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Photoreduction of Viologens by Visible Light in the Presence of Electron Donor and Hydrogen Evolution with Hydrogenase

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Photochemical redox systems have been developed for the purpose of solar energy utilization. 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]. Methyl viologen (1,1′-dimethyl-4,4′-bipyridinium chloride) has been used almost exclusively as an electron carrier, for it has sufficient redox potential to reduce water into hydrogen. Though methyl viologen is not photoexcited by visible light, irradiation or sunlight, some viologens such as ethyl-, propyl-, and 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 serve as a photosensitizer. We also 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.

All the chemicals (obtained from Tokyo Kasei Kogyo Co.) were of the highest available purity. Ethyl-, propyl-, and butyl-viologens were synthesized according to the literature [2]. Hydrogenase to the literature [2]. Hydrogenase from *Desulfovibrio vulgaris* (Miyazaki type) was purified according to Yagi's method [3]. The concentration of hydrogenase was not known, but it has the ability to produce 0.90 μmol of hydrogen by the reaction system: hydrogenase (0.5 dm^3)-methyl viologen (1.76 X 10^{-6} mol) – $Na_2S_2O_4$ (2.87 X 10^{-5} mol) in 6.0 ml of 0.1 *M* Tris-HCl buffer (pH 7.0) at 30 °C for 10 min.

The sample solution (which consisted of viologen dye and 2-mercaptoethanol (RSH) as an electron donor in Tris-HCl buffer (pH 7.0)), was deaerated by repeated freeze-pump-thaw cycles. A sample solution containing viologen dye (*ca.* 5 X 10^{-3} mol•dm^{-3}) and RSH (0.43 mol•dm^{-3}) was irradiated continuously with light from a 200 W tungsten lamp. Light of wavelengths less than 290 nm was removed by a Pyrex filter.

TABLE I. Hydrogen Evolution on Irradiation of Viologen-RSH-Hydrogenase System. The Solution (6.5 dm^3) Contains Viologen Dye, RSH (0.39 mol•dm^{-3}) and Hydrogenase (0.5 dm^3). Ethyl viologen, 4.49 X 10^{-3} mol•dm^{-3}; Propyl viologen, 4.54 X 10^{-3} mol•dm^{-3}; Butyl viologen, 4.40 X 10^{-3} mol•dm^{-3}.

Time (h)	Ethyl Viologen	Propyl Viologen H_2 evolved (μmol)	n-Butyl Viologen
8	0.14	0.14	0.06
16	0.29	0.22	0.15
24	0.26	0.30	0.16
3 days[a]	1.06	0.78	0.66

[a]Irradiated by sunlight.

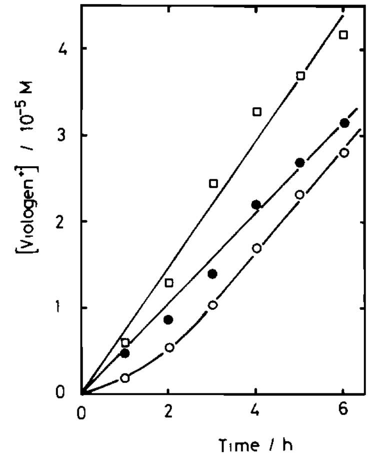

Fig. 1. Time dependence of reduced viologen concentration by irradiation. The solution (6.0 dm^3) contains viologen dye and RSH (0.43 mol•dm^{-3}); ethyl viologen, 4.87 X 10^{-3} mol•dm^{-3} (□); propyl viologen, 4.93 X 10^{-3} mol•dm^{-3} (●); butyl viologen, 4.77 X 10^{-3} mol•dm^{-3} (○).

When an aqueous solution containing viologen dyes and RSH was irradiated, the growth of the corresponding cation radicals of ethyl-, propyl-, and butyl-viologens, which have respective absorption bands at 603, 601, and 600 nm, were observed. As shown in Fig. 1, 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.

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As the reduced form of these viologens have high enough redox potentials for the decomposition of water, they may be useful as electron carriers to evolve hydrogen from water. In practice, hydrogen evolution by the reduction of water has been confirmed by the addition of hydrogenase as a catalyst to the reduced viologens formed by the reduction with $Na_2S_2O_4$.

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 the Table. Hydrogen evolution was also observed by the irradiation of 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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