containing Zn-$TPPS_3$, viologen dye and RSH, hydrogen evolution was observed (shown in Fig. 5). It is evident that all the viologens used in this experiment can serve as electron carriers for photoinduced hydrogen evolution. Hydrogen evolution rates with the systems with methyl- and ethyl-viologens were greater than those of propyl- and n-butyl-viologens. The rate order is almost the same as the photoreduction rates of viologens. Thus the rate determining step

TABLE II. Hydrogen Evolution by the Irradiation of Viologen–RSH (3.9×10^{-1} *M*)–Hydrogenase (0.5 ml) System.

Time/h	ethyl viologen (4.49×10^{-3} *M*)	propyl viologen (4.54×10^{-3} *M*)	n-butyl viologen (4.40×10^{-3} *M*)
8	0.14 μmol	0.14 μmol	0.06 μmol
16	0.29	0.22	0.15
24	0.26	0.30	0.16
3d[a]	1.06	0.78	0.66

[a]Irradiation of sunlight instead of tungsten lamp.

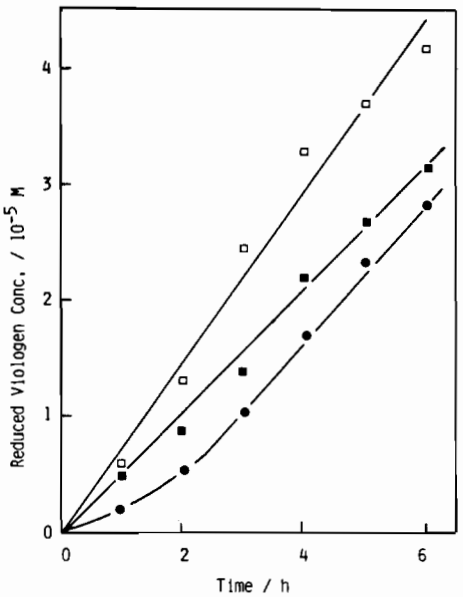

Fig. 6. Time dependence of reduced viologen concentration by the irradiation of viologen–RSH (4.3×10^{-1} *M*) system. □: ethyl viologens (4.87×10^{-3} *M*); ■: propyl viologen (4.93×10^{-3} *M*); ●: n-butyl viologen (4.77×10^{-3} *M*).

of photoinduced hydrogen evolution is the step of the photoreduction of viologens (under our experimental conditions).

Photoreduction of Viologen Dyes without Zn-TPPS$_3$ and Hydrogen Evolution with Hydrogenase

When an aqueous solution containing viologen dyes and RSH was irradiated, the growth of the corresponding cation radicals of ethyl-, propyl-, and n-butyl-viologens, (respective absorption bands at 603, 601, 600 nm) were observed. As shown in Fig. 6, the concentration of the reduced form of viologen dyes increased almost linearly with irradiation time. These viologens are photoexcited by the irradiation of visible light and photoreduced in the presence of RSH.

Hydrogen is evolved as a result of water reduction on the addition of hydrogenase to the photo-irradiation system which contains viologen dye and RSH, as shown in Table II. Hydrogen evolution was also observed by the irradiation by sunlight instead of the tungsten lamp. Thus these viologens serve not only as photosensitizers but also as electron carriers, and two component redox systems are developed for photochemical utilization of solar energy.

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References

1 J. M. Lehn and J. P. Sauvage, *Nouv. J. Chim., 1,* 449 (1977);
M. Kirch, J. M. Lehn and J. P. Sauvage, *Helv. Chim. Acta, 62,* 1345 (1979);
K. Kalyanasundaram, J. Kiwi and M. Grätzel, *ibid., 61,* 2720 (1978);
K. Kalyanasundaram and M. Grätzel, *J Chem. Soc. Chem. Comm.,* 1137 (1979);
A. Moradpour, E. Amouyal, P. Keller and H. Kagan, *Nouv. J. Chim., 2,* 547 (1978);
A. I. Krasna, *Photochem. Photobiol., 29,* 267 (1979);
I. Okura and N. Kim-Thuan, *J. Mol. Catal., 5,* 311 (1979);
I. Okura, S. Nakamura, N. Kim-Thuan and K. Nakamura, *ibid., 6,* 261 (1979);
I. Okura and N. Kim-Thuan, *J. Chem. Soc. Chem. Comm.,* 84 (1980);
I. Okura and N. Kim-Thuan, *J. Chem. Soc. Faraday Trans. I, 76,* 2209 (1980).
2 A. G. Evans, J. P. Evans and M. W. Baker, *J. Chem. Soc. Perkin Trans. II,* 1787 (1977).
3 T. Yagi, *J. Biochem., 68,* 694 (1970).