CHEMISTRY LETTERS, pp. 1199-1202, 1977. Published by the Chemical Society of Japan

STUDIES ON PHOTOACTIVATED ELECTRON-TRANSPORT SYSTEMS. I. REDUCTION OF HEMIN AND ANTHRAQUINONESULFONATE AS MEDIATED BY PYRIDINIUM IONS AND PHOTOEXCITED RUTHENIUM(II) COMPLEXES[1)]

Keisuke TAKUMA, Makoto KAJIWARA, and Taku MATSUO*
Department of Organic Synthesis, Faculty of Engineering,
Kyushu University, Hakozaki, Fukuoka 812

Photoexcited state of tris(2,2'-bipyridine)ruthenium(II) ion serves as a good reducing agent, if EDTA is present in the solution. Pyridyl radical and 4,4'-bipyridinium cation radical were obtained by this means of photoirradiation, and proved to be useful as mediators for catalytic reduction of Hemin and 9,10-anthraquinone-1-sulfonate.

Electron-transport systems play very important roles in biological energy-conversion as illustrated in the case of photosynthesis. Then, it may be very useful to organize a biomimetic electron-transport system as a first step to construct a man-made energy conversion system. An electron-transport cycle of this type was successfully activated by the use of visible lights, and the results are reported here.

In analogy to the chlorophyll at the photosystem I reaction center, man-made metal chelates would also be expected to play the role of an activation center for energy conversion from light into chemical energies. In this regard, Ru(II) complexes appear to be quite promising as reported by several groups.[2)] In addition, the mechanistic details of the photoinduced oxidation of Ru(II) complexes have been well investigated by the use of flash photolysis.[3)] In the presence of 1,1'-dimethyl-4,4'-bipyridinium dichloride (methylviologen dichloride), for example, an electron-transfer from photoexcited triplet state of tris(2,2'-bipyridine)ruthenium dichloride (denoted as $Ru(bpy)_3Cl_2$, hereafter) to methylviologen ion (abbreviated to MV^{2+}) easily takes place in a diffusion-controlled rate in acetonitrile solutions. The cation radical of MV, thus obtained, is reoxidized via back-electron transfer to $Ru(bpy)_3^{3+}$, and no net product is observed unless flash photolysis techniques are utilized. In the present experiment, on the other hand, the growth of the cation radical of MV was clearly observed, when the steady photoirradiation was carried out in the presence of EDTA as shown in Fig. 1.

An aqueous solution containing $Ru(bpy)_3Cl_2$ (5×10^{-5} M), EDTA (1×10^{-3} M), and MV (5×10^{-4} M) was deaerated by freeze-pump-thaw cycles and placed in an optical cell with 1 cm pathlength for spectroscopic measurements. The sample was irradiated with a collimated beam from 500 W high-pressure mercury lamp. The lights with wavelength shorter than 375 nm were completely removed by the use of a V-Y42 filter. Under this condition, the concentration of $Ru(bpy)_3Cl_2$ remained perfectly unchanged

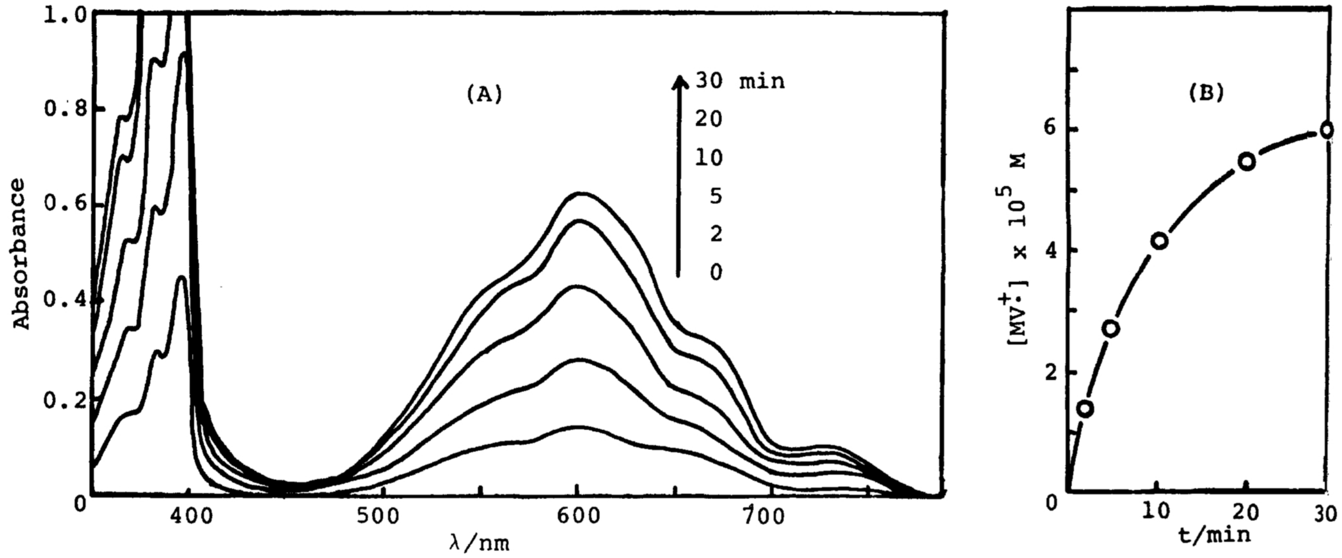
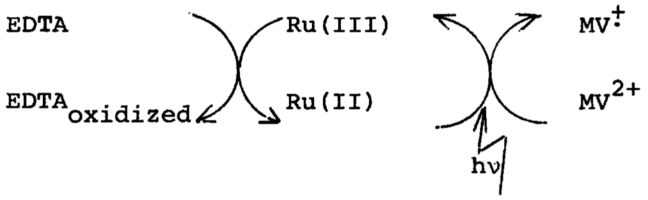


Fig. 1. The growth of $MV^{+\cdot}$ along the irradiation of an aqueous solution containing $Ru(bpy)_3Cl_2$, MV, and EDTA. (A) Variation of the difference spectra. (B) The rate of formation of $MV^{+\cdot}$.



throughout the irradiation period. The absorption spectra of the products were in good agreement with the reported spectra of $MV^{+\cdot}$ 4) and disappeared on exposure to the air. Since the luminescence from the Ru(II) complex was not quenched by EDTA, the primary photoreaction can not be the reduction of the Ru(II) complex but the formation of Ru(III) complex. The Ru(III) complex, thus produced, is apparently reduced by EDTA back to the Ru(II) complex, which is repeatedly photoexcited to give $MV^{+\cdot}$. Benzylviologen (BV) was also photoreduced under the same condition as the above, and the reaction rate was approximately twice as that of MV. The difference in the reaction rate may be ascribed to the fact that the redox potential of MV^{2+} ($E_{pH=5.2}$, -0.34 V) is lower than that of MV^{2+} ($E_{pH=5.2}$, -0.24 V).

The photoreduction of BV was also investigated in the presence of a surfactant micelles, which possess $Ru(bpy)_3^{2+}$ as the counter ions. The concentration of the surfactant, $(CH_3(CH_2)_{10}COO^-)_2Ru(bpy)_3^{2+}$, was adjusted to a value (1×10^{-2} M) a little above the second CMC (0.7×10^{-2} M),5) and the rate of formation of $BV^{+\cdot}$ was compared with that of the non-micellar solution which contained the same amounts of $Ru(bpy)_3Cl_2$ (1×10^{-2} M). The rate of formation of $BV^{+\cdot}$ in the micellar system was increased by a factor of 3.5 in comparison with the non-micellar system. A part of the micellar effect may be due to the increased local concentration of MV^{2+} at the micellar surface.

The photoreduction of 9,10-anthraquinone-1-sulfonate (AQαS) was analogously mediated by the combination of BV and $Ru(bpy)_3Cl_2$. Aqueous solutions of AQαS (1×10^{-4} M) were irradiated under the similar conditions as described above.

Formation of 9,10-dihydroxyanthracene-1-sulfonate was followed by the change in the difference spectra, which were identified with that of the authentic sample.
In the presence of EDTA, the photoreduction of AQαS slowly proceed without BV^{2+}.
The rate of reduction was enhanced by a factor of 14 by the addition on BV (5×10^{-4} M). As far as the redox potentials of the species concerned, an electron-transfer to AQαS should be more exothermic than that to BV^{2+}. Then the fact that BV^{2+} is much more efficient in removing an electron from the excited Ru(II) complex than AQαS may be ascribed to the difference in the electronic charge between them: BV^{2+} retains a positive charge while AQαS bears two negative charges after receiving an electron from the excited Ru(II) complex.

All of the above experiments indicate that MV^{2+} works as a good electron carrier from the photoactivated Ru(II) complex to electron acceptors of various types. As an application of this system, an attempt was made to reduce Hemin by the use of the electron transport system devised here. A solution containing Hemin (5×10^{-5} M), as solubilized by the use of non-ionic surfactant (Triton X-100, 0.5 %(v/v)) and pyridine (0.1 %(v/v)), was irradiated under the same condition as the above. In this case, $MV^{\dot{+}}$ was not detected but Hemin was smoothly reduced along the irradiation of the Ru(II) complex (Fig. 2.). The photoreduction of Hemin did not take place, if the irradiation was carried out in the absence of either EDTA or MV^{2+}. Then, it is clear that the following, cyclic redox reactions are induced by the irradiation of the Ru(II) complex:

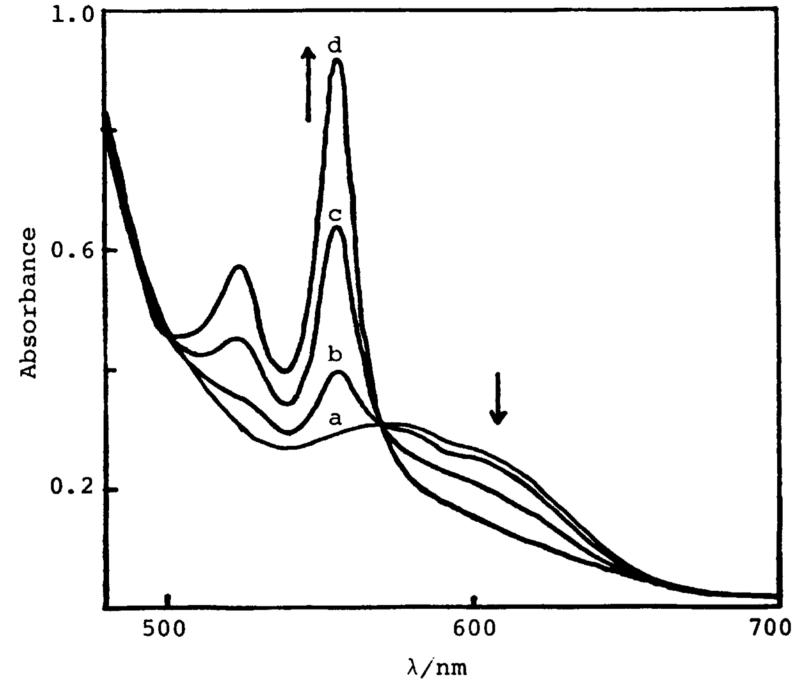
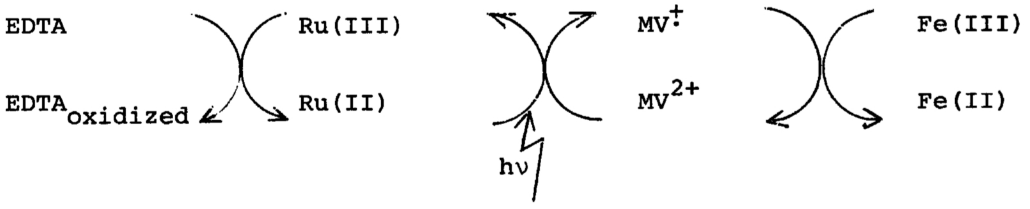


Fig. 2. Photoreduction of Hemin as mediated by MV^{2+} and $Ru(bpy)_3Cl_2$ in aqueous solution containing EDTA. (a), 0 sec; (b), 15 sec; (c), 45 sec; (d), 75 sec.



The rate of the photoreduction was increased by more than 50 % by replacing MV^{2+} with BV^{2+}. Pyridinium ions of various types could also be used as the electron carrier as summarized in Table 1.

Table 1. Relative Reduction Rates of Hemin as Mediated by Various Pyridinium Ions[a] and Photoexcited $Ru(bpy)_3Cl_2$

Pyridinium Ion	BV^{2+}	MV^{2+}	$4NA^+$ [b]	$3NA^+$ [c]	$2NA^+$ [d]
Relative Rate of Hemin Reduction	100	70	10	1	0.5

a) All of the pyridinium ions were used as the chlorides.
b) 1-Methyl-4-carbamoylpyridinium chloride. c) 1-Benzyl-3-carbamoylpyridinium chloride. d) 1-Methyl-2-carbamoylpyridinium chloride.

The relatively low efficiencies of the above 1-alkylcarbamoylpyridinium chlorides are correlated to the fact that the luminescence of $Ru(bpy)_3Cl_2$ is not so effectively quenched by these pyridinium ions as compared with the reported case of MV^{2+}.[6)]

In a summary, the excitation energy of photoirradiated $Ru(bpy)_3Cl_2$ was found to be used for redox reactions if EDTA and pyridinium ions such as BV^{2+} are present in the solution. An electron provided by the photoexcited Ru(II) complex is transported by an electron carrier ($BV^{+\cdot}$, for example) to oxidants, while the photooxidized ruthenium complex is reduced back to the original Ru(II) state. The basic idea of cyclic electron-transport system, as described above, will be quite useful in designing various types of photoinduced redox processes, which include the primary process of converting lights into chemical energies.

REFERENCES AND NOTES

* To whom any correspondence should be addressed.

1) Contribution No.442 from the Department of Organic Synthesis , Faculty of Engineering, Kyushu University.

2) (a) G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch, and D. G. Whitten, J. Am. Chem. Soc., 98, 2337 (1976). (b) S. O. Kobayashi, N. Furuta, and O. Simamura, Chem. Lett., 1976, 503.

3) R. C. Young, T. J. Meyer, and D. G. Whitten, J. Am. Chem. Soc., 98, 286 (1976).

4) E. M. Kosower and J. L. Cotter, J. Am. Chem. Soc., 86, 5524 (1964).

5) Synthesis and behaviors of this surfactant were presented, in part, at the regional meeting of the Chemical Society of Japan, Fukuoka, July, 1977. The details will be reported in other paper.

6) C. R. Bock, T. J. Meyer, and D. C. Whitten, J. Am. Chem. Soc., 96, 4710 (1974).

(Received July 23, 1977)