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Difference in Kinetic Behavior on the Photosensitized Decomposition of the Tris(oxalato)cobaltate(III) Ion by Tris(2,2′-bipyridine)ruthenium(II) and Bis(3,3′-biisoquinoline) (2,2′-bipyridine)ruthenium(II)

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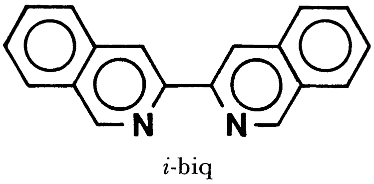
Synopsis. The photo-sensitized decomposition of $[Co(ox)_3]^{3-}$ (ox=oxalate) was performed using $[Ru(bpy)_3]^{2+}$ (bpy=2,2′-bipyridine) and $[Ru(i\text{-biq})_2(bpy)]^{2+}$ (*i*-biq=3,3′-biisoquinoline). The dramatic difference in the decomposition behavior appeared between them. In appearance, the decomposition rate obeys first-order with respect to the $[Co(ox)_3]^{3-}$ concentration for $[Ru(i\text{-biq})_2(bpy)]^{2+}$ system, whereas zero-order for the $[Ru(bpy)_3]^{2+}$ system. The cause was discussed on the basis of the kinetic analysis.

It is widely known that the tris(2,2′-bipyridine)ruthenium(II) complex, $[Ru(bpy)_3]^{2+}$, acts as a useful homogeneous photocatalyst for many photochemical systems. The photosensitized reductive decomposition of the tris(oxalato)cobaltate(III) ion, $[Co(ox)_3]^{3-}$, is one of the typical examples.[1] In our previous work, it was found that the rate of the decomposition is of zero-order with respect to the concentration of $[Co(ox)_3]^{3-}$ and is proportional to the incident light-intensity only.[2] For the purpose of comparing the catalytic behavior, we have been used several analogous ruthenium(II) complexes in place of $[Ru(bpy)_3]^{2+}$ as photosensitizers of the reaction. $[Ru(i\text{-biq})_2(bpy)]^{2+}$ (*i*-biq=3,3′-biisoquinoline) contains only one bpy ligand on which an excited electron can be populated in the lowest MLCT excited state. As *i*-biq ligands in the complex hardly affect the lowest excited state, the photophysical properties such as emission energy and emission lifetime of $[Ru(i\text{-biq})_2(bpy)]^{2+}$ are very similar to those of $[Ru(bpy)_3]^{2+}$.[3,4] Nevertheless, the dramatic difference between $[Ru(i\text{-biq})_2(bpy)]^{2+}$ and $[Ru(bpy)_3]^{2+}$ was observed in the decomposition behavior of $[Co(ox)_3]^{3-}$ in appearance. Thus we have carried out the kinetic approach in order to explain the difference between them.



i-biq

Experimental

$[Ru(bpy)_3]Cl_2\cdot 6H_2O$[5] and $K_3[Co(ox)_3]\cdot 3H_2O$[6] were prepared according to the literatures and recrystallized twice. 3,3′-Biisoquinoline and the $[Ru(i\text{-biq})_2(bpy)]^{2+}$ complex were available from previous investigation.[3] To obtain higher solubility in water, chloride of the complex was prepared by the anion exchange (Dowex 1-X8). The other chemicals used are of guaranteed reagent grade.

The sample solution for the photo-sensitized decomposition was prepared as follows: 2×10^{-5} mol dm^{-3} of the ruthenium(II) complex, 3×10^{-3} mol dm^{-3} of $[Co(ox)_3]^{3-}$, 0.095 mol dm^{-3} of HCl, and 0.2 mol dm^{-3} of NaCl. For the solution that sodium oxalate was added, the concentration of NaCl was lowered to keep the ionic strength constant. The solution was irradiated continuously with visible light (>400 nm) at 25 °C using the same apparatus as reported previously.[2] The reaction solution was purged of oxygen by bubbling pure nitrogen gas through it. Aliquot samples were withdrawn at appropriate times to measure the absorbance of $[Co(ox)_3]^{3-}$ at 602 nm (ε=148 mol^{-1} dm^3 cm^{-1}). While, the concentration of the ruthenium(II) complexes was checked by the absorption spectra after removal of the $[Co(ox)_3]^{3-}$ ion by the anion-exchange resin (Dowex 1-X8).

Results and Discussion

Figure 1 shows plots of the absorbance of $[Co(ox)_3]^{3-}$ vs. time under three different conditions. In the presence of $[Ru(bpy)_3]^{2+}$, $[Co(ox)_3]^{3-}$ decomposed efficiently in proportion to the time (Fig. 1A). When $[Ru(i\text{-biq})_2(bpy)]^{2+}$ was used instead of $[Ru(bpy)_3]^{2+}$ as a photosensitizer under the same acid conditions, the decomposition of $[Co(ox)_3]^{3-}$ was as slow as the self-decomposition by the intramolecular electron transfer, showing the very small photosensitizing effect (Fig. 1C). In the system, absorbance at 395 nm of $[Ru(i\text{-biq})_2(bpy)]^{2+}$ decreased with time and a new

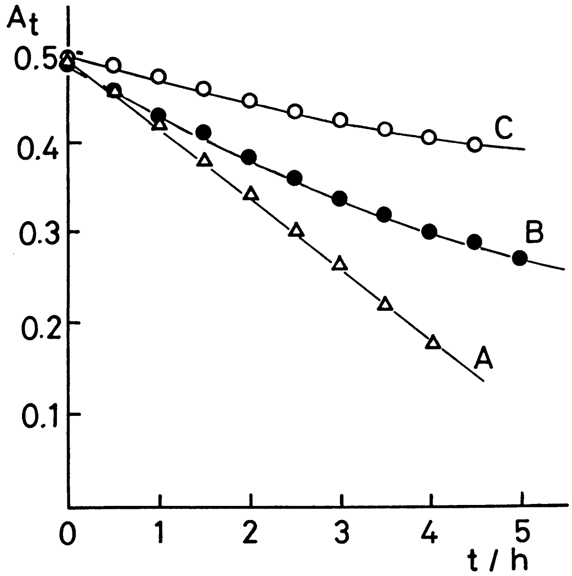


Fig. 1. Plots of the absorbance of $[Co(ox)_3]^{3-}$ vs. time in the presence of: (A) 2×10^{-5} mol dm^{-3} of $[Ru(bpy)_3]^{2+}$, (B) 2×10^{-5} mol dm^{-3} of $[Ru(i\text{-biq})_2(bpy)]^{2+}$ and 0.05 mol dm^{-3} of $Na_2C_2O_4$, (C) 2×10^{-5} mol dm^{-3} of $[Ru(i\text{-biq})_2(bpy)]^{2+}$.

absorption band at 370 nm appeared instead. The peak corresponds to the spectrum of a tervalent complex, $[\mathrm{Ru}(i\text{-biq})_2(\mathrm{bpy})]^{3+}$ obtained by the oxidation of $[\mathrm{Ru}(i\text{-biq})_2(\mathrm{bpy})]^{2+}$ using $\mathrm{PbO_2}$ in a 1 mol dm^{-3} sulfuric acid. This indicates that $[\mathrm{Ru}(i\text{-biq})_2(\mathrm{bpy})]^{3+}$, generated due to the oxidative quenching by $[\mathrm{Co(ox)_3}]^{3-}$, accumulated during the reaction time. This phenomenon for the mixed ligand complex results from a little higher stability of the tervalent state of the ruthenium ion than that for the tris(bipyridine) complex. The standard redox potentials are 1.26 V and 1.17 V vs. NHE for $[\mathrm{Ru(bpy)_3}]^{2+}$ and $[\mathrm{Ru}(i\text{-biq})_2(\mathrm{bpy})]^{2+}$, respectively.[7] In the case of the tris(bipyridine) complex, $[\mathrm{Ru(bpy)_3}]^{3+}$ can be reduced rapidly to the bivalent state by the oxalate ion released by the reductive decomposition of $[\mathrm{Co(ox)_3}]^{3-}$. Thus when sodium oxalate as a reductant of ruthenium(III) species was beforehand added to the sample solution with $[\mathrm{Ru}(i\text{-biq})_2(\mathrm{bpy})]^{2+}$, the decomposition of $[\mathrm{Co(ox)_3}]^{3-}$ proceeded smoothly keeping the constant concentration of $[\mathrm{Ru}(i\text{-biq})_2(\mathrm{bpy})]^{2+}$ (Fig. 1B). However, the apparent kinetic behavior was quite different from that for the $[\mathrm{Ru(bpy)_3}]^{2+}$ catalysis. In the case of $[\mathrm{Ru}(i\text{-biq})_2(\mathrm{bpy})]^{2+}$ catalysis, the decomposition rate of $[\mathrm{Co(ox)_3}]^{3-}$ seems to be of first-order rather than of zero-order with respect to the $[\mathrm{Co(ox)_3}]^{3-}$ concentration.

To explain the difference , we carried out the kinetic approach. The photo-sensitized decomposition takes place as shown in Scheme 1. According to the scheme, the kinetic expression can be described as Eq. 1

$$-\mathrm{d}[\mathrm{Co}']/\mathrm{d}t=(k_{\mathrm{et}}+k_{\mathrm{en}})[{}^*\mathrm{Ru}][\mathrm{Co^{III}}] - k_{\mathrm{be}}[\mathrm{Ru^{III}}\cdots\mathrm{Co^{II}}]-k_{\mathrm{d}}[\mathrm{Ru^{II}}\cdots{}^*\mathrm{Co}] \qquad (1)$$

where $[\mathrm{Co}']$ represents the total concentration of $[\mathrm{Co(ox)_3}]^{3-}$ involving an encounter complex in the ground state denoted by $[\mathrm{Ru^{II}}\cdots\mathrm{Co^{III}}]$: $[{}^*\mathrm{Ru}]$, $[\mathrm{Co^{III}}]$, $[\mathrm{Ru^{III}}\cdots\mathrm{Co^{II}}]$, and $[\mathrm{Ru^{II}}\cdots{}^*\mathrm{Co}]$ indicate the concentrations of the excited species of the ruthenium complexes, $[\mathrm{Co(ox)_3}]^{3-}$, and encounter complexes generated by electron- and energy-transfer, respectively: The rate constant on each step is defined as shown in Scheme 1. The association constant for $[\mathrm{Ru(bpy)_3}]^{2+}$ with $[\mathrm{Co(ox)_3}]^{3-}$ on the ground state was reported to be 1900 mol^{-1} dm^3 at zero ionic strength.[7] Using the value and 2×10^{-5} mol dm^{-3} for the $[\mathrm{Ru(bpy)_3}]^{2+}$ concentration, it is estimated that only a few percents of $[\mathrm{Co(ox)_3}]^{3-}$ are paired with $[\mathrm{Ru(bpy)_3}]^{2+}$. Under the experimental conditions of much higher ionic strength, the ion pairing of the ground state species would be negligible. The assumption of the steady state concentration for $[{}^*\mathrm{Ru}]$, $[\mathrm{Ru^{III}}\cdots\mathrm{Co^{II}}]$ and $[\mathrm{Ru^{II}}\cdots{}^*\mathrm{Co}]$ leads to Eq. 2:

$$[\mathrm{Co}']+k_0/k_{\mathrm{q}}\ln[\mathrm{Co}']=-Bt+C. \qquad (2)$$

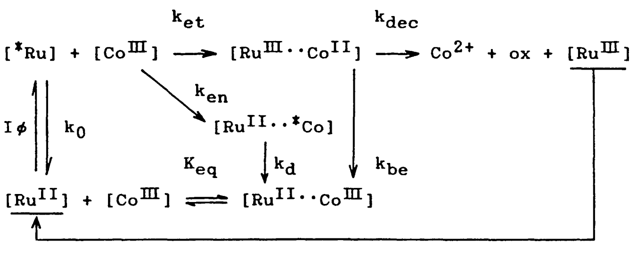
In this equation, k_{q} is the bimolecular quenching rate constant:

$$k_{\mathrm{q}}=k_{\mathrm{et}}+k_{\mathrm{en}}, \qquad (3)$$

and B is a constant related to the quantum yield of the reaction:

$$B=I\phi k_{\mathrm{et}}k_{\mathrm{dec}}/(k_{\mathrm{et}}+k_{\mathrm{en}})(k_{\mathrm{dec}}+k_{\mathrm{be}}). \qquad (4)$$

Equation 2 indicates that the reaction obeys the zero order rate law under the conditions of $[\mathrm{Co}']\gg|k_0/k_{\mathrm{q}}\ln[\mathrm{Co}']|$, while the first-order rate law under the conditions of $[\mathrm{Co}']\ll|k_0/k_{\mathrm{q}}\ln[\mathrm{Co}']|$. Thus the data for both $[\mathrm{Ru(bpy)_3}]^{2+}$ and $[\mathrm{Ru}(i\text{-biq})_2(\mathrm{bpy})]^{2+}$ were analyzed on the basis of Eq. 2. The decomposition data were corrected for the self-decomposition of $[\mathrm{Co(ox)_3}]^{3-}$. The decay rate constant (k_0) of $[\mathrm{Ru(bpy)_3}]^{2+}$ was fixed to the value of 1.7×10^{6} s^{-1}.[8] On the other hand, a similar value of k_0 is also expected for $[\mathrm{Ru}(i\text{-biq})_2(\mathrm{bpy})]^{2+}$ from the data in acetonitrile (1.0×10^{6} s^{-1}).[8] As shown in Fig. 2, both data were well fitted by Eq. 2 with reasonable values of k_0 and k_{q}. The result indicates that the quenching rate constant of $[\mathrm{Ru}(i\text{-biq})_2(\mathrm{bpy})]^{2+}$ in the system is smaller than that for $[\mathrm{Ru(bpy)_3}]^{2+}$. It would be related to the existence of the bulky ligands which do not participate in the lowest excited states for $[\mathrm{Ru}(i\text{-biq})_2(\mathrm{bpy})]^{2+}$. Such a situation particularly makes the intermolecular elec-



$[\mathrm{Ru^{II}}]$ = Ruthenium(II) Complexes

$[\mathrm{Co^{III}}]$ = $[\mathrm{Co(ox)_3}]^{3-}$

ox = $(\mathrm{COO})_2{}^{2-}$

Scheme 1.

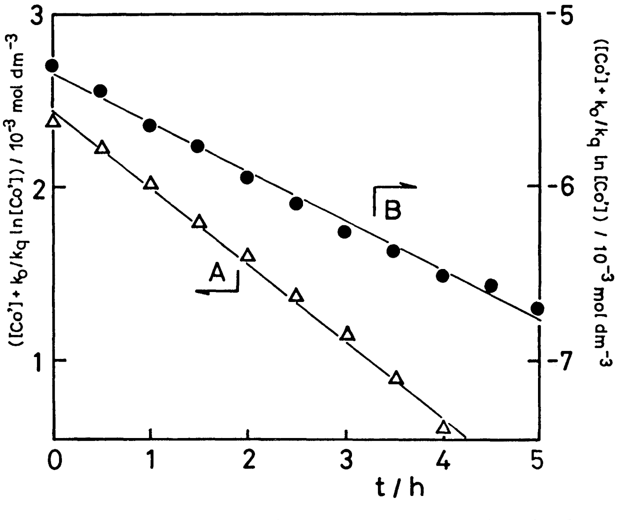


Fig. 2. Plots of ($[\mathrm{Co}']+k_0/k_{\mathrm{q}}\ln[\mathrm{Co}']$) vs. time in the systems of (A) $[\mathrm{Ru(bpy)_3}]^{2+}$ and (B) $[\mathrm{Ru}(i\text{-biq})_2(\mathrm{bpy})]^{2+}$. The straight lines are the least-square-fitting lines on the basis of Eq. 2: (A) $k_0=1.7\times10^{6}$ s^{-1}, $k_{\mathrm{q}}=1\times10^{10}$ mol^{-1} dm^3 s^{-1}, $B=7.4\times10^{-6}$ mol dm^{-3} s^{-1}, (B) $k_0=1.5\times10^{6}$ s^{-1}, $k_{\mathrm{q}}=1\times10^{9}$ mol^{-1} dm^3 s^{-1}, $B=4.7\times10^{-6}$ mol dm^{-3} s^{-1}.

tron transfer (i.e. k_{et}-path) much more difficult.

$[Ru(i\text{-biq})_2(bpy)]^{2+}$ has several advantages as a photosensitizer compared with $[Ru(bpy)_3]^{2+}$. For example, the lowest excited state of $[Ru(i\text{-biq})_2(bpy)]^{2+}$ could act as a stronger reductant than that for $[Ru(bpy)_3]^{2+}$, since the oxidation potential of the excited species is estimated to be −0.95 V and −0.79 V vs. NHE for $[Ru(i\text{-biq})_2(bpy)]^{2+}$ and $[Ru(bpy)_3]^{2+}$, respectively, from the potential of the ground state and the zero-zero excitation energy. The wider and stronger absorption bands in the visible region due to charge transfer to both *i*-biq and bpy ligands for $[Ru(i\text{-biq})_2(bpy)]^{2+}$ is another merit as a photosensitizer. Nevertheless, $[Ru(i\text{-biq})_2(bpy)]^{2+}$ is not so effective as $[Ru(bpy)_3]^{2+}$ as indicated by the B values (7.4×10^{-6} mol dm^{-3} s^{-1} for $[Ru(bpy)_3]^{2+}$ and 4.7×10^{-6} mol dm^{-3} s^{-1} for $[Ru(i\text{-biq})_2(bpy)]^{2+}$). The smaller value for the $[Ru(i\text{-biq})_2(bpy)]^{2+}$ system would come from the yield in the electron transfer step, the part of $k_{et}/(k_{et}+k_{en})$ in the B value (Eq. 4). For the $[Ru(bpy)_3]^{2+}$ system, the limiting quantum yield of the photosensitized decomposition of $[Co(ox)_3]^{3-}$ was reported to be 0.85 in 0.05 mol dm^{-3} H_2SO_4.[1] Such a high yield suggests that $k_{et}/(k_{et}+k_{en})$ in Eq. 2 must be a fairly high value near one. This results in a relation of $k_{et}>k_{en}$ for the $[Ru(bpy)_3]^{2+}$ system. On the other hand, k_q (i.e. $k_{et}+k_{en}$) for the $[Ru(i\text{-biq})_2(bpy)]^{2+}$ system has been estimated to be smaller than that for the $[Ru(bpy)_3]^{2+}$ system by one order as discussed above. Assuming that k_{en} is similar between both systems, there is a possibility that k_{et} is comparable to k_{en} in the $[Ru(i\text{-biq})_2(bpy)]^{2+}$ system. A sensitive change in $k_{et}/(k_{et}+k_{en})$ and thus the B value can occur in the situation. As for the part of $k_{dec}/(k_{dec}+k_{be})$ in Eq. 4, the higher value is expected for the $[Ru(i\text{-biq})_2(bpy)]^{2+}$ system rather than the $[Ru(bpy)_3]^{2+}$ system because the bulkiness for $[Ru(i\text{-biq})_2(bpy)]^{2+}$ makes the stability of the encounter complex, $[Ru^{III}\cdots Co^{II}]$, weaker.

In conclusion, the different behavior on the photosensitized decomposition of $[Co(ox)_3]^{3-}$ by $[Ru(bpy)_3]^{2+}$ and $[Ru(i\text{-biq})_2(bpy)]^{2+}$ can be explained in terms of the difference in the electron transfer step (k_{et}) from the ruthenium complexes to $[Co(ox)_3]^{3-}$.

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