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Electron-transfer Reaction from Sodium Benzenethiolate to Acceptors Assisted by Photo-excited Tris(2,2'-bipyridine)ruthenium(II)

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The photo-excited tris(2,2'-bipyridine)ruthenium(II) ($Ru(bpy)_3^{2+*}$) was effectively quenched by sodium benzenethiolate in acetonitrile (Stern-Volmer constant=4860 dm^3 mol^{-1}). The flash photolysis of a solution containing $Ru(bpy)_3^{2+}$ and benzenethiolate (excitation wavelength (λ)>480 nm) produced transient species absorbing *ca.* 510 nm; this species was identified as $Ru(bpy)_3^+$ and decayed with first-order kinetics with $k=3.0$ s^{-1}. This slow decay of $Ru(bpy)_3^+$ implies that the back-electron-transfer reaction was suppressed. The decay of $Ru(bpy)_3^+$ was accelerated by the addition of water, suggesting the possibility of the reaction between $Ru(bpy)_3^+$ and water, though no H_2 was detected. The steady irradiation of a solution containing $Ru(bpy)_3^{2+}$, benzenethiolate, and an electron-acceptor produced the radical anion of the added acceptor, which was detected with ESR spectroscopy.

Recently there has been considerable interest in photo-induced electron-transfer reactions in a solution containing $Ru(bpy)_3^{2+}$ from the viewpoint of solar energy conversion.[1-6] $Ru(bpy)_3^{3+}$ and $Ru(bpy)_3^+$ generated by the electron-transfer quenching of photo-excited tris(2,2'-bipyridine)ruthenium ($Ru(bpy)_3^{2+*}$) (Eqs. 1 and 2) are thermodynamically capable of

$$Ru(bpy)_3^{2+*} + Q \rightleftharpoons Ru(bpy)_3^{3+} + Q^{\cdot -} \quad (1)$$

$$Ru(bpy)_3^{2+*} + Q \rightleftharpoons Ru(bpy)_3^{+} + Q^{\cdot +} \quad (2)$$

oxidizing water to O_2 and of reducing water to H_2, respectively. However, the practical utility of these

$$Ru(bpy)_3^{2+} + e^- \rightleftharpoons Ru(bpy)_3^{+} \qquad E_{1/2} = -1.33\ V^{7)}$$

$$Ru(bpy)_3^{3+} + e^- \rightleftharpoons Ru(bpy)_3^{2+} \qquad E_{1/2} = +1.29\ V^{8)}$$

reactions is limited by the energy-wasting back-electron-transfer of Eqs. 1 and 2.[8-10] One approach to suppressing the back-electron-transfer reaction is to remove the quenching products by rapid irreversible reactions coupled with quenching processes.

We have found that the life-time of $Ru(bpy)_3^+$ can be elongated when benzenethiolate is used as the electron-donor for the quenching of $Ru(bpy)_3^{2+*}$. The thiyl radical formed in the electron-transfer from benzenethiolate to $Ru(bpy)_3^{2+*}$ can disappear upon rapid dimerization into disulfide,[11] which has a high redox (more negative) potential,[12] leading to the result that the back-electron-transfer can be suppressed. This paper reports the photo-induced reduction of $Ru(bpy)_3^{2+}$ in the presence of sodium benzenethiolate and the electron-transfer reaction from the $Ru(bpy)_3^+$ generated to some organic electron-acceptors.

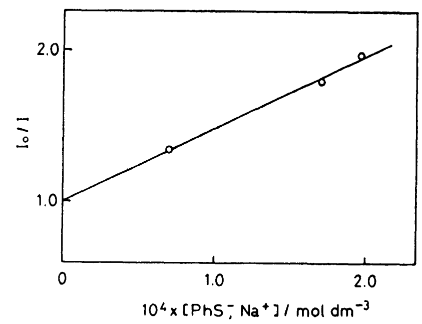


Fig. 1. Stern-Volmer plots for the quenching of the $Ru(bpy)_3^{2+*}$ luminescence (610 nm) by sodium benzenethiolate in acetonitrile. $[Ru(bpy)_3^{2+}] = 1.4 \times 10^{-5}$ mol dm^{-3}, excitation at 450 nm.

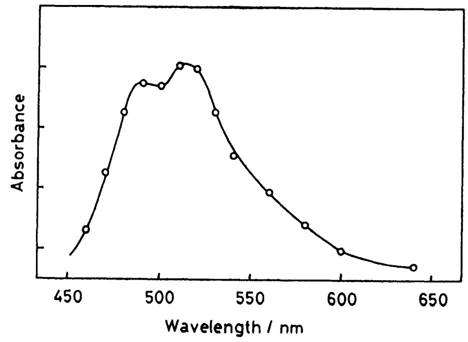


Fig. 2. Transient absorption spectrum in flash photolysis of acetonitrile solution containing $Ru(bpy)_3^{2+}$ (1×10^{-5} mol dm^{-3}) and sodium benzenethiolate (1×10^{-4} mol dm^{-3}).

Results and Discussion

The quenching experiments of the luminescence of $Ru(bpy)_3^{2+*}$ by sodium benzenethiolate were carried out in a highly degassed acetonitrile solution. The emission maximum of $Ru(bpy)_3^{2+*}$ was not shifted by the addition of benzenethiolate, and only the intensity of emission (I) decreased. The plot of I_0/I *vs.* the concentration of benzenethiolate (Stern-Volmer plot) is shown in Fig. 1. The Stern-Volmer quenching constant, K_{SV}=4860 dm^3 mol^{-1}, was obtained from the slope in Fig. 1. The quenching-rate constant (k_q) was calculated to be 5.7×10^9 dm^3 mol^{-1} s^{-1} from the Stern-Volmer constant, assuming that the rate constant for the natural deactivation of $Ru(bpy)_3^{2+*}$ (k_0) is 1.18×10^6 s^{-1} in acetonitrile.[13]

The flash photolysis of acetonitrile solutions containing $Ru(bpy)_3^{2+}$ (1—4$\times 10^{-5}$ mol dm^{-3}) and benzenethiolate (1—5$\times 10^{-4}$ mol dm^{-3}) gave the transient absorption spectrum shown in Fig. 2, which was assigned to $Ru(bpy)_3^+$. Similar spectra have been reported in pulse-radiolysis,[14] laser-photolysis,[15] and electrochemical studies.[7] The absorbance of transient species at a given wavelength was not changed on repetitive flashing (up to 20 flashes were tested). The photoanation reaction of $Ru(bpy)_3^{2+}$ by thiocyanate has been reported, although the quantum yield is low.[16] Our above results concerning repetitive flashing and both the absorption and emission spectra showed that such a photoanation reaction did not occur. The transient species decayed with first-order kinetics and had a long life-time ($\tau = 1/k = 333$ ms). These results imply that the back-electron-transfer reaction was effectively suppressed, because the decay of $Ru(bpy)_3^+$ by the back-electron-transfer reaction should obey second-order, equal-concentration kinetics.[13] When Eu(II) or aromatic amine was used as a quencher, the decays of $Ru(bpy)_3^+$ obeyed second-order kinetics, and the rate constants were 2.7×10^7 for Eu(II)[17] and 10^7—10^{10} $dm^3\ mol^{-1}\ s^{-1}$ for amines.[13] Whitten *et al.*[18] have found the very long-lived $Ru(bpy)_3^+$, which was generated by the quenching of $Ru(bpy)_3^{2+*}$ with triethylamine in dry acetonitrile. Since the triethylamine cation radical formed in the quenching as a counterpart of $Ru(bpy)_3^+$ was removed by an irreversible reaction with a solvent (CH_3CN), the back-electron-transfer reaction was almost entirely avoided. The irreversible reactions and their products were complex, whereas the irreversible product in our system was diphenyl disulfide, which could reproduce benzenethiolate (see below).

The results obtained here can be explained by a mechanism (Eqs. 3—6) in which the $Ru(bpy)_3^+$ formed in the reductive quenching of $Ru(bpy)_3^{2+*}$ (Eq. 4) may transfer an electron to disulfide, not to thiyl radicals (back-electron-transfer reaction), which dimerize each other to disulfide with $k_d = 10^9\ dm^3\ mol^{-1}\ s^{-1}$ (Eq. 5):[11]

$$Ru(bpy)_3^{2+} \underset{k_0}{\overset{h\nu}{\rightleftharpoons}} Ru(bpy)_3^{2+*} \qquad (3)$$

$$Ru(bpy)_3^{2+*} + PhS^- \xrightarrow{k_q} Ru(bpy)_3^+ + PhS\cdot \qquad (4)$$

$$PhS\cdot + PhS\cdot \xrightarrow{k_d} PhSSPh \qquad (5)$$

$$Ru(bpy)_3^+ + PhSSPh \xrightarrow{k_{et}} Ru(bpy)_3^{2+} + PhS^- + PhS\cdot \qquad (6)$$

The pseudo-first-order rate constant for the decay of $Ru(bpy)_3^+$ varied upon an added concentration of diphenyl disulfide (Fig. 3), showing the occurrence of an electron-transfer reaction, as is shown in Eq. 6. The rate constant (k_{et}) for the electron-transfer reaction was found to be $9.6 \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$. This slow electron-transfer reaction is due to the high redox potential of diphenyl disulfide ($E_{peak} = -1.6$ V *vs.* 10^{-3} mol dm^{-3} Ag^+/Ag).[12]

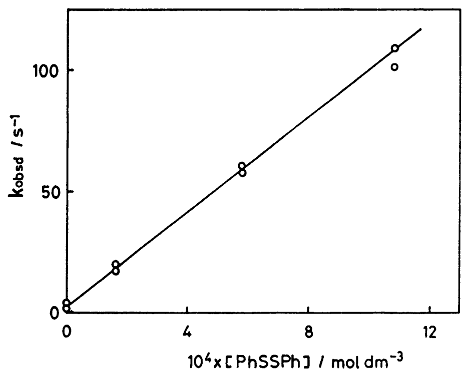


Fig. 3. Dependence of first-order rate constants for the decay of $Ru(bpy)_3^+$ (510 nm) on the concentration of added diphenyl disulfide.

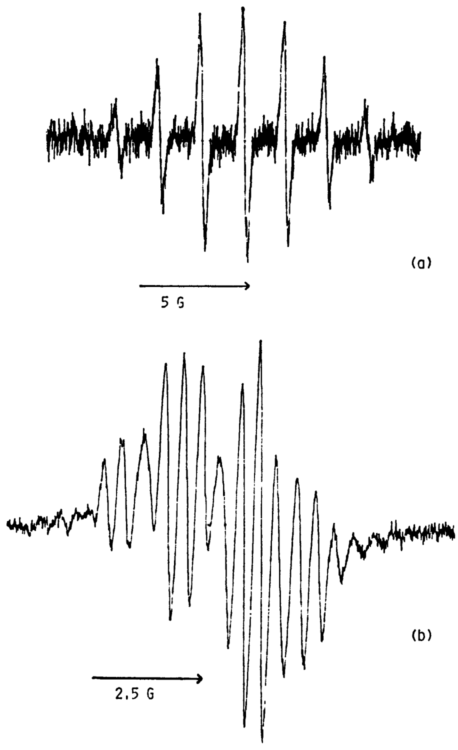


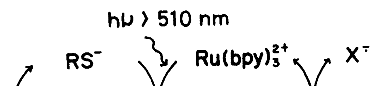
Fig. 4. ESR spectra of duroquinone radical anion (a) and benzil radical anion (b) in acetonitrile.

TABLE 1. PHOTO-INDUCED ELECTRON-TRANSFER FROM SODIUM BENZENETHIOLATE IN THE PRESENCE OF $Ru(bpy)_3^{2+}$ IN ACETONITRILE

Acceptor(X)	$E_{1/2}/V^{a)}$	Formation of $X^{\overline{\cdot}}$
Duroquinone	-0.69[23]	Yes, $a_H = 1.88$ G (Septet)
Acenaphthene-quinone	-0.96	Yes, $g = 2.0045$(Multiplet)
Benzil	-1.21	Yes, $g = 2.0048$(Multiplet)[24]
9-Fluorenone	-1.26	Very small
Azobenzene	-1.36	No

a) *vs.* SCE and used $(n\text{-}C_4H_9)_4NClO_4$ as a supporting electrolyte in acetonitrile.

The steady irradiation (wavelengths longer than 510 nm) of an acetonitrile solution containing $Ru(bpy)_3^{2+}$, benzenethiolate, and an electron-acceptor produced the radical anion of the added acceptor, which was detected with ESR spectroscopy (Table 1) (*e.g.*, the ESR spectra of duroquinone and benzil radical anions are shown in Fig. 4). As can be seen from Table 1, acceptors with a potential more positive than the $E_{1/2}$ of the $Ru(bpy)_3^+$/$Ru(bpy)_3^{2+}$ couple ($E_{1/2} = -1.33$ V *vs.* SCE) were reduced to radical anions. The irradiation in the absence of either $Ru(bpy)_3^{2+}$ or benzenethiolate produced no acceptor's radical anion, and the mixing of $Ru(bpy)_3^{2+}$, benzenethiolate, and acceptor in the dark produced no radical anion, either. The results suggest the following electron-transfer cycle:



where X is an electron-acceptor. Benzenethiolate could be reproduced with the reduction of disulfide.[19] The RS⁻/RSSR redox couple is known to be biologically important in an electron-transport system in ferredoxin or other iron-sulfur proteins.[20]

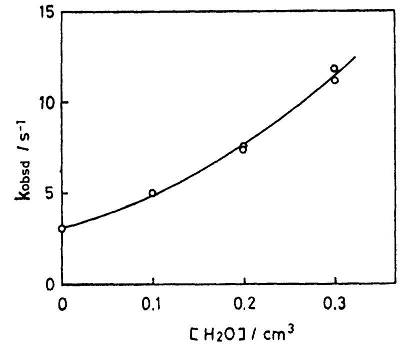


Fig. 5. Effect of added water on the rate constants for the decay of $Ru(bpy)_3^+$ (510 nm); total volume was 10 cm^3.

Although the decay of $Ru(bpy)_3^+$ was accelerated by the addition of water (Fig. 5), the formation of H_2 could not be detected.[21] Meyer *et al.*[6] have reported that there was no production of H_2 in the reaction of water with $Ru(bpy)_3^+$, whereas the reaction with $Ru(bpy)_3^0$ could produce H_2. This has been explained by the difference in two-electron reducing capability between $Ru(bpy)_3^+$ and $Ru(bpy)_3^0$:

$$Ru(bpy)_3^+ \rightleftharpoons Ru(bpy)_3^{3+} + 2e^- \qquad E = 0.00\ V\ vs.\ NHE$$

$$Ru(bpy)_3^0 \rightleftharpoons Ru(bpy)_3^{2+} + 2e^- \qquad E = -1.42\ V\ vs.\ NHE.$$

Although our system could not succeed in the formation of H_2, the electron-transport cycle described above shows the possibility of applying this system to other reduction reactions. An experiment for the application to the photo-galvanic cell of this system using the $Ru(bpy)_3^+/Ru(bpy)_3^{2+}$ couple is also undertaken.

Experimental

$Ru(bpy)_3Cl_2 6H_2O$ was synthesized according to published procedures.[22] Commercially available (reagent-grade) acceptors (duroquinone, acenaphthenequinone, benzil, 9-fluorenone, and azobenzene) were recrystallized twice from ethanol and sublimed under high vacuum (about 10^{-3} Pa). The preparation of sodium benzenethiolate was described previously.[19] The concentration of benzenethiolate in acetonitrile was determined from the absorbance at 298 nm ($\varepsilon = 1.8 \times 10^4$ $dm^3\ mol^{-1}\ cm^{-1}$). The solutions for the experiments of the flash photolysis, the quenching, and the ESR measurement were prepared by a high-vacuum-line technique.[19] The prepared sodium benzenethiolate solution was introduced through a breakseal to a solution containing $Ru(bpy)_3^{2+}$ and acceptor which had been degassed by the freeze-thaw-cycle method.

The quenching experiment of $Ru(bpy)_3^{2+*}$ by benzenethiolate was carried out with a Shimadzu RF 501 fluorescence spectrophotometer. The FSR measurements were carried out with a Varian E-4 ESR spectrometer. The steady irradiation for the photo-ESR study was obtained using a 500-W xenon lamp. The light shorter than 510 nm was cut off with a filter (Toshiba L-51).

The flash apparatus delivered a flash with an energy of 98 J and a half-peak duration of 10 μs from xenon lamps. The filter was used to cut off flash light shorter than 480 nm.

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