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Letter

Micellar-promoted Stereoselective Photoreduction of Potassium Ethylenediaminetetraacetatocobaltate(III) by a Long-chain Chiral Ruthenium(II) Complex

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Although extensive research on the photo-induced electron transfer reactions of $Ru(bpy)_3^{2+}$ (bpy = bipyridine) has recently centered around the micellar-promoted [1, 2] or stereoselective [3, 4] photoreactions of Δ (or Λ)-$Ru(bpy)_3^{2+}$ or Ru(bpy $deriv)_3^{2+}$ (bpy deriv = long-chain bipyridine derivatives), there is no report dealing with the micellar-promoted stereoselective photoreaction of long-chain ruthenium(II) complexes. This paper describes the micellar-accelerated chiroselective photoreduction of potassium ethylenediaminetetraacetatocobaltate(III), KCo(edta), by the following long-chain chiral ruthenium(II) complex with ionic or nonionic surfactants of cetyltrimethylammonium bromide (CTAB), polyoxyethylene (9.5) octylphenol (Triton X), and sodium dodecylsulfate (SDS). (See overleaf for reactions).

The ligand of bpy—Men (or bpy—C_{12}) was obtained via the esterification of 4,4′-dicarboxy-2,2′-bipyridine with l-menthol (or dodecyl alcohol), and $[Ru(bpy{-}Men)_2(bpy{-}C_{12})]^{2+}Cl_2$ was prepared by the reaction of bpy—C_{12} and $[Ru(bpy{-}Men)_2]^{2+}Cl_2$ which was obtained from $RuCl_3$ and bpy—Men. Since $Ru(bpy{-}Men)_2(bpy{-}C_{12})^{2+}$ has a CTTL (charge transfer to ligand) excitation at 470 nm ($\epsilon = 18\,000$ mol^{-1} dm^2; emission spectrum at 615 nm) in EtOH, the present photoreaction of $Ru(bpy{-}Men)_2(bpy{-}C_{12})^{2+}$ and (+) or (−)-$Co(edta)^-$ ($\lambda_{max}(\epsilon) = 385$ (229) and 538 nm (324 mol^{-1} dm^2)) was carried out in the range of $h\nu > 430$ nm with a cut-off filter, as described below.

The homogeneous 10 vol.% $EtOH{-}H_2O$ solution containing Ru-$(bpy{-}Men)_2(bpy{-}C_{12})^{2+}$ (2.7×10^{-5} mol dm^{-3}), (+)- or (−)-$Co(edta)^-$ (4.0×10^{-4} mol dm^{-3}) and/or the surfactant ($(0 - 6.0) \times 10^{-3}$ mol dm^{-3}) was irradiated by a 500 W xenon lamp ($h\nu > 430$ nm) without stirring at 28 °C in a nitrogen atmosphere, and the reaction rate was followed by the determination of the reacted amount of $Ru(bpy{-}Men)_2(bpy{-}C_{12})^{2+}$ at 470 nm.

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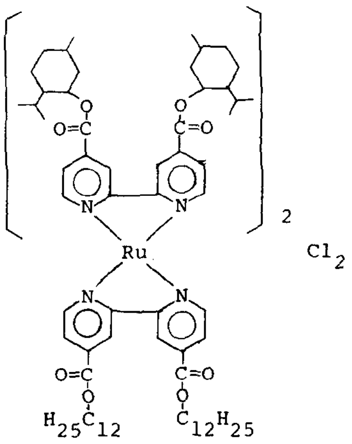
$$\left.\begin{array}{l}\mathrm{Ru(bpy{-}Men)_2(bpy{-}C_{12})^{2+} + (+)\text{-}Co(edta)^-} \\ \mathrm{Ru(bpy{-}Men)_2(bpy{-}C_{12})^{2+} + (-)\text{-}Co(edta)^-}\end{array}\right\rangle \xrightarrow{h\nu\ (>430\ \mathrm{nm})}$$

$$\mathrm{Ru(bpy{-}Men)_2(bpy{-}C_{12})^{3+} + Co(edta)^{2-}}$$

$[\mathrm{Ru(bpy{-}Men)_2(bpy{-}C_{12})]^{2+}Cl_2}$ =



As can be seen from a typical example of the rate of the present reaction (Fig. 1), the photoreaction obeyed a second-order rate law during the initial stage of the reaction (conversion $\leq$10%), but it proceeded in more complicated fashion after the initial reaction stage. Probably, the energetically favorable reduction potential (1.26 V [5]) of $\mathrm{Ru^{3+}/Ru^{2+}}$ and oxidation potential (0.38 V [6]) of $\mathrm{Co(edta)^-/Co(edta)^{2-}}$ promoted the reverse reaction, $\mathrm{Ru(bpy{-}Men)_2(bpy{-}C_{12})^{3+} + Co(edta)^{2-} \rightarrow Ru(bpy{-}Men)_2(bpy{-}C_{12})^{2+} + Co(edta)^-}$, on the cationic micellar surface. It is worth noting here that the second-order rate constants estimated from the linear relationship in Fig. 1 ($k^+ = 4.80 \times 10^{-2}\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$ for the (+)-Co(edta)$^-$ reduction and $k^- = 3.65 \times 10^{-2}\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$ for the (—)-Co(edta)$^-$ reduction) are apparently different between the k^+ and k^- values, and that the enantiomer rate ratio $k^+/k^- = 1.32$ supports the stereoselective photoreduction of (+)- and (—)-Co(edta)$^-$ by the chiral ruthenium(II) complex. More detailed aspects of the present stereoselective photoreaction were then investigated through the quenching of photo-excited triplet-state $[\mathrm{Ru(bpy{-}Men)_2(bpy{-}C_{12})^{2+}}]^*$ by (+)- or (—)-Co(edta)$^-$ at 470 nm (25 °C).

The present photo-induced electron transfer from $\mathrm{Ru(bpy{-}Men)_2(bpy{-}C_{12})^{2+}}$ (abbreviated by Ru(III)) to Co(edta)$^-$ (denoted by Co(III)) can be simplified as follows:

$$\mathrm{Ru(II)} \xrightarrow{h\nu} \mathrm{Ru(II)^*}$$

$$\mathrm{Ru(II)^*} \xrightarrow{k_e} \mathrm{Ru(II)} + h\nu$$

$$\mathrm{Ru(II)^*} \xrightarrow{k_\mathrm{i}} \mathrm{Ru(II)} + \Delta$$

$$\mathrm{Ru(II)^*} \xrightarrow{k_\mathrm{di}} \mathrm{Ru(II)}$$

$$\mathrm{Ru(II)^*} + \mathrm{Co(III)} \xrightarrow{k_\mathrm{r}} [\mathrm{Ru(III)\cdot Co(II)}]^*$$

$$[\mathrm{Ru(III)\cdot Co(II)}]^* \xrightarrow{k_\mathrm{b}} \mathrm{Ru(II)} + \mathrm{Co(III)}$$

$$[\mathrm{Ru(III)\cdot Co(II)}]^* \xrightarrow{k_\mathrm{p}} \mathrm{Ru(III)} + \mathrm{Co(II)}$$

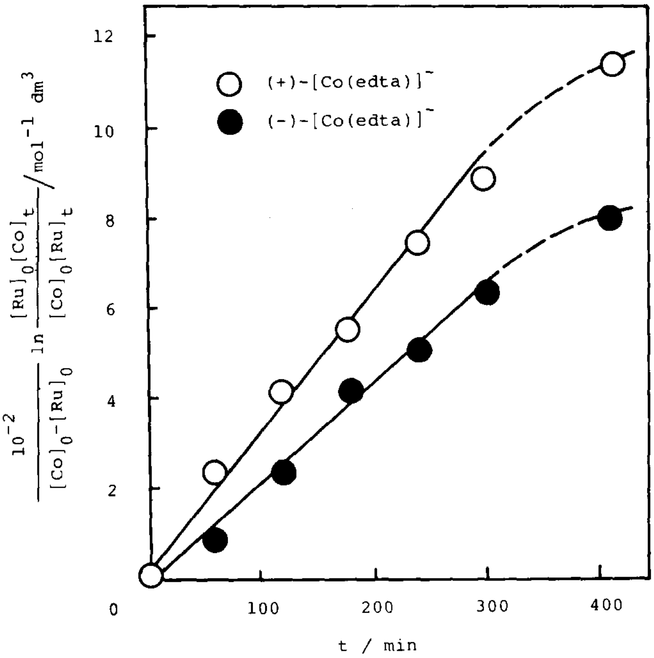


Fig. 1. Second-order plots for the photoreduction of (+)- or (−)-Co(edta)$^-$ (4.0×10^{-5} mol dm^{-3}) by Ru(bpy—Men)$_2$(bpy—C$_{12}$)$^{2+}$ (2.7×10^{-5} mol dm^{-3}) with CTAB (2.0×10^{-3} mol dm^{-3}) in 10 vol.% EtOH–H$_2$O at 28 °C.

The quantum yield of emission in the presence or absence of Co(III) (ϕ_e or $\phi_\mathrm{e}'^0$ respectively) was given as $\phi_\mathrm{e} = k_\mathrm{e}/(k_\mathrm{e} + k_\mathrm{r}[\mathrm{Co(III)}] + k_\mathrm{d} + k_\mathrm{i})$ or $\phi_\mathrm{e}^0 = k_\mathrm{e}/(k_\mathrm{e} + k_\mathrm{d} + k_\mathrm{i})$ by the assumption of the stationary-state concentration of [Ru(II)]*. The ratio of emission intensity in the absence of Co(III) to that in the presence of Co(III), I^0/I, was then expressed by the following equation:

$$\frac{\phi_e{}^0}{\phi_e} = \frac{I^0}{I} = \frac{k_r}{k_e + k_i + k_d}[\mathrm{Co(III)}] + 1 = k_r\tau[\mathrm{Co(III)}] + 1$$

(τ (lifetime of Ru(II)*) = $1/(k_e + k_i + k_d)$)

As is indicated in Fig. 2, the emission intensity ratio I^0/I was directly affected by the surfactant micelles; that is, the cationic CTAB micelles accelerated the quenching of photoactivated $\mathrm{Ru(bpy{-}Men)_2(bpy{-}C_{12})^{2+}}$ by $\mathrm{Co(edta)^-}$ via the condensation of the long-chain Ru(II) complex (through hydrophobic forces) and the anionic Co(III) complex (through charge-attraction forces). Notably, such a positive micellar effect of CTAB on the quenching reaction also results from lengthening the lifetime of photoexcited long-chain Ru(II) complex by the surfactant micelles, probably through depression of the vibrational relaxation of the excited species incorporated into the micelles (see Fig. 3). However, the change in the lifetime of Ru(II)* by the surfactant micelles was directly influenced by the aggregation number of the surfactant; that is, increasing the concentration of Ru(II)* on the micelles promotes the internal conversion of Ru(II)* so as to decrease the apparent lifetime of Ru(II)*. The order of the concentration of incorporated Ru(II) complex per micelle unit ($[\mathrm{Ru(bpy{-}Men)_2(bpy{-}C_{12})^{2+}}]/[\mathrm{micelle}]$) paralleled that of the ratio of lifetimes (τ'/τ), as shown in Table 1.

In regard to the Stern–Volmer relationship, the linear relation between I^0/I and [Co(III)] was well established, and the $k_r\tau$ values obtained as slopes of the straight lines were different between the enantiomers of $\mathrm{Co(edta)^-}$

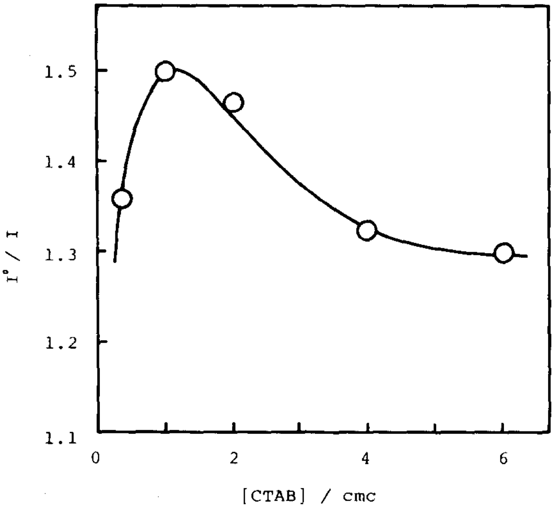


Fig. 2. Micellar effect on emission intensity ratio (I^0/I) in the quenching of photoactivated $\mathrm{Ru(bpy{-}Men)_2(bpy{-}C_{12})^{2+}}$ (2.7×10^{-5} mol dm^{-3}) by (+)-$\mathrm{Co(edta)^-}$ (4.0×10^{-5} mol dm^{-3}) in the presence of CTAB (*cmc* = 1.0×10^{-3} mol dm^{-3}).

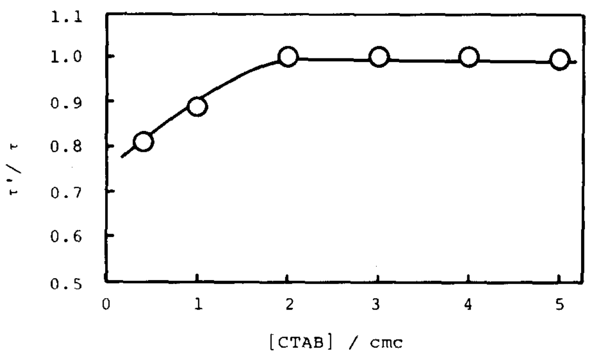


Fig. 3. Ratio of lifetime (τ') of $[Ru(bpy{-}Men)_2(bpy{-}C_{12})^{2+}]^*$ to that (τ) in the presence of CTAB (2.0 × *cmc*). (*cmc* = 1.0×10^{-3} mol dm^{-3}).

TABLE 1

Kinetic parameters[a]

Surfactant	$[Ru(bpy{-}Men)_2(bpy{-}C_{12})^{2+}]$[b] / [micelle]	Lifetime ratio	$k_r\tau$		k_r^+/k_r^-
			(+)-Co(edta)$^-$	(−)-Co(edta)$^-$	
CTAB (2.0 × *cmc*)	2.2	1.00	6273	2935	2.14
SDS (2.0 × *cmc*)	0.2	1.16	~50	~50	1.0
Triton X (2.0 × *cmc*)	12.3	0.63	3238	2803	1.16

[a] Quenching of photoactivated $Ru(bpy{-}Men)_2(bpy{-}C_{12})^{2+}$ (2.7×10^{-5} mol dm^{-3}) by (+)- or (−)-Co(edta)$^-$ (4.0×10^{-5} mol dm^{-3}) with CTAB (*cmc* = 1.0×10^{-3} mol dm^{-3}), SDS (*cmc* = 8.0×10^{-3} mol dm^{-3}) or Triton X (*cmc* = 3.0×10^{-4} mol dm^{-3}) at 25 °C in 10 vol.% $EtOH{-}H_2O$.

[b] [micelle] = ([surfactant] − *cmc*)/aggregation number (aggregation number = 80 (CTAB), 62 (SDS), or 137 (Triton X)).

and between the surfactants used (Fig. 4). The order of the $k_r\tau$ values (CTAB > Triton X ≫ SDS), which was not in accord with that of the lifetime ratio (SDS > CTAB > Triton X), is mainly caused by the difference in the k_r values; that is, the cationic CTAB micelles capable of accelerating the quenching reaction by the condensation of Co(edta)$^-$ result in the largest k_r value among the surfactant micelles, while the anionic SDS micelles incapable of promoting the reaction by inhibiting the approach of Co(edta)$^-$ toward the micelles bring about the smallest k_r value. At any rate, the stereoselection of the enantiomeric Co(edta)$^-$ substrates in the present reaction was well reflected in the enantiomer rate ratio (k_r^+/k_r^-) observed in the quenching experiments, and both the condensation of the substrate (electron

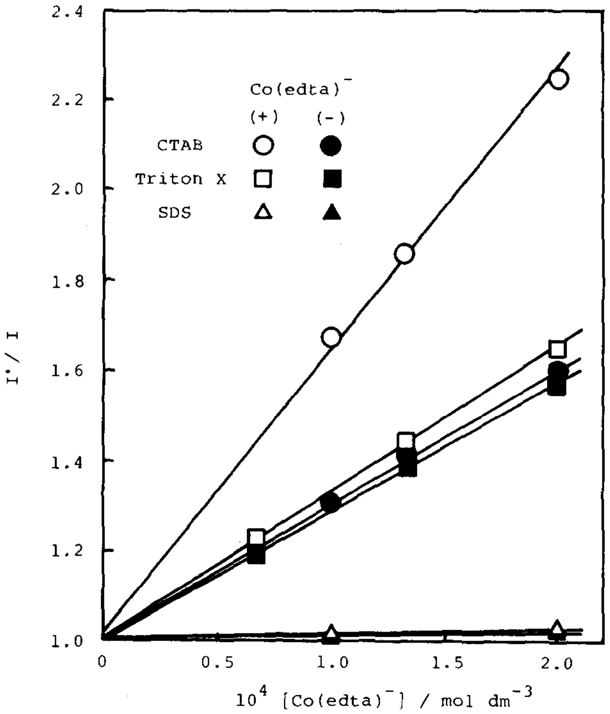


Fig. 4. Stern–Volmer plots of I^0/I *vs.* [Co(edta)$^-$]. ([Ru(III)] = 2.7 × 10^{-5} mol dm^{-3}, [CTAB] = [Triton X] = [SDS] = 2.0 × *cmc*. *cmc* = 1.0 × 10^{-3} (CTAB), 3.0 × 10^{-4} (Triton X), or 8.0 × 10^{-3} mol dm^{-3} (SDS)).

acceptor) and the lengthening of the lifetime of the excited species (electron donor) by the surfactant micelles play an important role in the promotion of the stereoselective photoinduced electron transfer reaction.

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