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PHOTOREDUCTION AND REDOX CATALYSIS OF AN AMPHIPATHIC DERIVATIVE OF TRIS(2,2'-BIPYRIDINE)RUTHENIUM(II) AT THE MICELLAR SURFACE$^{1)}$

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On the flash photolysis of an amphipathic derivative of tris(2,2'-bipyridine)ruthenium(II), the highest yield for photoreduction of the complex by N,N'-dimethylaniline was obtained with the micellar solutions of a cationic surfactant (CTAC). The kinetic studies proved that catalytic reduction of various substrates smoothly proceeded via the reduced ruthenium complex at the micellar surface.

Photochemical behaviors of polypyridine complexes of ruthenium(II) have called attention of investigators working for conversion and storage of solar energy.$^{2)}$ One of the most important features of the polypyridine complexes is the fact that the luminescent excited state plays a role of either strongly reducing or oxidizing agent,$^{3)}$ which may be useful as a catalyst for photochemical splitting of water into hydrogen and oxygen molecules. The catalytic reaction of the ruthenium complexes proceeding via the oxidized state have been well investigated.$^{4)}$ Rather scarce knowledge has been accumulated, on the other hand, as to the catalytic reactions involving the reduced species of the ruthenium complex, which is easily obtained by the photoirradiation in the presence of mild reductants.$^{5)}$ The basic requirement for photoexcited states to be used as a redox catalyst is highly efficient charge separation of the ion-pair produced by electron-transfer reactions between the photoexcited state and substrates. The efficiency of the charge separation is mainly limited by the extent of back electron transfer which inevitably follows the initial electron transfer involving the photoexcited state. The charge separation of the ion pair produced by the photoredox reactions in various donor-acceptor systems have been enhanced by the use of micellar surface.$^{6)}$ Several amphipathic ruthenium complexes, on the other hand, have been reported to be promising as catalysts for photoinduced redox reactions.$^{7)}$ However, no kinetic data on the charge separation processes are available. Then, photoinduced redox behaviors of an amphipathic ruthenium complex at the interface between bulk water and hydrophobic region provided by micelles were studied by flash techniques, and the results are reported here.

The amphipathic ruthenium complex used in this experiment was (N,N'-di(dodecyl)-2,2'-bipyridine-4,4'-dicarboxamide)-bis(2,2'-bipyridine)ruthenium(II)$^{2+}$ (abbreviated to $RuC_{12}B^{2+}$, hereafter),$^{8)}$ which is a homologue of that reported by Calvin and his associates.$^{7d)}$ The flash photolysis experiments were carried out in the same manner as previously described.$^{6c)}$

Charge Separation at the Micellar Surfaces

The formation of ion radical pairs just after excitation of $RuC_{12}B^{2+}$ and the decay via back electron transfer process were studied by flash photolysis. The sample solution contained $RuC_{12}B^{2+}$ (1×10^{-5} M) and N,N'-dimethylaniline (DMA, 2×10^{-3} M), as the electron donor, together with appropriate amounts of surfactants. The sample solutions were degassed and the flash lights with wavelength longer than 340 nm were irradiated. Formation of $RuC_{12}B^{+}$, the reduced product, was confirmed by the transient absorption which closely resembled the reported spectra of the corresponding ruthenium complex without aliphatic side chains.$^{5)}$ The decay of $RuC_{12}B^{+}$ was followed by the absorption at 515 nm as shown in Fig. 1.

The decay curves followed the second order reaction kinetics with rate constants (k_d), which indicated that the back electron transfer was remarkably retarded in micellar solutions of CTAC (a cationic surfactant,$^{9)}$ $k_d = 2.6 \times 10^7\ M^{-1}s^{-1}$) and Triton X-100 (a nonionic surfactant, $k_d = 1.5 \times 10^8\ M^{-1}s^{-1}$) in comparison with that in acetonitrile ($k_d = 7.8 \times 10^9\ M^{-1}s^{-1}$). In the case of anionic surfactant (SDS),$^{10)}$ on the other hand, $RuC_{12}B^{+}$ was hardly detected even at the beginning of the oscilloscope trace. The rate constant for the back electron transfer in the acetonitrile solution is close to the diffusion-controlled limit. Then, the extremely low yield of $RuC_{12}B^{+}$ in SDS solution indicates that the ion pair (DMA^{+}-$RuC_{12}B^{+}$) is not separated far enough to produce free DMA^{+}. The reason may be ascribed to electrostatic binding of DMA^{+} to the negatively charged micellar surface where the ion pair was produced. It is rather surprising that the rate constant for Triton X-100 system is not very far from that in CTAC system. In the case of pyrene radical anion-DMA^{+} systems, on the other hand, nonionic surfactant have been reported to be much less effective than cationic surfactant.$^{5)}$ The difference may be that the ion pair bears the same charge in the present experiment in contrast to the pyrene-DMA system. In other words, Coulombic repulsion between DMA^{+} and $RuC_{12}B^{+}$ aids the charge separation at the initial step, and the free DMA^{+} thus produced, appears to be located at more or less hydrophylic region. The positive charges at the cationic micellar surface is responsible to the additional increase in the life time of $RuC_{12}B^{+}$.

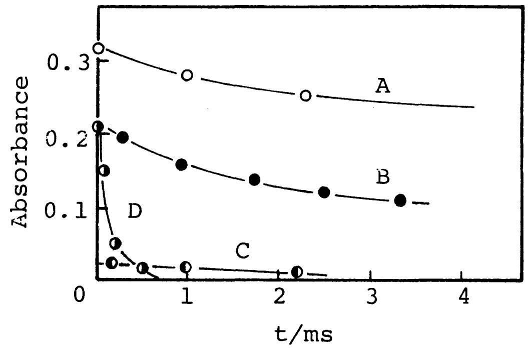

Fig. 1. The absorption decay curves of $RuC_{12}B^{+}$ measured at 515 nm on the flash photolysis (50 J) of the following solutions: A, [CTAC] = 0.01 M; B, [Triton X-100] = 1.0 %(v/v); C, [SDS] = 0.01M; and D, acetonitrile.

Electron Transfer Catalysis of $RuC_{12}B^{+}$ at the Micellar Surface

Electron transfer across the interface was studied by the flash photolysis of the micellar solution, which contained methyl viologen ion (MV^{2+}, 5×10^{-4} M), in addition to DMA and $RuC_{12}B^{2+}$. The transient absorptions at 80 μs and 10 ms after the flash photolysis were identified with those of $RuC_{12}B^{+}$ and MV^{+}, respectively (Fig. 2a).

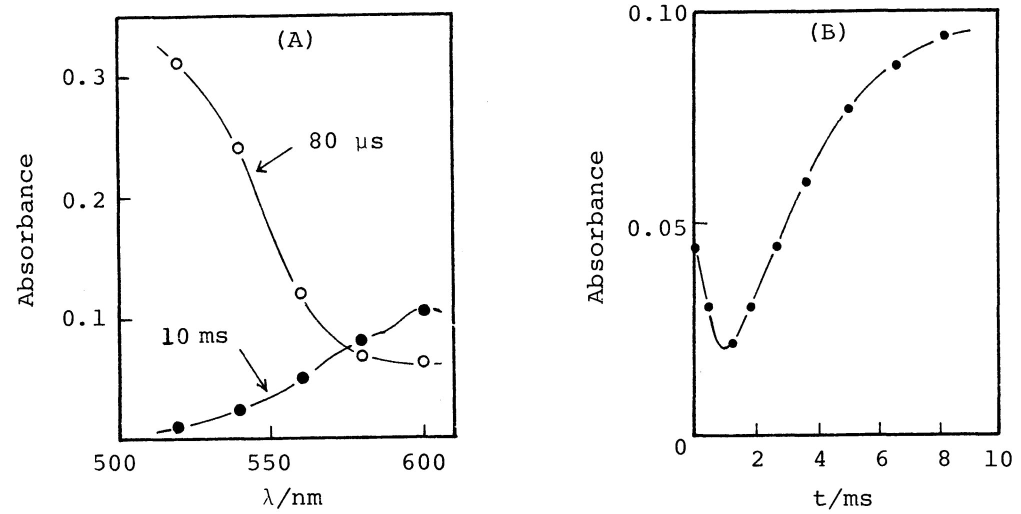

Fig. 2. Transient absorptions observed on the flash photolysis of DMA-$RuC_{12}B^{2+}$-MV^{2+} system in the micellar solution of CTAC. (A) The absorption bands at 80 μs (—o—) and 10 ms (—●—) after the photolysis. (B) The growth of MV^+ as detected by the absorption at 600 nm.

In other words, it is clear that MV^{2+} is reduced by $RuC_{12}B^+$. The growth of MV^+ was observed by the absorption at 600 nm (Fig. 2b) since 1 ms after the flash photolysis, and the curve was best fitted by the second order reaction kinetics with respect to the concentrations of MV^{2+} and $RuC_{12}B^+$. The kinetic analysis showed that the electron transfer from $RuC_{12}B^+$ to MV^{2+} proceeded with a rate constant ($k = 2 \times 10^5$ $M^{-1}s^{-1}$), which is much less than the diffusion-controlled value. This result is just as expected from the Coulombic repulsions between MV^{2+} and the surface of CTAC micelles where $RuC_{12}B^+$ is located. Under the experimental condition for the photolysis as shown in Fig. 2, approximately 30 % of $RuC_{12}B^+$ was used to reduce MV^{2+} and the remaining fraction appeared to be consumed by the recombination with DMA^+.

An amphipathic analogue of MV^{2+} was prepared by replacing the methyl groups in MV^{2+} with n-dodecyl groups.[11] Dodecylviologen (1,1'-dodecyl-4,4'-bipyridinium^{2+}, $C_{12}V^{2+}$), thus obtained, was easily solubilized into CTAC micelles. An example of the flash photolysis of the micellar solution containing $RuC_{12}B^{2+}$ (1×10^{-5} M) and $C_{12}V^{2+}$ (1×10^{-5} M) is shown in Fig. 3. The analysis of the decay curve for $RuC_{12}B^+$ ($k_d = 9.6 \times 10^7$ $M^{-1}s^{-1}$) and the growth of $C_{12}V^+$ indicates that $C_{12}V^+$ could be obtained in an almost quantitative yield as evaluated from the initially produced $RuC_{12}B^+$ (Fig. 3a). The extremely high electron transfer efficiency, as compared with the case of MV^{2+}, may be mainly ascribed to the enrichment of $C_{12}V^{2+}$ into the micellar volume, which increases the effective concentration of the electron acceptor than otherwise. It should also be noticed that $C_{12}V^+$, thus produced, survives for surprisingly long period of time ($k_d = 4.6 \times 10^6$ $M^{-1}s^{-1}$) as shown in Fig. 3b. The collision between $C_{12}V^+$ and DMA^+ is apparently retarded in the CTAC solution. Thus, it is evident that the micellar surface provides a very good microenviornment for keeping the photoirradiated system in a metastable state.

In conclusion, the above data suggest that photoreduction of amphipathic

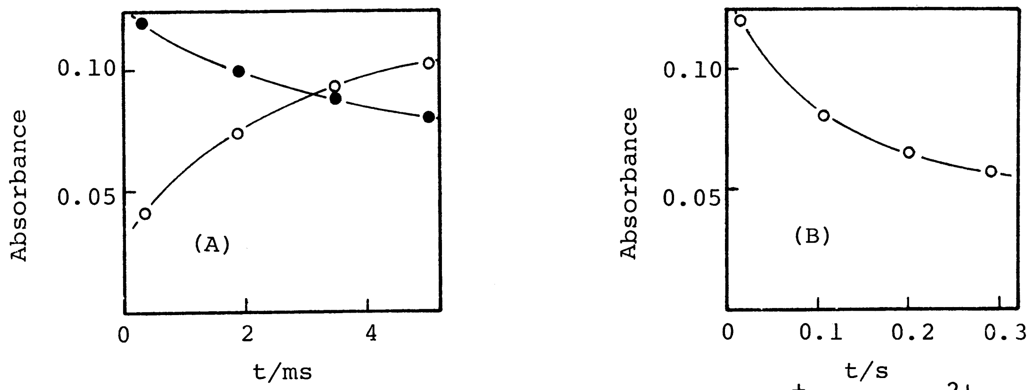

Fig. 3. The electron transfer reactions between $RuC_{12}B^+$ and $C_{12}V^{2+}$ as detected by the transient absorptions on the flash photolysis of the CTAC solution. (A) The decay of $RuC_{12}B^+$ at 515 nm (—●—) and the growth of $C_{12}V^+$ at 600 nm (—o—) in shortly after the photolysis. (B) The decay of $C_{12}V^+$ at the later part of the reaction.

derivatives of tris(2,2'-bipyridine)ruthenium(II) at the interfaces between water and organic microenvironment may be one of the most promising processes for energy conversion from photons into chemical potentials.

REFERENCES AND NOTES

1) a) Contribution No.516 from the Department of Organic Synthesis, Faculty of Engineering, Kyushu University, b) Presented, in part, at the annual meeting of the Chemical Society of Japan, Tokyo, April, 1978 and also at the discussion meeting on the photochemistry, Kyoto, November, 1978, c) Supported in part by *the Grant-in-Aid for Scientific Research (No.347068) from the Ministry of Education.*
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8) The details of the synthesis will be reported in other paper. Absorption maximum, 482 nm; fluorescence maximum, 664 nm in the CTAC micellar solutions.
9) CTAC stands for hexadecyltrimethylammonium chloride.
10) Sodium dodecyl sulfate is abbreviated to SDS.
11) The details of the synthesis will be reported in other paper. mp. 240°C (decomp.).

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