Hydrogen Generation by Visible Light with Ruthenium(II)carbonyltetraphenylporphyrin in Aqueous Micellar Solution Catalysed by Hydrogenase

By ICHIRO OKURA* and NGUYEN KIM-THUAN
(*Department of Chemical Engineering, Tokyo Institute of Technology, Meguro-ku, Tokyo,* 152, *Japan*)

Summary Hydrogen generation from the decomposition of water resulted from visible light irradiation in the presence of hydrogenase–ruthenium(II)carbonyltetraphenylporphyrin–methyl viologen–reducing agent systems.

HYDROGENASE is an enzyme which catalyses the decomposition of water in the presence of an electron-donating agent which should be a substrate of the enzyme and which should also have a high enough redox potential for the decomposition of water. The reduced form of methyl viologen (1,1′-dimethyl-4,4′-bipyridylium chloride) is a suitable electron-donating agent for this purpose and the reduction of methyl viologen with the aid of light energy has been reported[1–5] in the presence of some reducing agents and photosensitizers. Photoexcited states of divalent ruthenium complexes and porphyrin compounds serve as good reducing agents[1–3] and the photosensitizers are labile to oxidation in the presence of methyl viologen, so a ruthenium(II) porphyrin complex would be expected to play an efficient role in light energy conversion. We report here the reduction of methyl viologen by irradiation of rutheniumcarbonyltetraphenylporphyrin [Ru(TPP)CO] and hydrogen generation catalysed by hydrogenase.

Desulfovibrio vulgaris cells were cultured according to the literature.[6] The hydrogenase from *D. vulgaris* was purified by Yagi's method.[7] Ru(TPP)CO was synthesized[8] by refluxing TPP and $Ru_3(CO)_{12}$ in acetic acid under a nitrogen atmosphere.† The surfactant Triton X-100 was used to dissolve Ru(TPP)CO in water in the ratio 3:7 (v/v) Triton

† Methyl viologen and $Ru_3(CO)_{12}$ were purchased from Tokyo Kasei Kogyo Co. and Stream Chemicals, Inc., respectively. The other chemicals were of the highest available purity and obtained from Wako Pure Chemical Co.

X-100 water The following procedure, under anaerobic conditions, is typical To 2 35 × 10^{-7} mol of Ru(TPP)CO, 7 7 × 10^{-6} mol of methyl viologen, and mercaptoethanol (1 28 × 10^{-3} mol) or triethanolamine (8 0 × 10^{-4} mol), 1 ml of hydrogenase was added The concentration of the hydrogenase was not known, but 5 78 × 10^{-6} mol of hydrogen was generated by the following reaction system hydrogenase (0 5 ml)–methyl viologen (7 78 × 10^{-6} mol)–$Na_2S_2O_4$ (2 87 × 10^{-5} mol) in 3 ml of 0·02 M phosphate buffer (pH 7 0) at 30 °C for 10 min The mixture was adjusted to 5 ml with 0 02 M phosphate buffer (pH 7 0, a value suitable for hydrogenase) This solution was then irradiated (150 W slide projector tungsten lamp) in a Pyrex reaction vessel at 30 °C Light with wavelength shorter than 500 nm was excluded by the use of a Toshiba V-Y 50 filter A sample of the evolved hydrogen was collected with a sampling valve and was analysed by gas chromatography

The methyl viologen radical cation ($MV\cdot^+$), which has a characteristic absorption band at 605 nm, appeared when the micellar solution of Ru(TPP)CO was irradiated in the presence of a reducing agent The concentration of $MV\cdot^+$ increased gradually with time and reached a constant value as shown in the Figure

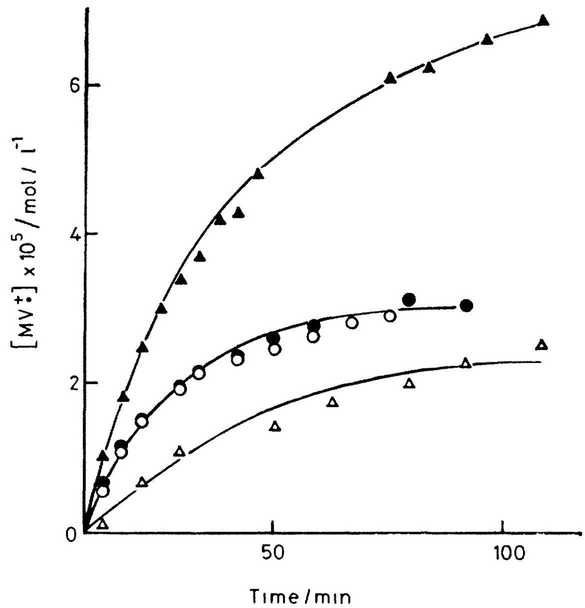


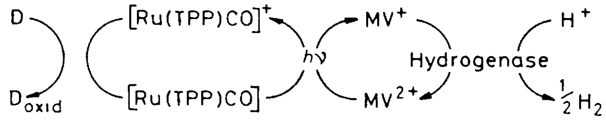
FIGURE Time dependence of methyl viologen cation radical formation Ru(TPP)CO (2 35 × 10^{-7} mol), additives (4 70 × 10^{-7} mol) MV (7 78 × 10^{-6} mol) and mercaptoethanol (1 28 × 10^{-3} mol) at 30 °C in Triton X-100 solution Ru(TPP)-CO + MV + mercaptoethanol (▲) Ru(TPP)CO + MV + mercaptoethanol + Pyrrole (○) Ru(TPP)CO + MV + mercaptoethanol + Imidazole (●) Ru(TPP)CO + MV + mercaptoethanol pyridine (△)

TABLE Hydrogen generation using hydrogenase–Ru(TPP)CO–methyl viologen (MV)–reducing agent systems by irradiation by visible light

System	Time/h	H_2/μmol	Turnover number
Ru(TPP)CO + hydrogenase	2	0 15	
+ MV + triethanolamine	3	0 38	
	5 67	0 69	
	7	1 07	4 6
Ru(TPP)CO + hydrogenase	2	0 68	
+ MV + mercaptoethanol	3	1 06	
	4	1 29	
	5	1 78	
	7	2 89	
	8	2 89	12 3

Two cases of hydrogen generation by the use of two electron-transfer systems which combine a photosensitizer and a methyl viologen photoirradiation system and hydrogenase as a catalyst were investigated (Table) Both systems are active generators of hydrogen From the turnover numbers in these systems, it is apparent that the reaction proceeds catalytically with respect to Ru-(TPP)CO concentration and the hydrogen generation rate strongly depends on the concentration of the reducing agent

By analogy with the photochemical properties[9] of a similar compound, Ru(TPP)(pyridine)$_2$, the quenching by methyl viologen should also proceed *via* an Ru(TPP)CO^+ intermediate (Scheme)



SCHEME D = electron donor

The effect of various additives on the photoreduction of methyl viologen was also studied, as shown in the Figure In the cases of imidazole and pyrrole the same quenching tendency was observed and a similar effect has been observed[10] during the reduction of Methylene Blue with Mn–hematoporphyrin The decrease in activity may be caused by the competitive co-ordination of the additives and methyl viologen at the central metal ion of the porphyrin, the quenching of the Ru(TPP)CO excited state by additives, or the change in ground state by co-ordination of the additives Imidazole and other bases, however, are known to form complexes easily with Ru(TPP)CO at the sixth co-ordination site which is vacant in this compound So, this effect may be due to the similarity in electron characters around nitrogen in heterocycles which co-ordinate the ruthenium ions competitively

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[1] I Okura and N Kim Thuan, *J Mol Catalysis*, 1979, **5**, 311
[2] I Okura and N Kim Thuan, *J Mol Catalysis*, 1979, **6**, 227
[3] I Okura and N Kim Thuan, *J Mol Catalysis*, in the press
[4] A A Krasnovskii, G P Brin, and V V Nikandrov, *Doklady Akad Nauk S S S R* , 1975, **220**, 1214
[5] K Takuma, M Kajiwara, and T Matsuo, *Chem Letters*, 1977, 1199
[6] T Yagi, M Honya, and N Tamiya, *Biochim Biophys Acta*, 1964, **92**, 52
[7] T Yagi *J Biochem* , 1970, **68**, 694
[8] B C Chow and I A Cohen, *Bioinorg Chem* , 1971 **1**, 57
[9] R C Young J K Nagle, T J Meyer, and D G Whitten *J Amer Chem Soc* , 1978, **100**, 4773
[10] I Okura, N Kim Thuan, and T Keii, *J Mol Catalysis*, 1979, **5**, 131