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Tris(2,2′-bipyridine)ruthenium(II)-photosensitized Reductions of Methyl Viologen and Molecular Oxygen in a Network of Water-swollen Cation-exchange Resin

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The visible-light-induced reduction of methyl viologen was found to occur in water-swollen cation-exchange resin, which adsorbed both $Ru(bpy)_3^{2+}$ and methyl viologen (RMCA resin) with the aid of triethanolamine (TEA) as a donor. With illumination, the generation of hydrogen peroxide proceeds in an oxygenated TEA solution containing RMCA resin. Hydrogen peroxide is produced *via* the superoxide ion, which is itself formed by the reaction of the methyl viologen radical in the resin with the oxygen molecule in the bulk of the solution. The $Ru(bpy)_3^{2+}$-photosensitized reaction processes leading to the generation of methyl viologen radical and hydrogen peroxide in the heterogeneous systems are discussed on the basis of the results obtained.

Many recent investigations[1–11] have been focussed on the quenching processes and visible-light-induced reactions *via* the photosensitized reactions of this type:

$$^*Ru(bpy)_3^{2+} + A \longrightarrow Ru(bpy)_3^{3+} + A^-,$$

where $^*Ru(bpy)_3^{2+}$ (bpy=2,2′-bipyridine) is the lowest excited state of $Ru(bpy)_3^{2+}$. The micellar systems have been examined with an eye to enhancing the charge-separation of this type of reaction.[1,7,10] In the case of a micellar solution, the kinetic features are considered to be different from those in a homogeneous solution. It has been suggested that, in a micellar system, no intermicellar exchange of $^*Ru(bpy)_3^{2+}$ and the acceptor molecules can take place; thus, the electron-transfer will occur within groups of only a few molecules that are compartmented within their host aggregate.[7]

Relatively little attention seems to have been paid to such heterogeneous reactions as those which occur in the networks of ion-exchange resins. The quenching of $^*Ru(bpy)_3^{2+}$ by various metal ions has been investigated in water-swollen cation-exchange resin (Shphadex-SP)[12] or in a cluster network of perfluorosulfonate membrane (Nafion 120).[13] However, little investigation of the $Ru(bpy)_3^{2+}$ photosensitized reduction in the network of the ion-exchange resin has been reported except for that in water-swollen iminodiacetic acid type chelate resin bead adsorbing $Ru(bpy)_3^{2+}$ and methyl viologen (MV^{2+}).[14] If we use a cation-exchange resin, photosensitizer and acceptor ions having more than two positive charges, such as $Ru(bpy)_3^{2+}$ and MV^{2+} respectively, could be accumulated in the domain of the resin. In such a system, an efficient electron-transfer from $^*Ru(bpy)_3^{2+}$ to the acceptor can be expected to occur if the resin is relatively transparent, and the back-reaction can be prevented by scavenging the oxidized species of the Ru(II) complex by a suitable donor, because the electron-transfer efficiency from the excited state of the chromophore to the acceptor should be enhance as a result of the intimate contact of these species in the domain of the resin.

In the present work, we have studied the photosensitized reduction of methyl viologen and the activation of the dissolved oxygen by use of a cation-exchange resin which adsorbs both $Ru(bpy)_3^{2+}$ and MV^{2+} (abbreviated as RMCA resin).

Experimental

The chloride salt of methyl viologen was recrystallized from methanol. The $[Ru(bpy)_3]Cl_2\cdot 6H_2O$[15] was prepared according to the literature method. The triethanolamine (TEA) and other reagents were of the best commercial grade available. The cation-exchange resin (Dowex 50-W-X-8, 100—200 mesh; sodium form) was used after conditioning by means of a column exchange, washing with water until the effluent was transparent in the UV region, and drying at 60 °C. The exchange capacity of the resin was determined to be 4.51 mequiv. g^{-1}. The concentrations of $Ru(bpy)_3^{2+}$ and MV^{2+} were determined by means of solution spectrometry at 456 nm (ε 13600 $M^{-1}\ cm^{-1}$, $1\ M = 1\ mol\ dm^{-3}$) and 257 nm (ε 21000 $M^{-1}\ cm^{-1}$) respectively. The cation-exchange resin adsorbing both $Ru(bpy)_3^{2+}$ and MV^{2+} was prepared as follows. The resin beads (5.0 g) in a 100-ml portion of the solution containing the Ru(II) and MV^{2+} were stirred for 1 h. By determining the concentrations of the Ru(II) and MV^{2+} remaining in the solution, the amounts of the adsorbed ions could be ascertained. The resulting resin beads were filtered, washed with water, and dried at 60 °C in the dark. The absorption spectra werer ecorded on a Hitachi Model 320 spectrophotometer. The reflectance spectral change in the RMCA resin was recorded as follows. A mixture of the RMCA resin beads (*ca.* 3 ml) and about 10-ml of the phosphate buffer (pH 7.0, 0.02 M) were bubbled with nitrogen gas for 30 min, and then the resin beads (*ca.* 2 ml) and small amounts of the buffer solution were packed into a photometer cell (10 mm × 10 mm) with a ground-glass cap in a thermostated cell holder at 30 ± 0.2 °C under nitrogen. The cell was illuminated with a 150-W slide projector with a UV cut-off filter (Kenko Skylight, L-40, UV). The reflectance spectra were recorded on a Hitachi Model 320 spectrometer equipped with an integrating sphere accessory (Model 210-2102), with aluminum oxide as the reference.

A typical procedure for the illumination of a mixture of the RMCA resin and aqueous solution was as follows. The pH of a mixture of 0.50 g of the RMCA resin and 30.0 ml of water in a 100-ml Ehrenmayer flask was adjusted to about 7 by the addition of several drops of dilute hydrochloric acid and, if necessary, dilute sodium hydroxide, by then adding 5.0 ml of a phosphate buffer (0.2 M), and ,finally, by adjusting the volume of the solution to 50.0 ml. The flask was kept in a thermostated water bath, made of transparent polyacrylic acid resin, at 30 ± 0.2 °C. Oxygen or air was flushed through the mixture for 20 min. The mixture was illuminated with a 150-W slide projector located below the water bath. During the illumination, the mixture was stirred by bubbling in oxygen or air. The concentration of hydrogen peroxide in the illuminated solution was determined colorimetrically using titanium oxalate.[16]

Results and Discussion

The cation-exchange resin adsorbs both $Ru(bpy)_3^{2+}$ and MV^{2+} in an aqueous solution well. When the total amounts (equiv. g^{-1} of the resin) of the adsorbed $Ru(bpy)_3^{2+}$ and MV^{2+} ions were less than 10% of the exchange capacity of the resin, no appreciable amounts of the adsorbed ions were eluted into the solution when the RMCA resin was kept in a 0.1 M TEA solution at pH 8.0 for 3 h at 30 °C. It was also ascertained that no detectable amounts of TEA were found to be adsorbed on the cation-exchange resin when 0.50 g of the cation-exchange resin was stirred in 50 ml of a 0.10 M TEA solution at pH 7 and 30 °C for 2 h.

When RMCA resin was illuminated in a deoxygenated aqueous solution of TEA, the resin turned from the original light brown through light green to dark blue. In the absence of TEA, however, no such color change was observed at all upon illumination.

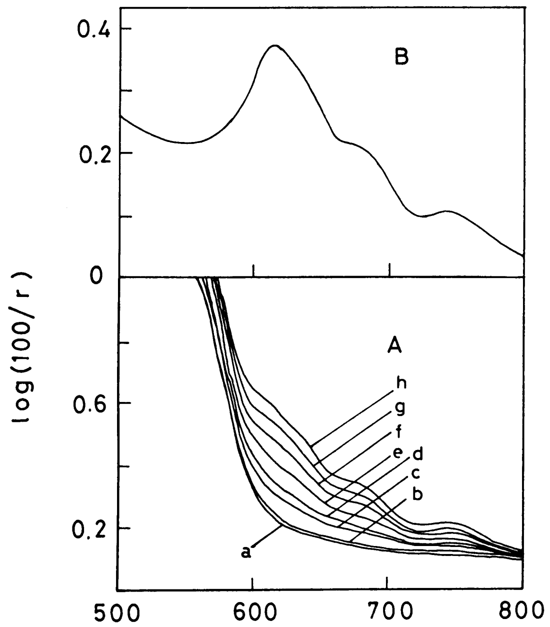

Fig. 1. Reflectance spectral change of the illuminated RMCA resin ($[Ru(II)]=2.3\times10^{-5}$ mol g^{-1}, $[MV^{2+}]=1.1\times10^{-4}$ mol g^{-1}) in N_2-saturated 0.10 M TEA solution with the illumination time (min) of 0 (a), 5 (b), 15 (c), 20 (d), 30 (e), 40 (f), 50 (g), and 60 (h) (A) and the differential spectrum of the 60 min illuminated RMCA resin (B) at pH 7.0 and 30 °C.

The reflectance spectral change in the RMCA resin in a deoxygenated solution (Fig. 1A) and the differential spectrum of the illuminated resin is essentially the same as the absorption spectrum of the methyl viologen radical in an aqueous solution in the region of 550—800 nm. It may be concluded that the $^*Ru(bpy)_3^{2+}$ produced by the photoexcitation of the adsorbed $Ru(bpy)_3^{2+}$ reacts with MV^{2+} to give the methyl viologen radical, MV^{+},[17] in the interior of the domain of the resin and that the oxydized psecies of the chromophore is scavenged by the TEA molecule present in the bulk of the solution. A bead of the illuminated (*ca.* 5 min) RMCA resin in a deoxygenated solution was cut into two hemispheres and then the cut surface was examined under a microscope. The dark blue color of the methyl viologen radical was found to spread homogeneously on the surface. This seems to indicate that the reaction proceeds almost homogeneously in the resin bead.

The photosensitized reduction of methyl viologen using RMCA resin can be explained by the scheme given in Eqs. 1—5. In these equations, the chemical species written in branckets with the suffix *r* represent those adsorbed on the resin, while *m* denotes the ratio of the average number of the MV^{2+} to one $Ru(bpy)_3^{2+}$:

$$[(Ru(II))(MV^{2+})_m]_r \xrightarrow{h\nu} [(^*Ru(II))(MV^{2+})_m]_r \qquad (1)$$

$$[(^*Ru(II))(MV^{2+})_m]_r \longrightarrow [(Ru(II))(MV^{2+})_m]_r + \Delta + h\nu' \qquad (2)$$

$$[(^*Ru(II))(MV^{2+})_m]_r \longrightarrow [(Ru(III))(MV^{+})(MV^{2+})_{m-1}]_r \qquad (3)$$

$$[(Ru(III))(MV^{+})(MV^{2+})_{m-1}]_r \longrightarrow [(Ru(II))(MV^{2+})_m]_r \qquad (4)$$

$$[(Ru(III))(MV^{+})(MV^{2+})_{m-1}]_r + TEA \longrightarrow [(Ru(II))(MV^{+})(MV^{2+})_{m-1}]_r + TEA_{ox}, \qquad (5)$$

where TEA_{ox} is the oxidized species of triethanolamine. The charge separation, *i.e.*, generation of MV^{+}, takes place as a result of the reduction of the Ru(III) by the TEA molecule *via* Eq. 5.

When RMCA resin was illuminated in an oxygenated solution of TEA, only a slight color change or, in some cases, no color change at all was seen, while the formation of hydrogen peroxide was observed in the bulk of the solution. These facts indicate that the hydrogen peroxide is produced by the reaction of the methyl viologen radical with the oxygen molecule.

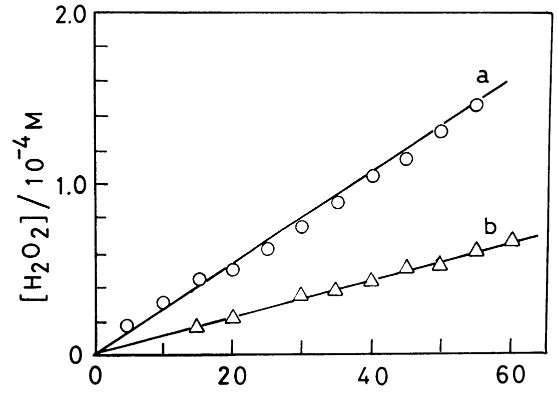

Fig. 2. Plots of the concentration of hydrogen peroxide with the illumination time in the mixture of 0.50 g of RMCA resin ($[Ru(II)]=2.3\times10^{-5}$ mol g^{-1}, $[MV^{2+}]=1.1\times10^{-4}$ mol g^{-1}) and 50 ml of the O_2-saturated (a) and air-saturated (b) 0.10 M TEA solutions at pH 7.0 and 30 °C.

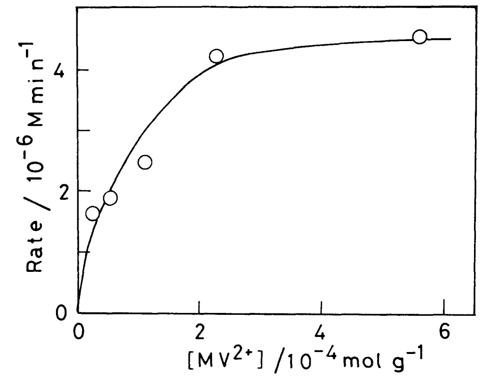

Fig. 3. Dependence of the rate of hydrogen peroxide formation on the concentration of MV^{2+} in the mixture of 0.50 g of RMCA resin ($[Ru(II)] = 2.3 \times 10^{-5}$ mol g^{-1}) and 50 ml of O_2-saturated 0.10 M TEA solution at pH 7.0 and 30 °C.

The concentration of hydrogen peroxide is plotted as a function of the illumination time in Fig. 2. The rate of hydrogen peroxide formation was determined from the slope of the plots of the hydrogen peroxide concentration *vs.* the illumination time. The results shown in Fig. 2 demonstrate that the rate depends on the concentration of the dissolved oxygen: the rate in the oxygen-saturated solution is about two times greater than that in the air-saturated solution under the conditions employed.

The rate also depends on the "concentrations"[19] of the adsorbed $Ru(bpy)_3^{2+}$ and MV^{2+}. The rate dependence on the concentration of MV^{2+} shows that the rate increases sharply at lower $[MV^{2+}]$ values and reaches the saturated value at $[MV^{2+}]$ values higher than about 2×10^{-4} mol g^{-1} (Fig. 3).

The rate is also affected by the concentration of the TEA: the rate increases with the concentration of the TEA and is hardly saturated even at 0.5 M (Fig. 4). The dependence of the rate on the concentration of the Ru(II) is presented in Fig. 5.

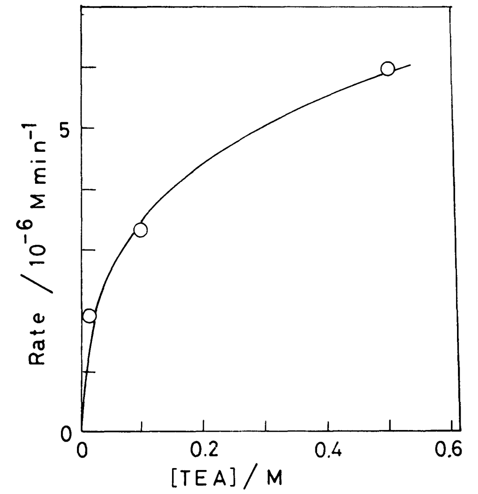

Fig. 4. Dependence of the rate of hydrogen peroxide formation on the concentration of TEA in the mixture of 0.50 g of RMCA resin ($[Eu(II)] = 2.3 \times 10^{-5}$ mol g^{-1}, $[MV^{2+}] = 1.1 \times 10^{-4}$ mol g^{-1}) and 50 ml of O_2-saturated TEA solution at pH 7.0 and 30 °C.

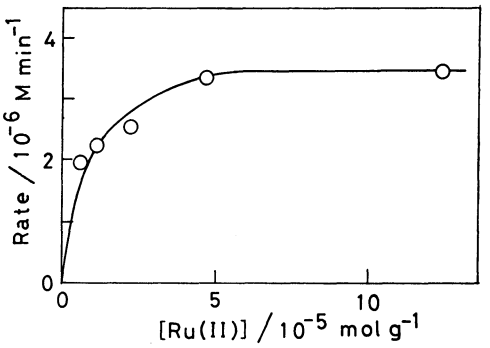

Fig. 5. Dependence of the rate of hydrogen peroxide formation on the concentration of $Ru(bpy)_3^{2+}$ in the mixture of 0.50 g RMCA resin ($[MV^{2+}] = 1.1 \times 10^{-4}$ mol g^{-1}) and 50 ml of O_2-saturated 0.10 M TEA solution at pH 7.0 and 30 °C.

The reaction scheme for the formation of hydrogen peroxide responsible for the results can be explained by Eqs. 1—5, 6, and the subsequent reduction of the superoxide ion, by Eqs. 7—9. Hydrogen peroxide is,

$$[(Ru(II))(MV^{+})(MV^{2+})_{m-1}]_r + O_2 \longrightarrow [(Ru(II))(MV^{2+})_m]_r + O_2^- \qquad (6)$$

probably, formed by the disproportionation reaction of the superoxide ions and the reaction of O_2^- with $^*Ru(bpy)_3^{2+}$, and/or MV^+. The rate dependence on the

$$O_2^- + O_2^- + 2H^+ \longrightarrow H_2O_2 + O_2 \qquad (7)$$

$$[^*Ru(II)]_r + O_2^- + 2H^+ \longrightarrow [Ru(III)]_r + H_2O_2 \qquad (8)$$

$$[MV^+]_r + O_2^- + 2H^+ \longrightarrow [MV^{2+}]_r + H_2O_2 \qquad (9)$$

oxygen concentration may be explained by the fact that the rate of the reaction of MV^+ with O_2 is relatively slow at low O_2 concentrations relative to that of the methyl viologen-radical formation: thus, the rate of hydrogen peroxide increases with an increase in the O_2 concentration in the lower-concentration region.

When 0.50 g of the RMCA resin ($[Ru(II)] = 2.3 \times 10^{-5}$ mol g^{-1} and $[MV^{2+}] = 1.1 \times 10^{-5}$ mol g^{-1}) in 50 ml of 0.10 M TEA was illuminated at 30 °C for 10 h, 1.4×10^{-3} M H_2O_2 was generated: thus, the turnover number for the Ru(II) and MV^{2+} were estimated to be about 10 and 2 respectively in this case (Fig. 6).

A experiment aimed at comparing the efficiencies of hydrogen peroxide formation in the heterogeneous system with the corresponding homogeneous one was

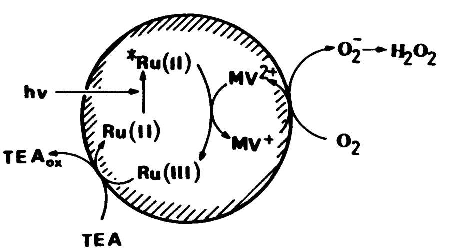

Fig. 6. Schematic representation of the generation of hydrogen peroxide in RMCA resin/O_2/TEA/H_2O system.

TABLE 1. COMPARISON OF THE RATE OF HYDROGEN PEROXIDE FORMATION IN THE RMCA RESIN SYSTEM WITH THE CORRESPONDING HOMOGENEOUS SYSTEM AT pH 7.0 AND 30 °C [a)]

System		$[Ru(bpy)_3{}^{2+}]$	$[MV^{2+}]$	[TEA]/M	$(d[H_2O_2]/dt)$/mol min^{-1}
Heterogeneous[b)]	1A	2.3×10^{-5}	1.1×10^{-4}	0.10	2.4×10^{-6}
	1B	5.9×10^{-6}	2.8×10^{-5}	0.012	1.3×10^{-6}
Homogeneous[c)]	2A	2.3×10^{-4}	1.1×10^{-3}	0.10	1.4×10^{-5}
	2B	5.9×10^{-5}	2.8×10^{-4}	0.012	1.5×10^{-6}

a) 1A and 1B correspond to 2A and 2B respectively. O_2-saturated solution at pH 7.0 and 30 °C. b) 0.50 g of the RMCA resins in 50 ml of the solution. The unit of the "concentrations" of the Ru(II) and MV^{2+} is represented by mol g^{-1}. c) The volume of the illuminated solutions was 50 ml. The unit of the concentrations of the Ru(II) and MV^{2+} is represented by mol dm^{-3}.

carried out; the results are presented in Table 1. In higher-concentration regions of the Ru(II), MV^{2+}, and TEA, the relative rate in the resin system is lower than that of the corresponding homogeneous system. However, in the lower-concentration regions of those species, the rate in the heterogeneous system was almost the same with that of the corresponding homogeneous system.

A system similar to that used in the present study may be used as a model for the visible light-induced generation of high-energy substances. It seems possible to make a system consinsting of an ion-exchange resin in which the photosensitizer, acceptor, and donor are all localized in its cluster network. When we use such a system, a more efficient model for solar-energy conversion may be designed. Moreover, if we could use a transparent thin film made of ion-exchange resin which adsorbed $Ru(bpy)_3{}^{2+}$ and a donor such as MV^{2+} instead of the RMCA resin, a more efficient charge-separation system than the present one could be made. Further experiments in this direction are now being undertaken.

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17) No appreciable amount of the MV^+ was eluted into the bulk of the solution during the illumination. Such a large adsorbability of the monopositive charged species of MV^+ on the cation-exchange resin may be attributable to both the electrostatic and hydrophobic interactions between the MV^+ and the resins.[18)]

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19) The amounts of $Ru(bpy)_3{}^{2+}$, MV^{2+}, and MV^+ adsorbed on the cation-exchange resin are conveniently represented as [Ru(II)], $[MV^{2+}]$, and $[MV^+]$ respectively, while the unit of the "concentration" is denoted by mol g^{-1}.