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PHOTOINDUCED ELECTRON TRANSFER BETWEEN AMPHIPATHIC RUTHENIUM(II) COMPLEX AND N,N-DIMETHYLANILINE IN SYNTHETIC BILAYER MEMBRANES AND PHOSPHOLIPID LIPOSOMES[1)]

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Photoreduction of amphipathic ruthenium(II) complex by N,N-dimethylaniline was studied by the flash photolysis in synthetic bilayer membranes and phospholipid liposomes. Back electron transfer was effectively retarded in these systems. The effect of phase transition on the rate of back electron transfer reaction was different in synthetic bilayers and in liposomes.

Photochemical reactions catalyzed by tris(2,2'-bipyridine)ruthenium(II) complex, $Ru(bpy)_3^{2+}$, have been extensively investigated, since this particular metal complex is considered to be as one of the most promising photocatalysts for chemical conversion of solar energy.[2)] Hydrogen evolution from water by the use of $Ru(bpy)_3^{2+}$ as a photosensitizer has recently been reported by several investigators.[3)] In order to photochemically decompose water into hydrogen and oxygen molecules, it is essential to separate reductive and oxidative processes and to link them with appropriate redox catalysts as found in the chloroplast.[4)] Therefore, it is very important to prepare appropriate microenvironments for the reaction as well as to study characteristics of photosensitizers. Some biomembrane models such as phospholipid liposomes, liquid membranes, or microemulsions are probably useful for such purposes. Very recently cationic, anionic, and nonionic surfactants containing two long alkyl chains have been found to form bilayer structure similar to that in phospholipid liposomes.[5)] These synthetic bilayer membranes may hopefully be used as a new microenvironment appropriate to control photochemical reactions.

In the present communication, results on photoinduced electron transfer between amphipathic ruthenium(II) complex and N,N-dimethylaniline(abbreviated to DMA) in synthetic bilayer membranes and phospholipid liposomes are reported. Comparisons will be made with photoinduced redox behavior of an amphipathic ruthenium complex in various micellar systems reported in the preceding paper.[6)]

The amphipathic ruthenium complex employed in this experiment was (N,N'-didodecyl-2,2'-bipyridine-4,4'-dicarboxamide)-bis(2,2'-bipyridine)ruthenium(II)$^{2+}$(abbreviated to $RuC_{12}B^{2+}$).[7)] Dihexadecyldimethylammonium bromide(abbreviated to $2C_{16}NB$), which was found to form bilayer structure, was kindly supplied by Prof. T. Kunitake of Kyushu University. An aqueous dispersion of $2C_{16}NB$ (1 mM) and $RuC_{12}B^{2+}$ (1×10^{-5} M) was sonicated at about 60 °C for 30 min to get a clear solution, to which DMA (2 mM) was added. Liposomes (1 mM) containing $RuC_{12}B^{2+}$ were prepared from dipalmitoylphosphatidylcholine(DPPC) and dimyristoylphosphatidylcholine(DMPC) according to a usual sonication method. These aqueous solutions were deaerated by a pump-thaw and Ar substitution method. The flash photolysis experiments were carried out by the use of a 340 nm cut-off filter in the similar manner as previously reported.$^{6)}$

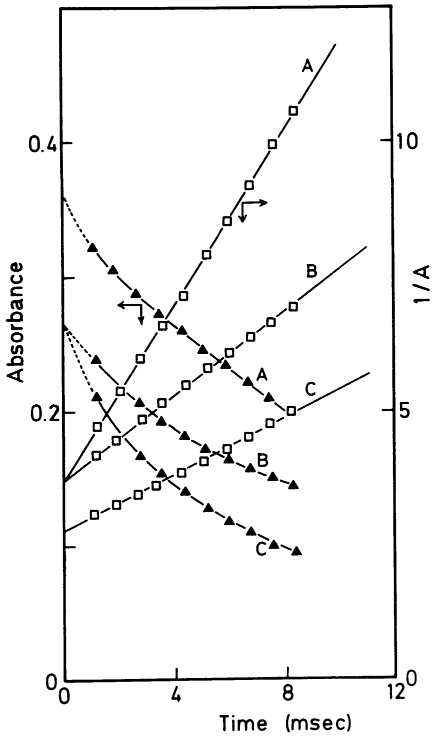

Fig. 1 Time dependences of absorbances at 515 nm and their reciprocals at (A) 50, (B) 25, and (C) 17 °C in a $2C_{16}NB$ bilayer system.

Photoinduced Charge Separation

Photoinduced electron transfer from DMA to $RuC_{12}B^{2+}$ was confirmed by the transient abosrption spectra which resembled the reported spectra of the corresponding $Ru(bpy)_3^+$, but shifted to a longer wavelength region by about 30 nm.$^{8)}$ The decay of $RuC_{12}B^+$ was followed by the transient absorption at 515 nm as shown in Fig. 1 for a synthetic bilayer ($2C_{16}NB$) system. The decay curves followed the second order reaction kinetics with rate constants, k_d. The values of k_d are listed in Table I. Photoinduced formation of $RuC_{12}B^+$ was also observed in phospholipid liposome systems containing DMA. The decay of $RuC_{12}B^+$ in liposomes was somewhat faster than in a $2C_{16}NB$ bilayer system and appeared to consist of two different processes as shown in Fig. 2. The second order reaction rate constants obtained in the initial and later regions are listed in Table I. Transient absorptions disappeared completely in each step, with no strange signals, and repeated flash photolysis generated them with a good reproducibility. Therefore, the decay of $RuC_{12}B^+$ was concluded to be caused by a back electron transfer reaction to DMA^+.

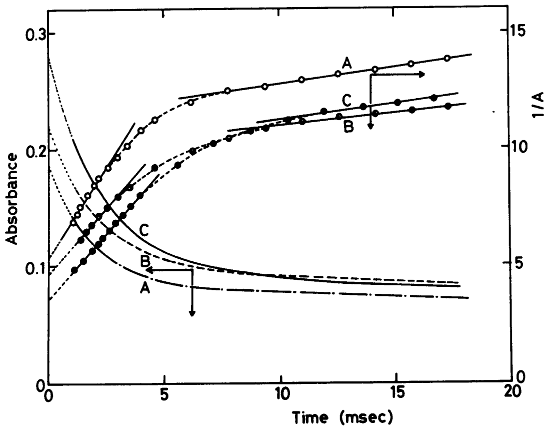

Fig. 2 The decay of transient absorptions at 515 nm at (A) 50, (B) 25, and (C) 13 °C in a DMPC liposome system.

Comparisons of k_d values obtained at 25 °C with that in a homogeneous acetonitrile solution indicate that the back electron transfer reaction between $RuC_{12}B^+$ and DMA^+ was remarkably retarded in these bilayer systems. Zwitterionic phospholipid liposomes with no net surface charges showed k_d values comparable to that observed in a nonionic Triton X-100 micellar system.$^{6)}$ This result supports the previous hypothesis that Coulombic repulsion between DMA^+ and $RuC_{12}B^+$ bearing the same positive charges is responsible to the initial charge separation and also, to some extent, to the retardation of the subsequent back electron transfer reactions.$^{6)}$ Positively charged interface of $2C_{16}NB$ synthetic bilayer membranes contributed to the additional retardation of back electron transfer reaction

Table I. Second order rate constant, k_d, of the back electron transfer reaction between $RuC_{12}B^+$ and DMA^+ in a synthetic bilayer and phospholipid liposome systems.

System	k_d ($M^{-1}s^{-1}$) first decay	second decay	temperature (°C)
$2C_{16}NB$ (1×10^{-3}M)	2.3×10^7	none	17
	3.3×10^7	none	25
	7.1×10^7	none	50
DPPC (1×10^{-3}M)	1.7×10^8	8.8×10^6	25
DMPC (1×10^{-3}M)	9.8×10^7	1.2×10^7	13
	9.8×10^7	9.1×10^6	25
	1.3×10^8	1.2×10^7	50
CTAC (1×10^{-2}M)	2.6×10^7	(ref. 6)	
Triton X-100 (1%(v/v))	1.5×10^8	(ref. 6)	
acetonitrile	7.8×10^9	(ref. 6)	

by preventing DMA^+ from approaching $RuC_{12}B^+$, just as in the case of a CTAC micellar system.6) Molecular motions of individual molecules were extermely restricted in a bilayer structure compared with those in micelles.5c) The exchange rate of molecules between free and aggregated states is known to be much slower in a bilayer structure than in micelles. Therefore, photoproduced $RuC_{12}B^+$ molecules are assumed to have little probability to escape from bilayer membrane where they were originally solubilized. The result that k_d value in micelles was almost identical with those in bilayer systems suggests that the rate of back electron transfer depends almost solely on the diffusion of once-repelled DMA^+ to re-encounter with $RuC_{12}B^+$.

Effect of Temperature on the Back Electron Transfer Reaction

The phase transition temperature (T_c) of $2C_{16}NB$ bilayers was determined to be 28 °C by thermal measurements.9) Liposomes from DPPC and DMPC show the phase transition at 41.4 and 23.9 °C, respectively.10) The temperature dependence of k_d values in $2C_{16}NB$ was found to be fitted approximately by the Arrhenius plot. Changes of k_d values in DMPC liposomes upon phase transition were even much smaller. The phase transition in phospholipid liposomes is known to be caused by the cooperative melting of aligned long alkyl chains alone, leaving head groups with zwitterionic interactions almost intact. Therefore, the mobility of and the microenvironment around head groups of $RuC_{12}B^{2+}$ solubilized in liposomes would hardly change upon phase transition. Such situation was most likely reflected in small changes of k_d values in DMPC liposomes observed below and above T_c. The chain packing in synthetic bilayers like $2C_{16}NB$ has been concluded to be much less compact than that in phospholipid liposomes from various experimental results.5c) NMR and thermal measurements indicated that the cooperativity of phase transition is much smaller in synthetic bilayers than in liposomes.9)11) The present results indicate that not only the aligned long alkyl chains but the head groups also would begin molecular motions with considerable amplitude near and above T_c in synthetic bilayers. The apparent lack of the effect of phase transition on k_d values in $2C_{16}NB$ was probably caused by a gradual disordering of the positively charged interface with increasing temperatures. The effect of phase transition with smaller cooperativity would be detected less sensitively in experiments where temperatures were gradually changed, attaining thermal equilibrium stepwise.

The nature of slower back electron transfer process in DPPC and DMPC cannot be clearly explained at this stage. One of the possible explanations would be the migration of DMA^+ to $RuC_{12}B^+$ solubilized in other liposomes at a distance.

From these results it can be concluded that synthetic bilayers and phospholipid liposomes which possess different aqueous phases separated by aligned hydrophobic layer could be effectively used as a photochemical reaction field to produce reduced species of amphipathic Ru(II) complex and to store it for a relatively long period of time. Further investigations on electron transfer reactions from $RuC_{12}B^+$ to appropriate acceptors are now in progress.

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