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Photoredox Reactions Using Ion-Exchange Resin-Adsorbed $Ru(bpy)_3{}^{2+}$. Photosensitized Reductions of Methyl Viologen and Molecular Oxygen Using Ion-Exchange Resin-Adsorbed Tris(2,2′-bipyridine)ruthenium(II)

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The $Ru(bpy)_3{}^{2+}$ photosensitized reduction of methyl viologen (MV^{2+}) proceeds rapidly in water-swollen iminodiacetic acid type chelate resin beads which adsorbed both $Ru(bpy)_3{}^{2+}$ and MV^{2+} (RM resin). Photosensitized electron-transfer reaction of $Ru(bpy)_3{}^{2+}$ with MV^{2+} takes place in the resin bead with the aid of polymer-bound iminodiacetic acid (PIDA) as a donor. The back-reaction of $Ru(bpy)_3{}^{3+}$ with the methyl viologen radical is prevented by the reduction of $Ru(bpy)_3{}^{3+}$ by PIDA. Photosensitized formation of hydrogen peroxide occurs in an aqueous solution containing RM resin and oxygen. Hydrogen peroxide is produced by the reaction of the adsorbed methyl viologen radical with the dissolved molecular oxygen in the heterogeneous system. The photosensitized reaction mechanisms leading to the formation of the methyl viologen radical and hydrogen peroxide in the water-swollen RM resin system are discussed based on the results obtained.

Introduction

Visible-light-induced chemical reactions with tris(2,2′-bipyridine)ruthenium(II), $Ru(bpy)_3{}^{2+}$, as a photosensitizer are currently under intensive study.[1] One of the well-known $Ru(bpy)_3{}^{2+}$ photosensitized reactions to generate methyl viologen radical, MV^+, involves the reduction of methyl viologen, MV^{2+}, with electron donors such as EDTA and triethanolamine (TEOA). Previously, we reported that the photosensitized formation of hydrogen peroxide proceeds in oxygen-containing aqueous solutions of $Ru(bpy)_3{}^{2+}$–$SbCl_3$[2] and $Ru(bpy)_3{}^{2+}$–ascorbic acid.[3] In these systems the hydrogen peroxide is generated from oxygen via the superoxide ion which is produced by the reaction of the lowest excited state of $Ru(bpy)_3{}^{2+}$, $^*Ru(bpy)_3{}^{2+}$, with O_2. The $SbCl_3$ and ascorbic acid act as an electron donor for the oxidized species of $Ru(bpy)_3{}^{2+}$.

It was reported that the cation-exchange resin Sephadex-SP[4] or the perfluorosulfonate membrane Nafion 120[5] adsorbed $^*Ru(bpy)_3{}^{2+}$ ions are quenched by various metal ions and the quenching reactions are dynamic processes and not static quenching in these environments. In the former case, the apparent increase in the quenching efficiency was attributed to the high local concentrations of the donor and quenchers in the domain of the polymer.[4] In the latter case, the quenching process in the cluster network of the membrane was found to be very similar to nonhomogeneous quenching in micellar systems.[5]

The luminescence behavior of $Ru(bpy)_3{}^{2+}$ in aqueous solution is affected in the presence of poly(stylenesulfonate) (PSS);[6] the luminescence intensity increases with increasing concentration of PSS along with a red-shift of the luminescence maximum. A "coooperative effect" was proposed in order to explain the relatively strong interaction between $Ru(bpy)_3{}^{2}$ and PSS polymer chains. Polymer-supported $Ru(bpy)_3{}^{2+}$ was synthesized and the quenching rates of the excited state of the polymer-bound $^*Ru(bpy)_3{}^{2+}$ analogue with some metal and metal complex ions were observed.[7] The enhancement of the quenching rate by the Cu^{2+} ion was attributed to the formation of a hybrid metal complex with the polymeric ligand.

No net redox reactions, however, occur in all of those systems because fast back-reactions of the oxidized species of $Ru(bpy)_3{}^{2+}$ with the reduced species of the acceptors take place.

In the $Ru(bpy)_3{}^{2+}$ photosensitized reduction of the acceptor, in order to promote charge separation, we are interested in increasing the rate of reaction of $^*Ru(bpy)_3{}^{2+}$ with the electron acceptor, while decreasing the rate of back-reaction. It was expected that in the former reaction $^*Ru(bpy)_3{}^{2+}$ would find itself in the neighborhood of the acceptor and for the latter reaction each $^*Ru(bpy)_3{}^{2+}$ would

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[1] (a) C. R. Bock, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **96**, 4710 (1974); (b) C. Creutz and N. Sutin, *Proc. Natl. Acad. Sci. U.S.A.*, 72, 2858 (1975); (c) R. C. Young, T. J. Meyer, and D. G. Whitten, *J. Am. Chem. Soc.*, **98**, 286 (1976); (d) K. Takuma, K. Kajiwara, and T. Matsuo, *Chem. Lett.*, 1199 (1977); (e) W. Ford, J. W. Otvos, and M. Calvin, *Nature (London)*, **274**, 507 (1978); (f) K. Kalyanasundarum, J. Kiwi, and M. Grätzel, *Helv. Chim. Acta*, **61**, 2720 (1978); (g) J. M. Lehn, J-P. Sauvage, and R. Ziessel, *Nouv. J. Chim.*, **3**, 423 (1979); (h) D. Meisel, M. S. Matheson, and J. Rabani, *J. Am. Chem. Soc.*, **100**, 117 (1978); (i) D. G. Whitten, *Acc. Chem. Res.*, **13**, 83 (1980); (j) S. F. Chan, M. Chou, C. Creutz, T. Matsubara, and N. Sutin, *J. Am. Chem. Soc.*, **103**, 369 (1981).

[2] Y. Kurimura and R. Onimura, *Inorg. Chem.*, **19**, 3516 (1980).

[3] Y. Kurimura, H. Yokota, and Y. Muraki, *Bull. Chem. Soc. Jpn.*, **54**, 2450 (1981).

[4] A. T. Thornton and G. S. Laurence, *J. Chem. Soc., Chem. Commun.*, 408 (1978).

[5] P. C. Lee and D. Meisel, *J. Am. Chem. Soc.*, **102**, 5477 (1980).

[6] Y. Kurimura, H. Yokota, K. Shigehara, and E. Tsuchida, *Bull. Chem. Soc. Jpn.*, **55**, 55 (1982).

[7] Y. Kurimura, N. Shinozaki, F. Ito, Y. Uratani, K. Shigehara, E. Tsuchida, M. Kaneko, and A. Yamada, *Bull. Chem. Soc. Jpn.*, **55**, 380 (1982).

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be surrounded by the scavenger of the oxidized product of it. Thus, we made an attempt to use the iminodiacetic acid type chelate resins which adsorbed both $Ru(bpy)_3^{2+}$ and MV^{2+} as photosensitizer and acceptor, respectively. In this system we would expect that the polymer-bound iminodiacetic acid acts as an electron donor.

Experimental Section

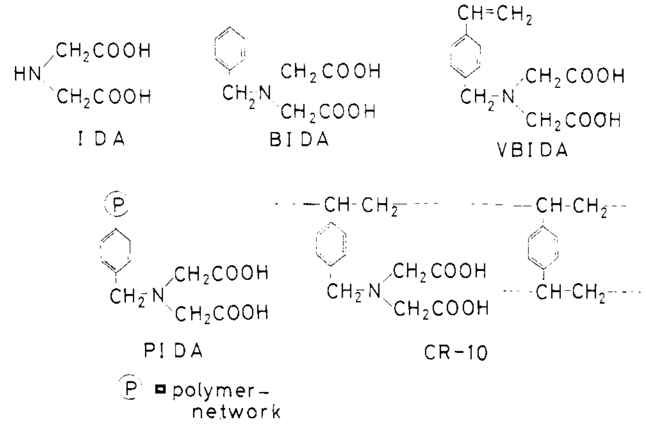
$[Ru(bpy)_3]Cl_2·6H_2O$ was prepared according to the literature method.[8] *N*-Vinylbenzyliminodiacetic acid (VBIDA)[9] and *N*-benzyliminodiacetic acid (BIDA)[9] were synthesized in a manner similar to that described elsewhere.[10] $CuSO_4·5H_2O$, the disodium salt of EDTA, and other reagents were the best commercial grade available. The ion-exchange resin used for the experiments was obtained as follows: the iminodiacetic acid type chelate resin (Diaion CR-10, the sodium form, 15–40 mesh) was washed with about a 20-fold volume of 1 M hydrochloric acid and then washed with a large amount of water. The resin was then washed with 1 M sodium sulfate until no chloride ions were detected in the effluent. Finally, the resin was washed with water until the effluent was transparent in the UV region and dried at 60 °C. The exchange capacity of the chelate resin determined by means of column exchange chromatography with Cu^{2+} ions at pH 6.2 and 25 ± 0.1 °C was 1.98×10^{-3} equiv g^{-1} of dry resin.[11] The amounts of uptake of $Ru(bpy)_3^{2+}$ and MV^{2+} were determined spectrophotometrically from the concentrations of these in the solution after equilibrium. The concentration of Cu^{2+} was determined by means of an atomic absorption spectrometer with a Hitachi Model 200-10 spectrometer. The concentrations of $Ru(bpy)_3^{2+}$ and MV^{2+} were determined by solution spectrophotometry at 456 ($\epsilon = 13600$ M^{-1} cm^{-1}) and 257 nm ($\epsilon = 21000$ M^{-1} cm^{-1}), respectively, with a Hitachi Model 320 spectrophotometer. The ion-exchange resin beads which adsorbed $Ru(bpy)_3^{2+}$ and MV^{2+} (abbreviated as RM resin) were prepared from iminodiacetic acid type chelate resin beads (CR resin, the sodium form), $[Ru(bpy)_3]Cl_2·6H_2O$, and the chloride salt of methyl viologen. The resin beads were equilibrated with a stirred solution containing the desired amounts of these solutes for at least 2 h. These solutes were found to be quantitatively adsorbed on the resin under the conditions employed (the total amount of solutes <30% of the exchange capacity of the resin). The resulting resin beads were filtered, washed with water, and dried at 60 °C in darkness. The reflectance spectrum of the methyl viologen radical in RM resin was recorded on a Hitachi Model 320 spectrometer equipped with an integrating sphere accessory Model 210-2102 with a glass cell (10 mm × 10 mm), in which the RM resin and, usually, buffer solution (acetate or phosphate) were filled compactly, with aluminum oxide as a reference. The RM resin and the buffer solution were packed into the cell and the cell was illuminated with a 150-W slide projector with UV cutoff filter (Kenko Skylight L-40, UV) at 25 ± 0.5 °C. The distance from the center of the tungsten lamp to the surface of the cell wall was 120 mm. A procedure typical of kinetic experiments for the formation of hydrogen peroxide was used as follows: To 50 mL of buffer solution in a 100-mL Erlenmeyer flask was added 0.20 g of the RM resin beads and the mixture was allowed to stand for 1 h in darkness. The flask was kept in a water bath thermostated at 25 ± 0.2 °C, which was made of a transparent poly(acrylic acid) resin, then, oxygen or air or, in some cases, an O_2–N_2 mixture was bubbled through the solution. The mixture was illuminated with the same light source as used for methyl viologen reduction. The light source was located below the water bath and the mixture of the resin beads and aqueous solution were well stirred by bubbling the gas. The distance from the center of the tungsten lamp and the bottom of the flask was 120 mm. Aliquots of the illuminated solution were poured into a column (10 mm diameter and 20 mm length) of cation-exchange resin (Dowex 50-W-X-8, 100–200 mesh, sodium form)[12] followed by washing with water. The concentration of hydrogen peroxide in the eluate was determined colorimetrically.[13] The types of chelating agents used as donors and the resins used for the experiments except for EDTA are summarized in Table I and Chart I.

TABLE I: Types of Chelating Agents[a] and Resins Used for the Experiments

abbrev	substance	note
	Chelating Agent	
IDA	iminodiacetic acid	*b*
BIDA	*N*-benzyliminodiacetic acid	*b*
VBIDA	*N*-vinylbenzyliminodiacetic acid	*b*
PIDA	polymer-supported iminodiacetic acid of CR-10	1 g of dry CR-10 contains ca. 1.0×10^{-3} mol unit of PIDA[b]
	Resin	
CR-10 resin	iminodiacetic acid type chelate resin (Diaion CR-10)	white, translucent, exchange capacity is 1.0×10^{-3} mol g^{-1} for Cu^{2+} [b]
Cr-Cu resin	CR-10 resin absorbing Cu^{2+}	blue
RMC resin	CR-10 resin absorbing $Ru(bpy)_3^{2+}$ and MV^{2+}	light orange

[a] Except for EDTA. [b] Structures are given in Chart I.

Chart I



Results and Discussion

In an aqueous solution, both $Ru(bpy)_3^{2+}$ and MV^{2+} were found to be well adsorbed on the iminodiacetic acid type chelate resin. The uptake of $Ru(bpy)_3^{2+}$ and MV^{2+} was followed by determinations of the concentrations of Ru-

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(8) R. Palmer and T. S. Piper, *Inorg. Chem.*, 5, 864 (1966).

(9) VBIDA (disodium salt) used was a mixture of *p*- and *m*-vinylbenzyliminodiacetic acid and used without separation.

(10) A. Uehara, E. Kyuno, and R. Tsuchiya, *Bull. Chem. Soc. Jpn.*, 43, 1394 (1970).

(11) About 1.0×10^{-3} mol of the PIDA units are attached to 1 g of the chelate resins since the exchange capacity of the CR-10 resins is 1.98×10^{-3} equiv g^{-1}.

(12) The cation-exchange resins were used to remove the $Ru(bpy)_3^{2+}$ and MV^{2+} which were contained in small amounts in the prolonged time-illuminated solutions.

(13) E. B. Sandell, "Colorimetric Determination of Trace of Metals", 2nd ed, Interscience, New York, 1950, p 572.

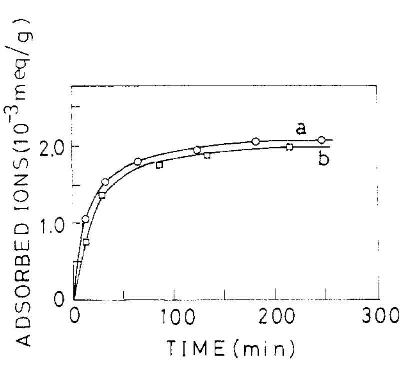

Figure 1. Adsorption of $\mathrm{Ru(bpy)_3^{2+}}$ or $\mathrm{MV^{2+}}$ on the chelate resin (0.050 g) in 10 mL of an aqueous solution containing 0.10 M $\mathrm{Ru(bpy)_3^{2+}}$ (a) or 0.10 M $\mathrm{MV^{2+}}$ (b) at 25 °C.

$\mathrm{(bpy)_3^{2+}}$ and $\mathrm{MV^{2+}}$, respectively, in the solution. The amount of adsorbed $\mathrm{Ru(bpy)_3^{2+}}$ and $\mathrm{MV^{2+}}$ on the resin beads is plotted as a function of time in parts a and b of Figure 1, respectively. From the results shown in this figure, the exchange capacities of the chelate resin for $\mathrm{Ru(bpy)_3^{2+}}$ and $\mathrm{MV^{2+}}$ are estimated to be about 1.9×10^{-3} and 2.0×10^{-3} mequiv $\mathrm{g^{-1}}$, respectively. Throughout all experiments the total amounts of adsorbed $\mathrm{Ru(bpy)_3^{2+}}$ and $\mathrm{MV^{2+}}$ were usually kept less than 2.0×10^{-4} mol $\mathrm{g^{-1}}$ which corresponds to about 20% of the exchange capacity of the resin. Under such conditions, no appreciable amount of the adsorbed ions was eluted into the bulk solution when 1 g of the resins were kept in 50 mL of the buffer solution (pH 7.4, $\mu = 0.03$) over night.

Formation of Methyl Viologen Radicals in RM Resin. With illumination of RM resin beads in deaerated water, the color of the beads turned rapidly from light orange to a dark violet through a light green as the result of formation of methyl viologen radicals. The cation-exchange resin (Dowex-50W-X-8, sodium form) was also found to adsorb both $\mathrm{Ru(bpy)_3^{2+}}$ and $\mathrm{MV^{2+}}$. However, no photosensitized reduction of $\mathrm{MV^{2+}}$ occurred in the resin at pH 3–8. Therefore, it may be concluded that the polymer-bound iminodiacetic acid acts as the electron donor for the oxidized species of the chromophore in the RM resin.

The reflectance spectral change of the RM resin with illumination is presented in Figure 2. The shape of the reflectance spectrum of the nonilluminated RM resin (spectrum b) is very similar to that of the absorption spectrum of $\mathrm{Ru(bpy)_3^{2+}}$ in aqueous solution ($\lambda_{\mathrm{max}} = 456$ nm) although it was slightly red shifted (ca. 10 nm). In this figure, a rapid increase in the spectral band ($\lambda_{\mathrm{max}} = 608$ nm) is seen as the result of the progressive formation of the methyl viologen radical. The shape and the maximum of the reflectance spectrum of the adsorbed methyl viologen radical in the visible region are similar to those of the absorption spectrum. One of the 1-min illuminated RM resins had been dried under darkness and cut into two hemispheres. The cut surface was then examined under a microscope. The dark violet color of the methyl viologen radical was found to have spread homogeneously on the surface. The observation seems to indicate that the reaction proceeded almost homogeneously and/or the rate of the exchange of the methyl viologen radicals is rapid at least in a given resin bead.

The results are best interpreted by a mechanism in which the back-reaction of $\mathrm{Ru(bpy)_3^{3+}}$ with $\mathrm{MV^+}$ is prevented by the reaction of Ru(III) with polymer-bound iminodiacetic acid (PIDA). Under the conditions employed, as the number of PIDA units are sufficiently larger than that of the $\mathrm{Ru(bpy)_3^{2+}}$ and the latter should contact intimately with at least one or two of the PIDA moieties, thus, the scavenging reaction of the oxidized species of $\mathrm{Ru(bpy)_3^{2+}}$ by PIDA would occur efficiently. The main features of the reaction scheme for the photosensitized reduction of methyl viologen are represented by eq 1–6.

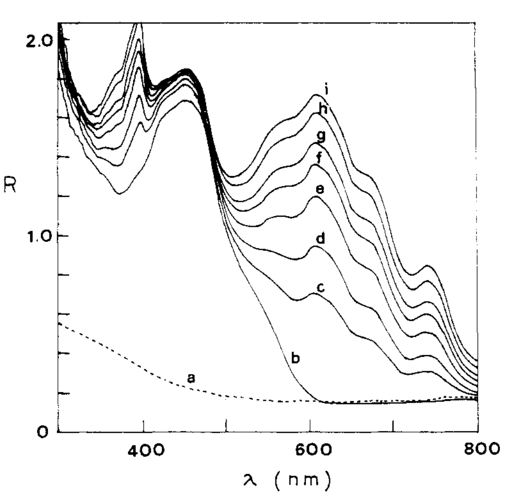

Figure 2. Reflectance spectra of the chelate resin (a) and reflectance spectral change of the RM resin (1.0×10^{-5} mol $\mathrm{g^{-1}}$ of Ru(II), 5.0×10^{-5} mol $\mathrm{g^{-1}}$ of $\mathrm{MV^{2+}}$) in $\mathrm{N_2}$-saturated water at 25 °C. Illumination times (s) were as follows: (b) 0; (c) 15; (d) 39; (e) 60; (f) 90; (g) 120; (h) 180; (i) 240.

$$[\mathrm{Ru(II)(MV^{2+})}_m\mathrm{(PIDA)}_n]_\mathrm{r} \xrightarrow{h\nu} [{}^*\mathrm{Ru(II)(MV^{2+})}_m\mathrm{(PIDA)}_n]_\mathrm{r} \tag{1}$$

$$[{}^*\mathrm{Ru(II)(MV^{2+})}_m\mathrm{(PIDA)}_n]_\mathrm{r} \rightarrow [\mathrm{Ru(II)(MV^{2+})}_m\mathrm{(PIDA)}_n]_\mathrm{r} + \Delta + h\nu' \tag{2}$$

$$[{}^*\mathrm{Ru(II)(MV^{2+})}_m\mathrm{(PIDA)}_n]_\mathrm{r} \rightarrow [\mathrm{Ru(III)(MV^{+})(MV^{2+})}_{m-1}\mathrm{(PIDA)}_n]_\mathrm{r} \tag{3}$$

$$[\mathrm{Ru(III)(MV^{+})(MV^{2+})}_{m-1}\mathrm{(PIDA)}_n]_\mathrm{r} \rightarrow [\mathrm{Ru(II)(MV^{2+})}_m\mathrm{(PIDA)}_n]_\mathrm{r} \tag{4}$$

$$[\mathrm{Ru(III)(MV^{+})(MV^{2+})}_{m-1}\mathrm{(PIDA)}_n]_\mathrm{r} \rightarrow [\mathrm{Ru(II)(MV^{+})(MV^{2+})}_{m-1}\mathrm{(PIDA_{ox})(PIDA)}_{n-1}]_\mathrm{r} \tag{5}$$

$$[\mathrm{Ru(II)(MV^{+})(MV^{2+})}_{m-1}\mathrm{(PIDA)_{ox}(PIDA)}_{n-1}]_\mathrm{r} + \mathrm{M^+} \rightarrow [\mathrm{Ru(II)(M^{+})(MV^{2+})}_{m-1}\mathrm{(PIDA)_{ox}(PIDA)}_{n-1}]_\mathrm{r} + \mathrm{MV^+} \tag{6}$$

In these equations, the chemical species written in brackets with subscript r represent those adsorbed on the resin; the subscript m and n denote the ratios of the average number of $\mathrm{MV^{2+}}$ and PIDA to a $\mathrm{Ru(bpy)_3^{2+}}$ molecule in the resin, respectively; Ru(II), Ru(III), and *Ru(II) represent $\mathrm{Ru(bpy)_3^{2+}}$, $\mathrm{Ru(bpy)_3^{3+}}$, and $\mathrm{{}^*Ru(bpy)_3^{2+}}$, respectively; and $\mathrm{PIDA_{ox}}$ is the oxidized species of PIDA. The oxidative quenching reaction (eq 3) competes with the deactivation process of *Ru(II) (eq 2) and the scavenging reaction of Ru(III) by PIDA (eq 5) competes with the back-reaction (eq 4). Equation 6 represents the ion-exchange equilibrium of adsorbed $\mathrm{MV^+}$ with a simple cation ($\mathrm{M^+}$) such as $\mathrm{Na^+}$ or $\mathrm{H^+}$ in solution. In order to check the rate of discharge by the exchange of $\mathrm{MV^+}$ from the resin, we have carried out the following examination. Water-swollen RM resin beads were illuminated for 3 min and the reflectance spectra of the beads were recorded immediately after the illumination was stopped and the beads were allowed to stand for 5 min. However, notable differences between these was not observed. This indicates that the rate of discharge of the $\mathrm{MV^+}$ cations from the ion-exchange resin beads is relatively slow. If we use a solution containing a higher concentration of simple salt than that used in the present experiment, more rapid discharge of $\mathrm{MV^+}$ would occur. However, further experiments were not carried out.

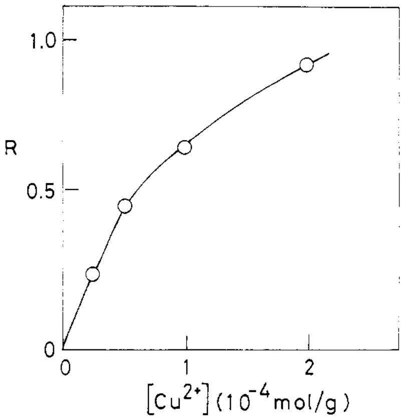

Figure 3. Plots of R vs. amounts of Cu^{2+} adsorbed on the chelate resin in aqueous solution at pH 6.4 and 25 °C.

As a relative measure of the concentration of the methyl viologen radicals in the RM resin beads, we take a value of R defined by

$$R = \log (100/r)$$

where r is the reflectance (%). If the conditions wherein the reflectance spectrum is observed are the same, the amount of methyl viologen radicals in the resins, which are located in the first layer of the cell interior where incident light from the photometer light source is absorbed and reflected, should be related to R. In this connection, a relationship between R and the concentration of the adsorbed metal ions on the resin was examined by using a Cu^{2+} adsorbed chelate resin (CR-Cu resin). About 3 mL of water-swollen CR-Cu resin beads and a small amount of the buffer solution (pH 6.2, $\mu \simeq 0.02$) were packed into the cell (10 mm × 10 mm); then, the reflectance, r, of the resin beads was determined at the band maximum (735 nm). In Figure 3, the value of R is plotted as a function of the amount of Cu^{2+} adsorbed which is defined by the "concentration" of Cu^{2+},[14] $[Cu^{2+}]$ (mol g^{-1}). This figure shows that the value of R is almost proportional to the concentration of Cu^{2+} in the resin beads when R is less than about 0.4. Thus, we concluded that the concentration of methyl viologen radical in the resin beads is regarded to be proportional to R at $\lambda_{max} = 608$ nm if it is smaller than about 0.4.

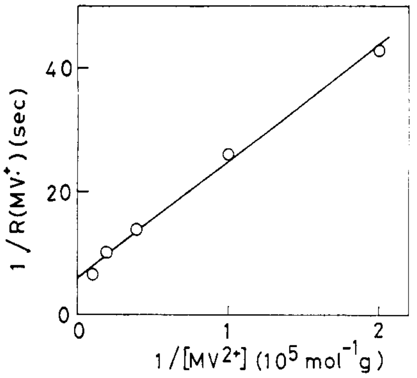

Figure 4. Plot of $1/R(MV^+)$ vs. $1/[MV^{2+}]$.

The relative rate of formation of methyl viologen radical, $R(MV^+)$ ($= dR/dt$), was determined from the slope of R vs. time plots at the initial state. A semiquantitative analysis of the reaction kinetics for methyl viologen radical formation in the RM resin beads–aqueous solution system by means of reflectance spectrum could be carried out if the assumption described below is made. The assumption that must be made is that the rates of the ion-exchange adsorption equilibrium reactions of MV^{2+}, $Ru(bpy)_3{}^{2+}$, and MV^+ in the interior of a given resin bead would be fast compared with those of the redox reactions occurring in the resin and, thus, the reactive species would be always distributed homogeneously, so the reactions occurring in the resins are regarded as well as those occurring in the homogeneous solution.[14] On the basis of this assumption and the reaction mechanism represented by eq 1–5, a steady-state approximation could be applied for the concentrations of $^*Ru(bpy)_3{}^{2+}$ and $Ru(bpy)_3{}^{3+}$; the steady-state concentrations of these are given by eq 7 and 8.[15] In

$$[^*\mathrm{Ru(II)}] = \frac{AI_0[\mathrm{Ru(II)}]}{k_2 + k_3[\mathrm{MV}^{2+}]} \tag{7}$$

$$[\mathrm{Ru(III)}] = \frac{k_3[^*\mathrm{Ru(II)}][\mathrm{MV}^{2+}]}{k_4[\mathrm{MV}^+] + k_5[\mathrm{PIDA}]} \tag{8}$$

these equations, A is a constant which is determined by the experimental conditions and I_0 is the light intensity; k_1, ..., k_5 are the rate constants of the corresponding reactions. The rate of formation of the methyl viologen radical defined by the moles of MV^+ formed per gram of resin per unit time, is given by

$$\mathrm{d}[\mathrm{MV}^+]/\mathrm{d}t = k_3[^*\mathrm{Ru(II)}][\mathrm{MV}^{2+}] - k_4[\mathrm{Ru(III)}][\mathrm{MV}^+] \tag{9}$$

From eq 7–9, we obtain

$$\frac{\mathrm{d}[\mathrm{MV}^+]}{\mathrm{d}t} = \left(\frac{k_3AI_0[\mathrm{Ru(II)}][\mathrm{MV}^{2+}]}{k_2 + k_3[\mathrm{MV}^{2+}]}\right)\left(\frac{k_5[\mathrm{PIDA}]}{k_4[\mathrm{MV}^+] + k_5[\mathrm{PIDA}]}\right) \tag{10}$$

When $k_4[MV^+] << k_5[PIDA]$, $d[MV^+]/dt$ is given by

$$\frac{\mathrm{d}[\mathrm{MV}^+]}{\mathrm{d}t} = \frac{k_3AI_0[\mathrm{Ru(II)}][\mathrm{MV}^{2+}]}{k_2 + k_3[\mathrm{MV}^{2+}]} \tag{11}$$

Equation 11 can be rewritten as

$$\frac{1}{\mathrm{d}[\mathrm{MV}^+]/\mathrm{d}t} = \frac{1}{AI_0[\mathrm{Ru(II)}]}\left(1 + \frac{k_2}{k_3[\mathrm{MV}^{2+}]}\right) \tag{12}$$

In the present case, as the relative rate of methyl viologen radical formation, $R(MV^+)$, should be proportional to the $d[MV^+]/dt$, eq 13 is obtained

$$\frac{1}{R(\mathrm{MV}^+)} = \frac{\alpha}{I_0[\mathrm{Ru(II)}]}\left(1 + \frac{k_2}{k_3[\mathrm{MV}^{2+}]}\right) \tag{13}$$

where α is a constant at a given experimental conditions. At a given [Ru(II)], plots of $1/R(MV^+)$ vs. $1/[MV^{2+}]$ should be linear if the reaction mechanism represented by eq 1–5 and the assumption made are valid. In Figure 4, the value of $1/R(MV^+)$ is plotted as a function of 1/

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[14] (a) The amounts of Cu^{2+}, $Ru(bpy)_3{}^{2+}$, MV^{2+}, and MV^+ adsorbed on the chelate resin are conveniently represented as [Ru(II)], $[MV^{2+}]$, and $[MV^+]$, respectively, and the unit of the "concentration" is denoted by mol g^{-1}. (b) In the following discussion, the apparent rate constants are represented by k_i and the units of k_i are s^{-1} for first-order reactions and mol g^{-1} s^{-1} for second-order reactions.

[15] In addition, the assumption is made that it could be safely concluded that the PIDA moieties are distributed uniformly in the resin.

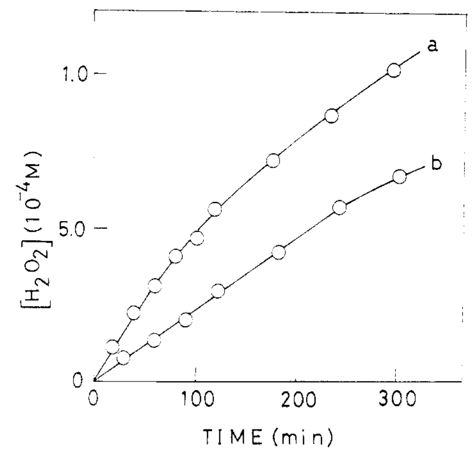

Figure 5. Generation of hydrogen peroxide with illumination of 0.20 g of the RM resin (1.0 × 10^{-5} mol g^{-1} of Ru(II), 5.0 × 10^{-5} mol g^{-1} of MV^{2+}) in 50 mL of O_2-saturated (a) and air-saturated (b) solutions at pH 7.4 and 25 °C.

$[MV^{2+}]$. An almost linear dependence of $1/R(MV^+)$ on $1/[MV^{2+}]$ is seen in Figure 4. This observation indicates that reactions 1–5 represent the main features of the photosensitized reduction of methyl viologen in the RM resin system and that the back-reaction (eq 4) could be ignored compared with the scavenging reaction of Ru(III) by PIDA in the initial stage.

The ratio of k_2/k_3 could be obtained from the values of the intercept and the slope of the $1/R(MV^+)$ vs. $1/[MV^{2+}]$ plots. The plot has an intercept of 6.5 s and a slope of 1.9 × 10^{-4} mol g^{-1} s. We then estimated that k_2/k_3 is 2.9 × 10^{-5} mol^{-1} g. The ratio of *Ru(II) that reacts with MV^{2+} can be represented by

$$\frac{V_3}{V_2 + V_3} = \frac{k_3[\text{*Ru(II)}][\text{MV}^{2+}]}{k_2[\text{*Ru(II)}] + k_3[\text{*Ru(II)}][\text{MV}^{2+}]} = \frac{1}{1 + \dfrac{k_2}{k_3[\text{MV}^{2+}]}} \quad (14)$$

where V_2 and V_3 are the rates of reactions 2 and 3, respectively. From eq 14 and the value of k_2/k_3, we obtain that about 87% of the excited-state chromophore reacts with the acceptor during its lifetime when $[MV^{2+}]$ = 2.0 × 10^{-4} mol g^{-1}.

Formation of Hydrogen Peroxide in the RM Resin–Aqueous Solution System. As is described in the previous section, the photoinduced rapid formation of the methyl viologen radical proceeds in the RM resin in deaerated aqueous solution. When oxygen gas was flushed into the mixture, the color of the methyl viologen radical rapidly faded and the simultaneous formation of hydrogen peroxide took place in the bulk solution. This suggests that the generation of hydrogen peroxide by the reaction of the methyl viologen radical with dissolved oxygen proceeds in the heterogeneous system. It was already reported that the quenching reaction of *Ru(bpy)_3^{2+} with O_2 gave the superoxide ion[16] (k_q = (3.3 ± 0.2) × 10^9 M^{-1} s^{-1}).[16b]

The rate depends on the concentration of dissolved oxygen (Figures 5 and 6). The rate is, however, relatively insensitive to the oxygen concentration at higher concentrations of oxygen. The results shown in Figures 5 and 6 seem to indicate that the reaction of methyl viologen radicals with oxygen molecules proceeds almost completely

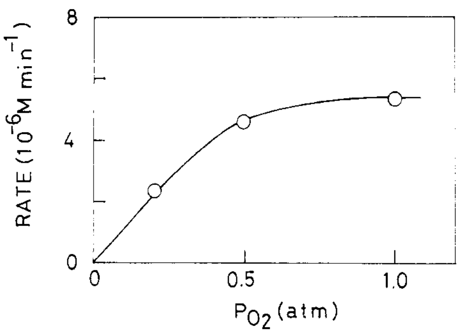

Figure 6. Dependence of the rate of hydrogen peroxide formation on p_{O_2} in 0.20 g of the RM resin (1.0 × 10^{-5} mol g^{-1} of Ru(II), 5.0 × 10^{-5} mol g^{-1} of MV^{2+})–O_2-saturated aqueous solution (50 mL) at pH 7.4 and 25 °C.

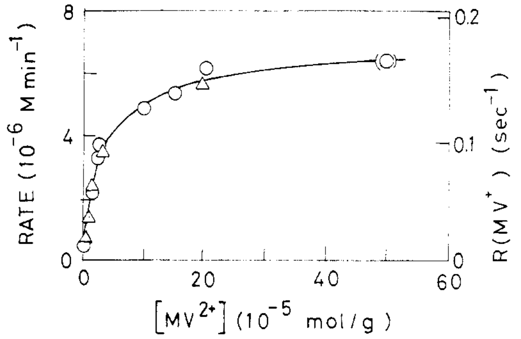

Figure 7. Dependence of the rate of hydrogen peroxide formation on $[MV^{2+}]$ in 0.20 g of the RM resin (1.0 × 10^{-5} mol g^{-1} of Ru(II))–O_2-saturated aqueous solution (50 mL) at pH 7.4 and 25 °C (○) and the relationship between $R(MV^+)$ and $[MV^{2+}]$ (△). In the case represented by –(○)–, about 5% of the adsorbed species was eluted into the solution after 100 min of illumination.

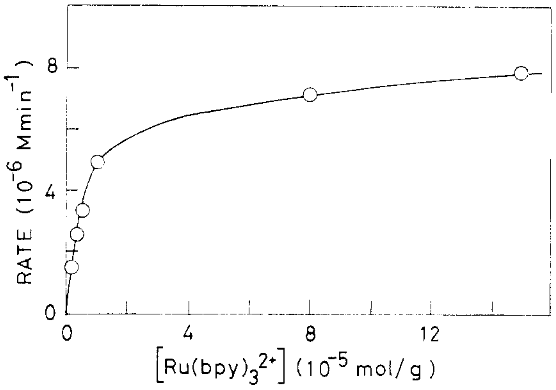

Figure 8. Dependence of the rate of hydrogen peroxide formation on [Ru(II)] in 0.20 g of the RM resin (5.0 × 10^{-5} mol g^{-1} of MV^{2+})–O_2-saturated aqueous solution (50 mL) at pH 7.4 and 25 °C.

in oxygen-saturated solutions under the present experimental conditions.

The effect of the concentration of methyl viologen on the rate is shown in Figure 7. Hydrogen peroxide was formed at a slow rate even if the methyl viologen was absent from the resin. This suggests that direct electron-transfer between the adsorbed *Ru(II) and the dissolved O_2 takes place when the concentration of methyl viologen is small with the aid of PIDA. Such a dependence of the rate on the concentration of methyl viologen is, probably, accounted for by the dependence of $R(MV^+)$ on $[MV^{2+}]$ (see Figure 7). Consequently, the rate profile in Figure 7 is very similar to the $R(MV^+)$ vs. $[MV^{2+}]$ plots as shown in the same figure. A relationship between the rate of formation of hydrogen peroxide and the concentration of Ru(II) in the resin is also shown in Figure 8.

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[16] (a) G. P. Anderson, D. J. Salmon, T. J. Mayer, and R. C. Young, *J. Am. Chem. Soc.*, **99**, 1980 (1977); (b) D. Meisel and M. S. Matheson, *ibid.*, **99**, 6577 (1977).

TABLE II: Comparison of the Rate of Hydrogen Peroxide Formation between the Heterogeneous and Homogeneous Systems at pH 7.4 and 25 °C[a]

system	heterogeneous[b] (RM resin)	homogeneous[c]			
donor	PIDA	IDA	VBIDA	BIDA	EDTA
$d[H_2O_2]/dt$[d]	$(3.8 \pm 0.3) \times 10^{-6}$	[e]	$(8.9 \pm 0.6) \times 10^{-7}$	$(8.3 \pm 0.5) \times 10^{-7}$	$(4.2 \pm 0.8) \times 10^{-7}$

[a] The reaction rates were measured in oxygen-saturated solution (50.0 mL). In all the systems, the amounts (in mol) of Ru(II), MV^{2+}, and the donors in the solutions were adjusted to be the same, i.e., 2.0×10^{-6} mol (Ru(II), 1.0×10^{-5} mol MV^{2+}, and 2.0×10^{-4} mol donor, respectively. [b] 0.20 g of RM resin (1.0×10^{-5} mol g^{-1} of Ru(II), 5.0×10^{-5} mol g^{-1} of MV^{2+}, and ca. 1.0×10^{-4} mol unit of PIDA) in 50 mL of oxygen-saturated solution. [c] 4.0×10^{-5} M of Ru(II), 2.0×10^{-4} M of MV^{2+}, and 2.0×10^{-3} of M donor in 50 mL of oxygen-saturated solution. [d] Units are mol min^{-1}. [e] No detectable amount of H_2O_2 was observed.

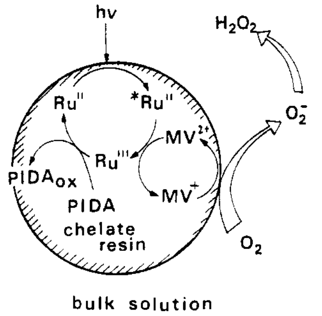

Figure 9. Schematic representation of the generation of hydrogen peroxide in RM resin–O_2-containing aqueous solution.

Probable photoinduced reaction steps leading to hydrogen peroxide formation in the RM resin system are outlined as follows:

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

$$[{}^*Ru(II)(MV^{2+})_m(PIDA)_n]_r \rightarrow [Ru(II)(MV^{2+})_m(PIDA)_n]_r + \Delta + h\nu' \quad (2)$$

$$[{}^*Ru(II)(MV^{2+})_m(PIDA)_n]_r + O_2 \rightarrow [Ru(II)(MV^{2+})_m(PIDA_{ox})(PIDA)_{n-1}]_r + O_2^- \quad (15)$$

$$[{}^*Ru(II)(MV^{2+})_m(PIDA)_n]_r \rightarrow [Ru(III)(MV^+)(MV^{2+})_{m-1}(PIDA)_n]_r \quad (3)$$

$$[Ru(III)(MV^+)(MV^{2+})_{m-1}(PIDA)_n]_r \rightarrow [Ru(II)(MV^{2+})_m(PIDA)_n]_r \quad (4)$$

$$[Ru(III)(MV^+)(MV^{2+})_{m-1}(PIDA)_n]_r \rightarrow [Ru(II)(MV^+)(MV^{2+})_{m-1}(PIDA_{ox})(PIDA)_{n-1}]_r \quad (5)$$

$$[Ru(II)(MV^+)(MV^{2+})_{m-1}(PIDA_{ox})(PIDA)_{n-1}]_r + O_2 \rightarrow [Ru(II)(MV^{2+})_m(PIDA_{ox})(PIDA)_{n-1}]_r + O_2^- \quad (16)$$

Hydrogen peroxide is formed from the supper oxide ions, probably, via the disproportionation reaction[3,17]

$$O_2^- + O_2^- + 2H^+ \text{ (or } HO_2 + HO_2) \rightarrow H_2O_2 + O_2 \quad (17)$$

Other probable reactions producing hydrogen peroxide are the reaction of O_2^- (or HO_2) with *Ru(II) or MV^+ which give H_2O_2 and Ru(III) or MV^{2+}, respectively. The main reactions that account for the photosensitized hydrogen peroxide generation in the heterogeneous system are illustrated schematically in Figure 9. When the RM resin (0.20 g) which adsorbed 1.0×10^{-5} mol g^{-1} of Ru(II), 5.0×10^{-5} mol g^{-1} of MV^{2+} in 50 mL of oxygen-saturated aqueous solution (pH 7.4) was illuminated for 7 h, 1.4×10^{-4} M hydrogen peroxide was formed. Therefore, it is estimated that the turnover numbers are about 7 with respect to all the $Ru(bpy)_3^{2+}$ adsorbed on the resin beads.

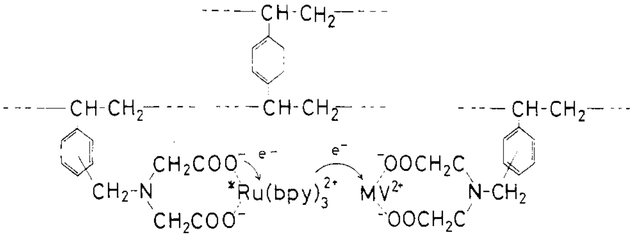

Figure 10. Schematics of the probable reaction mechanism for charge separation.

With illumination of the oxygenated solution (50.0 mL) containing 4.0×10^{-5} M $Ru(bpy)_3^{2+}$, 2.0×10^{-4} M MV^{2+}, and $4.0 \times 10^{-}3$ M iminodiacetic acid (IDA)[20] at pH 7.4 no detectable amounts of hydrogen peroxide were observed for 30 min whereas if we used EDTA, *N*-benzyliminodiacetic acid (BIDA), or its derivatives instead of IDA, some hydrogen peroxide was detected in the solution. The results shown in Table II indicate that the rate in the RM resin system is about four to ten times greater than those in the homogeneous systems. The results of the comparison experiments may be interpreted as follows. In the RM resin system, the iminodiacetic acid is attached to the resin at the nitrogen atom through the benzyl group, making it a tertiary amine, and providing stronger electron-donating properties than the iminodiacetic acid which has a secondary nitrogen atom. The high efficiency for hydrogen peroxide formation in the resin system may be mainly attributable to the following reasons: (1) acceleration of the forward reaction by attracting two positively charged reactants, (2) neutralization of the positive charges on the $Ru(bpy)_3^{2+}$ and MV^{2+} by the negatively charged carboxyl groups of the PIDA moieties (Figure 10), and (3) providing efficient donors for PIDA, which contacts intimately with Ru(II) by an electrostatic interaction, to scavenge the oxidized species of Ru(II) in the resin.

The RM resin and analogous systems may be used for other additional light-induced reactions. By use of such a system an efficient charge separation could be achieved.

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(17) The pK_a values of the following equilibrium reactions were reported to be 4.8[18] for eq 18 and 11.85[19] for eq 19.

$$HO_2 \rightleftarrows H^+ + O_2^- \quad (18)$$

$$H_2O_2 \rightleftarrows H^+ + HO_2^- \quad (19)$$

(18) D. Meisel and G. Czapski, *J. Phys. Chem.*, **79**, 1503 (1975).

(19) J. Jortner and G. Stein, *Bull. Res. Co. Isr.*, **6A**, 239 (1957).

(20) The concentrations of Ru(II), MV^{2+}, and the donor in the homogeneous systems correspond to the equivalent of the corresponding species in the heterogeneous system of 0.20 g of the RM resin (1.0×10^{-5} mol g^{-1} Ru(II), 5.0×10^{-5} mol g^{-1} MV^{2+}, about 1.0×10^{-3} mol of PIDA) in 50 mL of aqueous solution.