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COMPARISON OF RUTHENIUM COMPLEXES FOR PHOTOINDUCED METHYL VIOLOGEN REDUCTION AND HYDROGEN EVOLUTION FROM WATER BY HYDROGENASE

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Highly active photoinduced systems for methyl viologen reduction are developed by using ruthenium complexes with long lifetime at the photoexcited state. The system, which has the higher activity for methyl viologen reduction, has the higher activity for hydrogen evolution when hydrogenase [EC 1.12.2.1] was added.

Photochemical reduction of water to hydrogen with light absorbing species has been studied extensively as a means of solar energy storage, and the research being carried out focuses on the development of a highly active system for hydrogen production. As reported previously,[1-6] the photoexcited state of tris (2,2'-bipyridine) ruthenium (II) ($Ru(bpy)_3^{2+}$) serves as a good reducing agent, and is liable to be oxidized in the presence of a suitable oxidizing agent such as methyl viologen (MV^{2+}). The reduced form of MV^{2+}, which has a sufficient redox potential for the decomposition of water, is known to be an artificial cofactor for hydrogenase [EC 1.12.2.1]. It is required for a development of a highly active system to use a photosensitizer possessing not only a high reducing power but also a long lifetime to increase the quenching probability by MV^{2+} at the photoexcited state. In this study various ruthenium complexes with longer lifetimes than $Ru(bpy)_3^{2+*}$ were used as photosensitizers to develop more efficient system for MV^{2+} reduction, and also an attempt was made to reduce water to hydrogen by the use of electron transfer system containing Ru-complex, MV^{2+}, mercaptoethanol (RSH) and hydrogenase.

All reagents were obtained from commercial sources and were of the highest purity available. Ru-complexes were synthesized according to ref. 7. D. vulgaris cells were grown according to the literature[8] and the hydrogenase from D. vulgaris was purified by Yagi's method.[9] The hydrogenase activity was described elsewhere.[10] A typical experiment was performed as follows under anaerobic conditions. To 3.92×10^{-5} M of Ru-complex, 3.52×10^{-4} M of MV^{2+} and 1.94×10^{-1} M of RSH, 2 ml of hydrogenase is added if necessary. The mixture is adjusted to 6 ml with 0.02 M phosphate buffer (pH 7.0: this value is suitable for hydrogenase). The solution was then irradiated at 30°C with the light of wavelength 460 nm by using a Toshiba KL-46 filter. A portion of the evolved hydrogen was collected via a sampling valve and analyzed by g.l.c..

When an aqueous solution containing Ru-complex, MV^{2+} and RSH was irradiated, the growth of MV^{+} which has characteristic absorption bands at 395 and 605 nm was observed. The activities of photosensitizers for the reduction of MV^{2+} were compared as shown in the Table as well as the triplet state lifetimes of Ru-complexes.

Table Photoinduced Reduction of Methyl Viologen and Hydrogen Evolution in the Presence of RuL_3^{2+}

Ligand (L)	bpy	phen	Cl-phen	dime-phen
τ (ns)[a]	600	920	940	1740
$d[MV^+]/dt$ (10^{-6} M min^{-1})[b]	3.95	4.76	6.82	11.1
H_2 evolved (μmol)[c]	0.82	0.58	0.84	1.66

a) reference 12, b) See the text for the reaction conditions, c) In the presence of hydrogense the light of wavelength 460 nm was irradiated for 2 h at 30°C. $[MV^{2+}]$: 1.30×10^{-3} M.

In every photoirradiation system, the concentration of MV^+ increased linearly at the beginning of the reaction and reached a constant value. When irradiation ceased, the concentration of MV^+ decreased gradually and reached zero. The activities in the Table are expressed by the initial rates. The order of the activities is as follows: $Ru(dime\text{-}phen)_3^{2+} > Ru(Cl\text{-}phen)_3^{2+} > Ru(phen)_3^{2+} > Ru(bpy)_3^{2+}$, where dime-phen, Cl-phen and phen are 4,7-dimethyl-1,10-phenanthroline, 5-chloro-1,10-phenanthroline and 1,10-phenanthroline, respectively. It is appaent that the higher activity is obtained with the longer lifetime.

When hydrogenase was added in the system containing Ru-complex, MV^{2+} and RSH with continuous irradiation, hydrogen evolution was observed as shown in the Table. The higher activity for hydrogen evolution was observed on the system with the higher activity for the MV^{2+} reduction except for $Ru(phen)_3^{2+}$ system. The lower activity for hydrogen evolution in this system might be due to the inactivation of hydrogenase, for 1,10-phenanthroline inhibits hydroganse activity strongly.[11] Hydrogen evolution was also observed by the irradiation of sunlight, and these Ru-complexes with longer lifetimes seem to be regarded as being significant photosensitizers for solar energy storage.

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References

1) I. Okura and N. Kim-Thuan, J. Mol. Catal., 5, 311 (1979).
2) I. Okura, S. Nakamura, N. Kim-Thuan and K. Nakamura, J. Mol. Catal., 6, 261 (1979).
3) C. R. Bock, T. J. Meyer and D. G. Whitten, J. Am. Chem. Soc., 96, 4710 (1974).
4) R. C. Young, T. J. Meyer and D. G. Whitten, J. Am. Chem. Soc., 97, 4781 (1975).
5) K. Takuma, M. Kajiwara and T. Matsuo, Chem. Lett., 1979, 1199.
6) H. O. Gafney and A. W. Anderson, J. Am. Chem. Soc., 84, 8238 (1972).
7) S. Anderson and K. R. Seddon, J. Chem. Res. (S), 74 (1979).
8) T. Yagi, M. Honya and N. Tamiya, Biochim. Biophys. Acta, 153, 699 (1968).
9) T. Yagi, J. Biochem., 68, 649 (1970).
10) I. Okura, M. Takeuchi and N. Kim-Thuan, Chem. Lett., 1980, 765.
11) I. Okura, K. Nakamura and S. Nakamura, J. Mol. Catal., 6, 311 (1979).
12) C. T. Lin, W. Bottcher, M. Chon, C. Creutz and N. Sutin, J. Am. Chem. Soc., 98, 6536 (1976).

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