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Photoinduced Electron-transfer from Thiols to $[Ru(bpy)_3]^{2+}$ in Aqueous Solutions

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Synopsis. The quenching of photoexcited $[Ru(bpy)_3]^{2+}$ by water-soluble thiols was studied by steady-state and time-resolved measurements. 2-Mercaptobenzoic acid and 4-mercaptopyridine which give the delocalized thiolate ions in water quenched $[Ru(bpy)_3]^{2+*}$ effectively, and $[Ru(bpy)_3]^+$ was formed by the quenching. No quenching occurred with cysteine and 2-mercaptoethanol.

Photoinduced electron-transfer with $[Ru(bpy)_3]^{2+}$ (bpy=2,2′-bipyridine) has been extensively investigated.[1] Previously, we reported that a photoexcited $[Ru(bpy)_3]^{2+}$ was quenched by benzenethiolate ion in nonaqueous solution (acetonitrile) and that $[Ru(bpy)_3]^+$ absorbing around 510 nm was formed in good yield.[2] The back electron-transfer reaction from $[Ru(bpy)_3]^+$ to PhS· was suppressed by the rapid dimerization reaction of thiyl radicals and $[Ru(bpy)_3]^+$ could exist with a relatively long lifetime in this system. The overall reaction can be expressed by Eq. 1 and the reverse process (the back electron-transfer reaction to disulfide) is slow.

$$2[Ru(bpy)_3]^{2+} + 2PhS^- \underset{\text{slow}}{\overset{h\nu}{\rightleftharpoons}} 2[Ru(bpy)_3]^+ + PhSSPh \quad (1)$$

The application of this redox couple to photogalvanic cell was also reported.[3] Thermodynamically, $[Ru(bpy)_3]^+$ can reduce water to H_2.[4] In this letter we study the photoinduced electron-transfer from water-soluble thiols to $[Ru(bpy)_3]^{2+*}$ in order to search good redox couples used in aqueous solutions.

Experimental

$[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ was synthesized according to published procedures.[5] Commercially available thiols were purified by recrystallization. The steady-state emission intensity was measured with Shimadzu RF 503A spectrofluorophotometer. Laser photolysis experiments for the lifetime quenching were carried out with a frequency-doubled Q-switched ruby laser system (347.1 nm pulse: 20 ns pulse width). The xenon-flash apparatus delivered a flash (10 μs pulse) with 112.5 joule was used for the detection of transient $[Ru(bpy)_3]^+$.

Results and Discussion

The quenching experiments of $[Ru(bpy)_3]^{2+*}$ by cysteine, 2-mercaptoethanol, 4-mercaptopyridine, and 2-mercaptobenzoic acid were carried out by steady-state measurement in deoxygenated solution. Cysteine and 2-mercaptoethanol did not quench the emission of $[Ru(bpy)_3]^{2+*}$ under a wide variation in pH (6-11; Borax buffer), whereas 2-mercaptobenzoic acid and 4-mercaptopyridine showed effective quenchings (Table 1). The Stern-Volmer plots for them are shown

Table 1. The quenching of $[Ru(bpy)_3]^{2+*}$ by water-soluble thiols

Thiols	pK_a	Quenching at pH>pK_a(−SH)
2-Mercaptobenzoic acid	3.0 (-COOH)	
	8.5 (-SH)	k_q=1.7×10^9 dm^3 l^{-1} s^{-1}
4-Mercaptopyridine	10.6 (-SH)	k_q=5×10^7 dm^3 l^{-1} s^{-1}
Cysteine	1.7 (-COOH)	
	8.3 (-SH)	No quenching
	10.8 (-NH$_2$)	
2-Mercaptoethanol	10 (-SH)	No quenching

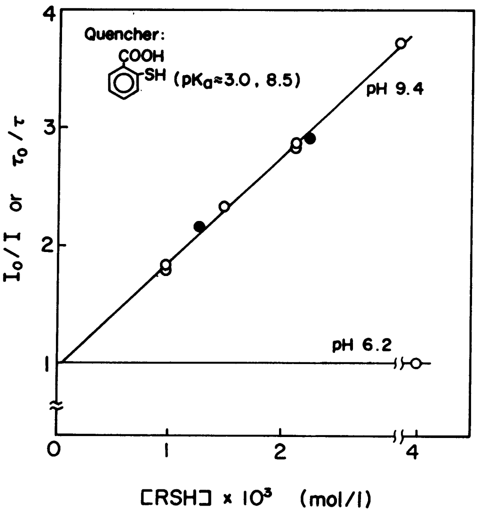

Fig. 1. Plots of I_0/I (○) and τ_0/τ (●) *vs.* [RSH] for quenching of $[Ru(bpy)_3]^{2+*}$ by 2-mercaptobenzoic acid.

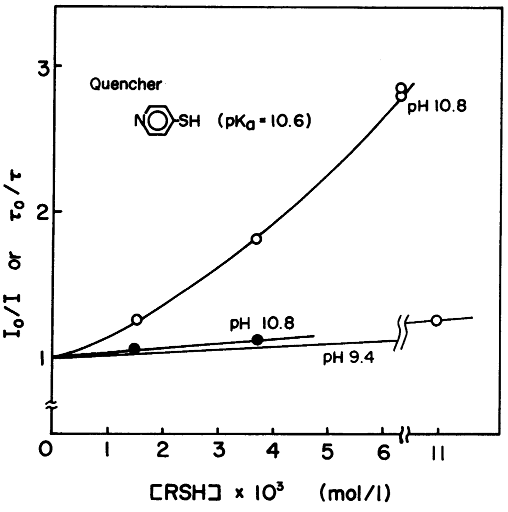

Fig. 2. Plots of I_0/I (○) and τ_0/τ (●) *vs.* [RSH] for quenching of $[Ru(bpy)_3]^{2+*}$ by 4-mercaptopyridine.

in Figs. 1 and 2. The quenchings are effective in pH region larger than their pK_a's. Apparently thiolate ion formed from the dissociation of -SH group is necessary for the quenching. The thiolate ions derived from 2-mercaptobenzoic acid and 4-mercaptopyridine are conjugated with aromatic moieties, and the delocalization is favorable to the orbital overlapping in electron-transfer process, resulting in the effective quenching.

The emission lifetimes were measured by exciting $[Ru(bpy)_3]^{2+}$ with a 347.1 nm-pulse (20 ns pulse width, ruby laser). The emission decays were single-exponential in the absence and the presence of quenchers, whose slopes varied with the concentration of the quencher. The plots of τ_0/τ *vs.* [RSH] were superimposed upon Figs. 1 and 2. The dynamic quenching rate constants for 2-mercaptobenzoic acid and 4-mercaptopyridine were obtained to be 1.7×10^9 (pH=9.4) and 5×10^7 dm^3 mol^{-1} s^{-1} (pH=10.8), respectively. As shown in Fig. 1, the slope of the plots of I_0/I *vs.* [RSH] was identical with that of the plots of τ_0/τ, suggesting that only dynamic quenching takes place and the quenching of $[Ru(bpy)_3]^{2+*}$ with *o*-sulfidobenzoate ion proceeds by the usual Stern-Volmer behavior. In contrast with this, the quenching by pyridinethiolate ion is almost static quenching (Fig. 2). Although the emission and the absorption spectra of $[Ru(bpy)_3]^{2+}$ were not changed in the presence of pyridinethiolate ion, somewhat association of $[Ru(bpy)_3]^{2+*}$ with the anion resulting in the static quenching seems to take place. The following xenon flash photolysis study is suggesting the association.

The formation of the transient species absorbing around 520 nm was detected by means of xenon flash photolysis of the aqueous solution (pH=9.4) containing $[Ru(bpy)_3]^{2+}$ and 2-mercaptobenzoic acid. The species can be assigned to $[Ru(bpy)_3]^+$ as shown elsewhere.[2,6] The decay profile is shown in Fig. 3. The decay obeyed good first-order kinetics with a rate constant $k=6.5\times10^3$ s^{-1}, which implies that the back electron-transfer reaction was suppressed. It has been reported that when Eu(II) and aromatic amines were used as quenchers, the decays of $[Ru(bpy)_3]^+$ obeyed second-order kinetics with rate constants 2.7×10^7 and 10^7—10^{10} dm^3 mol^{-1} s^{-1}, respectively.[7,8] On the other hand, the formation of $[Ru(bpy)_3]^+$ can not be detected in $[Ru(bpy)_3]^{2+}$-4-mercaptopyridine system. This may be caused by the rapid back electron-transfer in the static quenching pair.

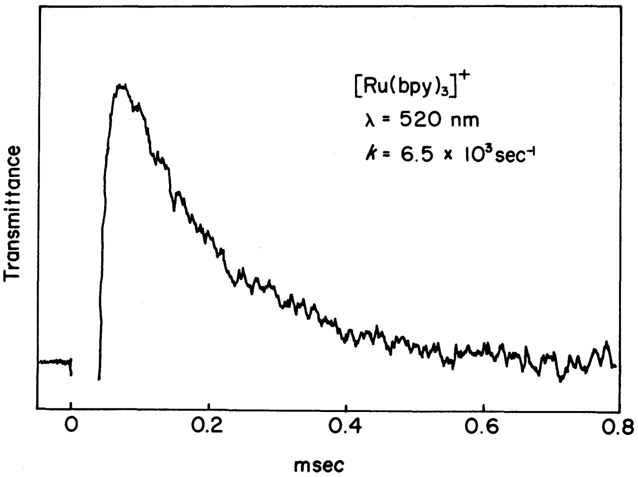

Fig. 3. Decay profile of transient absorption (λ=520 nm) of $[Ru(bpy)_3]^+$ in aqueous solution (pH=9.4; RSH: 2-mercaptobenzoic acid).

Steady-state irradiation on the buffer solution (pH=9.4) containing $[Ru(bpy)_3]^{2+}$, 2-mercaptobenzoic acid, and PtO_2 as preliminary experiments was carried out. H_2 evolution was confirmed by gas chromatography (Molecular sieves 5A, 60—80 mesh, 2 m, temp; 35 °C, carrier; N_2, TCD detector) though the yield is low.

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