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PHOTOINDUCED CHARGE SEPARATION, ELECTRON STORAGE AND ELECTRON TRANSPORT TO PLATINUM COLLOID BY THE USE OF VIOLOGEN POLYMER[1)]

Tatsuya OHSAKO, Tetsuo SAKAMOTO, and Taku MATSUO*

Department of Organic Synthesis, Faculty of Engineering,
Kyushu University 36, Hakozaki, Fukuoka 812

Viologen polymers were successfully used to collect photoliberated electron from polypyridineruthenium(II) complexes by the use of a zwitterionic viologen as an electron mediator. The collected electrons were successively trapped by platinum colloid supported on the viologen polymers. The viologen polymer thus proved to be an efficient electron transporting system from photoredox reaction center to multi-electron redox catalyst for chemical solar energy conversion.

Polypyridineruthenium(II) complexes, RuL_3^{2+}, have been well investigated as a possible photocatalyst for solar energy conversion system. In many of these studies, viologen have proved useful in delivering the photoliberated electron from RuL_3^{2+} to colloidal metal catalysts for hydrogen generation.[2-6)] Viologen polymers can be used for the same purpose.[7,8)] In addition, ESR spectra of the partially reduced viologen polymers indicate that the photoinjected electrons on the polymer are delocalized over the polymer chain by the electron exchange between the neighboring viologen units.[7)] This type of electron exchange was also observed in viologen units on other molecular assemblies such as micelles and bilayer membranes, and enhanced charge separation of the photoproduced primary ion pairs.[9-11)] Furthermore, viologen polymers were found to stabilize Pt colloid.[7)] On the basis of these characteristics, viologen polymer is expected to afford an efficient electron transport system which links photoreaction center and multi-electron redox site in the dark as observed in photosynthesis.

In the present experiment, an attempt is made to set up a model system by the use of a photoreaction center, which consists of RuL_3^{2+} and a zwitterionic propyl viologen sulfonate($PS^{2-}V^{2+}$),[12-14)] and electron-transporting viologen polymer in combination with colloidal platinum catalysts.

The reported procedures[7)] were used to prepare viologen polymer, zwitterionic viologen, ruthenium complexes as shown below. Platinum colloid was prepared by reducing H_2PtCl_6 with sodium citrate. Non-buffered aqueous solutions of RuL_3^{2+} (2×10^{-5}M), EDTA (1×10^{-3}M), and viologens were degassed, replaced by Ar and irradiated with 500 W super high pressure mercury lamp equipped with cut off filter (Toshiba L-42, $\lambda >$ 405 nm). The reduction of viologen units was followed by the difference spectra in the region between 500 and 650 nm. Flash photolysis was carried out as previously described.[15)]

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1 M = 1 mol dm^{-3}.

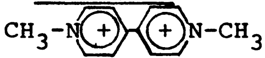
RUTHENIUM COMPLEXES

$Ru(bpy)_3^{2+}$; tris(2,2'-bipyridine)ruthenium(II)

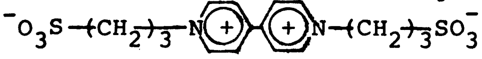
$Ru(phen)_3^{2+}$; tris(1,10-phenanthroline)ruthenim(II)

VIOLOGENS

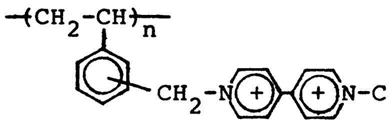
MV^{2+} ;



$PS^{2-}V^{2+}$; zwitterionic viologen



PV^{2+} ; viologen polymer



POLYCATION

PPy^{+} ;

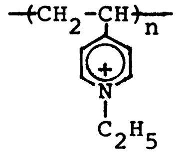


Table 1. Photoinduced reduction of viologens as sensitized by ruthenium complex a)

System No.	Ru complex	viologens	Eq % c)d)	ϕrel % e)
1	bpy b)	$PS^{2-}V^{2+}$	31	57
2	bpy	PV^{2+}	(13) f)	17
3	bpy	$PS^{2-}V^{2+}$ + PV^{2+}	31	151
4	bpy	$PS^{2-}V^{2+}$ + PPy^{+}	31	42
5	phen b)	$PS^{2-}V^{2+}$	46	77
6	phen	PV^{2+}	(16) f)	32
7	phen	$PS^{2-}V^{2+}$ + PV^{2+}	47	239

a) [Ru complex] = 2×10^{-5} M, $[PS^{2-}V^{2+}] = 5 \times 10^{-4}$ M, $[PV^{2+}] = 5 \times 10^{-4}$ M.

b) Bpy and phen stand for $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ respectively.

c) The luminescence quenching efficiency (Eq) is evaluated as $(I_o - I)/I_o$, where I_o and I stand for the luminescence intensities of $Ru(bpy)_3^{2+}$ in the absence and presence of viologen, respectively.

d) Obtained in the presence of NaCl (0.002 M).

e) ϕrel value for MV^{2+}(1×10^{-3}M) - $Ru(bpy)_3^{2+}$ was taken as the reference (100%).

f) Obtained with high NaCl concentraion (0.5 M).

The luminescence quenching of the ruthenium complexes by viologen and the sensitized reduction of the viologen units in the presence of EDTA as a sacrificial reagent were studied at first (Table 1). The relative quantum yield of reduced viologen, ϕrel, was evaluated from the initial rate of formation and was normalized to that of $Ru(bpy)_3^{2+}$- MV^{2+} system.16) In order to compare the results of these two types of experiments under the same ionic strength, the quenching behaviors of the ruthenium complexes were studied in the presence of appropriate amounts of NaCl (cf. Footnotes of Table 1). Under the ordinary ionic strength, the quenching due to the viologen polymer was too small to be detected with reasonable accuracy. Then, the Eq-value in Table 1 was obtained with 0.5 M NaCl solution. Even under this condition, the quenching by viologen polymer was still small and the relative quantum yield of the reduced viologen was inevitably low. Therefore, the quenching efficiency in System 3 may be completely ascribed to the coexisting zwitterionic viologen. The ϕrel value, remarkably increased in the system where the zwitterionic viologen coexisted with the viologen polymer (System No.3). Apparently, the same type of effects have been observed with $Ru(bpy)_3^{2+}$-sensitized reduction of the zwitterionic viologen on the addition of cationic micelles and bilayer membranes.17-19) The effect has been ascribed to trapping of the reduced viologen by the positively charged molecular assemblies, which suppresses the reverse electron transfer to the oxidized ruthenium complexes in the bulk aqueous phase. Polycation in the present experiments may be expected to be useful in this type of charge separation. No such effect could be detected, however, by the use of

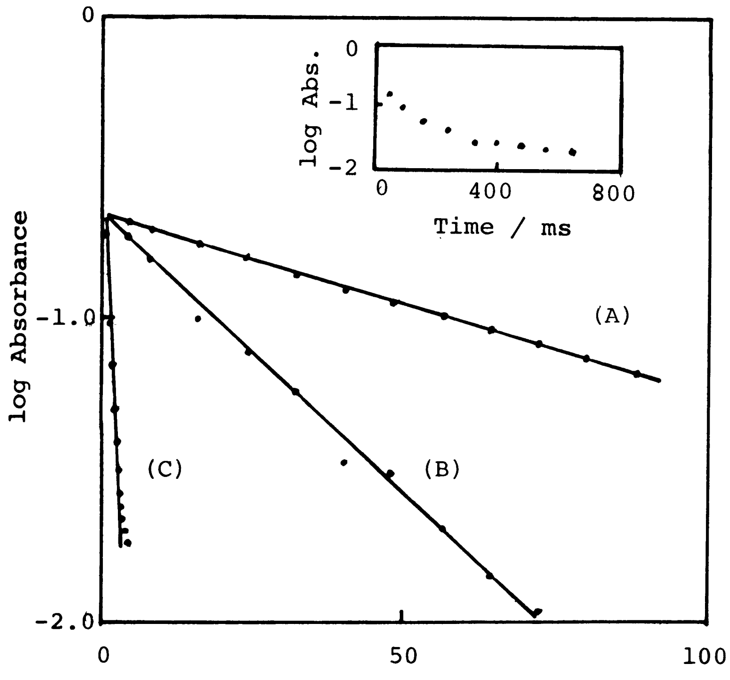


Fig. 1. The decay of viologen polymer radical at 603 nm under the following conditions:
(A) $[Ru(bpy)_3^{2+}] = 2 \times 10^{-5}M$, $[PS^{2-}V^{2+}] = 5 \times 10^{-4}M$, $[PV^{2+}] = 5 \times 10^{-4}M$.
(B) $[Pt] = 5 \times 10^{-5}$ M in addition to condition (A), and
(C) The sample (B) in 0.5 M H_2SO_4.
The inset figure corresponds to the decay of viologen polymer radical for longer period under condition (A).

poly(N-ethyl-4-vinylpyridinium) as shown by the ϕrel value for System No.4.

In addition, formation of viologen radical dimers was clearly observed with the difference absorption in system 3, which could not be detected in the absence of the viologen polymer.

Studies with tris(1,10-phenanthroline)ruthenium (II) complex analogously revealed the cooperation between the polymer and zwitterionic viologens as shown in Table 1 (Systems No.5-7).

On the basis of the above consideration, it is concluded that the zwitterionic viologens shuttle between the photoexcited ruthenium complexes and the viologen polymer as an efficient electron mediator. The viologen polymers thus store the photoliberated electrons and suppress the reverse electron transfer to the oxidized ruthenium complexes as elucidated by the flash spectroscopy described in the following section.

The decay of transient absorption due to the viologen cation radical was followed at 603 nm after the photolysis of $Ru(bpy)_3^{2+}$- zwitterionic viologen system by a Xenon flash (10 μs, 390 J, λ>405 nm). The transient absorption due to the reduced viologen disappeared within 160 μs in the absence of viologen polymer.$^{17)}$ In the presence of viologen polymer, however, the reduced viologen survived for extremely long period as shown in Fig. 1(A and the inset figure). The decay followed the first order reaction kinetics (τ = 52 ms) up to ca. 200 ms after the photolysis. Since most of the photoexcited ruthenium complexes are quenched by electron-transfer to the zwitterionic viologen at first, the electron must be further delivered to viologen polymer to survive the reverse electron transfer for such a long period. The viologen polymer thus plays a role of electron pool and the stored electrons must be slowly recaptured by the oxidized ruthenium complex via unidentified process corresponding to the first order reaction kinetics.

On the addition of Pt colloid, the decay of the viologen radical was enhanced while the first order reaction kinetics was still retained, (Fig. 1, B, τ = 16 ms). The increased rate of decay corresponds to that of electron transfer from the reduced viologen to platinum colloids. A remarkable increase in the decay rate was observed with the 0.5 M H_2SO_4 solution (C, τ = 1 ms), and it was almost independent of the concentration of Pt colloid in the investigated region ([Pt] = 3 - 50 μM). The decay rate is approximately two order of magnitude larger than that for MV^{2+} - Pt colloid stabilized by polyvinylalcohol ([Pt] = 2 μM) system at pH=1 as reported by Miller et al.20) These facts strongly indicate that the Pt colloids are well supported on the viologen polymer. The electron transfer from the viologen polymer radical to Pt colloids seems to be facilitated particularly at low pH region. Thus, one may expect that hydrogen will be generated under continuous irradiation of this system in the presence of electron donor at low pH region. The expectation was not fulfilled because many electron donors are inactive in such acidic region. In neutral pH region the hydrogen generation was observed in the presence of EDTA, although the rate was less than that for methyl viologen system in combination with Pt colloid stabilized by polyvinylalcohol, and the viologen polymer radical was accumulated. In this case, the reduction of protons to hydrogen on Pt colloid is obviously the rate-determining step. The reason may be ascribed to the shift of redox potential of proton on Pt colloid which could be regarded as "micro Pt electrode" surrounded by polycationic viologen polymer, because it was reported that the redox potential of proton shifted to negative on Pt electrode covered with ammonium salts.21)

In short, the photoredox center and multi-electron redox reaction site can be efficiently linked by the use of viologen polymer as "an electron pool", which is expected to play an important role in constructing molecular catalyst for artificial photosynthesis.

References

1) Contribution No. 704 from the Department of Organic Synthesis, Faculty of Engineering, Kyushu University.
2) K. Kirch, J. M. Lehn, and J. P. Sauvage, Helv. Chem. Acta., 62, 1345(1979).
3) M. Grätzel, Ber. Bunsenges. Chem., 84, 981(1980).
4) N. Sutin and C. Creutz, Pure App. Chem., 52, 2717(1980).
5) T. Matsuo, Pure App. Chem., 54, 1693(1982).
6) P. A. Brugger, P. Cuendet, and M. Grätzel, J. Am. Chem. Soc., 103, 2923(1981).
7) T. Nishijima, T. Nagamura, and T. Matsuo, J. Polym. Sci., Polym. Lett. Ed., 19, 65(1981).
8) R. C. Lee, M. S. Matheson, and D. Meisel, Israel J. Chem., 22, 133 (1982).
9) K. Takuma, T. Sakamoto, T. Nagamua, and T. Matsuo, J. Phys. Chem., 85, 619(1981).
10) T. Matsuo, T. Sakamoto, K. Takuma, K. Sakura, and T. Ohsako, J. Phys. Chem., 85, 1277(1981).
11) K. Sakura, T. Sakamoto, and T. Matsuo, Chem. Lett., 1982, 1651.
12) I. Willner, J. W. Otvos, and M. Calvin, J. Am. Chem. Soc., 103, 3203(1981).
13) I. Willner, J.-M. Yang, C. Laane, J. W. Otvos, and M. Calvin, J. Phys. Chem., 85, 3277(1981).
14) R. E. Sasoon and J. Rabani, Israel J. Chem., 22, 138(1982).
15) Y.Tsutsui, K.Takuma, T.Nagamura, and T. Matsuo, Chem. Lett., 1979, 617.
16) The rate of formation of $MV^{\dagger}$ in the standard system was obtained with 1 mM MV^{2+} solution.
17) T. Nagamura, T. Kurihara, T. Matsuo, M. Sumitani, and K. Yoshihara, J. Phys. Chem., 86, 4368(1982).
18) T. Nagamura, N. Takeyama, and T. Matsuo, Chem. Lett., 1983, 1341.
19) T. Nagamura, N. Takeyama, and T. Matsuo, J. Colloid Interface Sci., accepted for publication.
20) D. S. Miller and G. McLendon, J. Am. Chem. Soc., 103, 2923(1981).
21) J. L. Stickney, M. S. Soriaga, and A. T. Huhbard, J. Electroanal. Chem., 85, 179(1981).

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