CHEMISTRY LETTERS, pp. 45-48, 1978. Published by the Chemical Society of Japan

QUENCHING OF THE LUMINESCENT EXCITED STATE OF TRIS(2,2'-BIPYRIDYL)RUTHENIUM(II) WITH BROMONITROMETHANE

Sigero OISHI and Naoko FURUTA
Sagami Chemical Research Centre
Nishi-Ohnuma, Sagamihara, Kanagawa 229

Linear Stern-Volmer plots were obtained for cathodic photocurrents from the quenching of excited tris(2,2'-bypyridyl)ruthenium(II) with bromonitromethane at an SnO_2 electrode, and the resulting Ksv was in fair agreement with that for emission quenching, indicating that the quenching process occurs by the reductive cleavage of bromonitromethane. A nitromethylated product was formed in the presence of 1,4-dimethoxybenzene.

Organic quenchers such as methyl viologen[1)] and aromatic nitro compounds[2)] are known to deactivate the luminescent excited state of tris(2,2'-bipyridyl)ruthenium(II) ($*Ru(bpy)_3{}^{2+}$) by electron transfer quenching. The quenching reaction is followed by a rapid dark reaction which gives back the ground state $Ru(bpy)_3{}^{2+}$ and the starting quencher. We describe here the results which indicate that electron transfer quenching accompanied by irreversible decomposition occurs in the deactivation of $*Ru(bpy)_3{}^{2+}$ by bromonitromethane ($BrCH_2NO_2$) giving $Ru(bpy)_3{}^{3+}$ and nitromethyl radical ($\cdot CH_2NO_2$).

Photocurrents were measured potentiostatically at an SnO_2 electrode illuminated with visible light ($\lambda > 406$ nm) in a solution of $Ru(bpy)_3Cl_2$ (1.01 mM) and $BrCH_2NO_2$ (9.97 mM) in 0.1 N sulfuric acid under nitrogen. The resulting current-voltage curve is similar to that obtained from the quenching of $*Ru(bpy)_3{}^{2+}$ with dioxygen[3)], except for a wave at around +0.2 V[4)] (Fig. 1). The cathodic photocurrent amounted to 2.9 and 6.6 $\mu A/cm^2$ at electrode potentials of +0.5 and +0.1 V, respectively. On the other hand, without $BrCH_2NO_2$, we observed only small anodic photocurrents not greater than 0.15 $\mu A/cm^2$. Since the spectral distribution of cathodic photocurrents at an electrode potential of +0.5 V was nearly identical with the absorption spectrum of $Ru(bpy)_3{}^{2+}$, the photocurrent is obviously due to the light absorption by $Ru(bpy)_3{}^{2+}$.

Electronic excited states of $BrCH_2NO_2$ are too high for efficient quenching of $^*Ru(bpy)_3{}^{2+}$ by energy transfer, because even aromatic nitro compounds such as nitrobenzene and dinitronaphthalene have relatively high triplet energies (E_T > 57 kcal/mole)$^{5)}$ compared to $^*Ru(bpy)_3{}^{2+}$ (E_T = 49 kcal/mole)$^{6)}$. Therefore, reaction 4 (Scheme 1), which corresponds to electron transfer quenching accompanied by irreversible decomposition, probably is taking place. It is contrasted with the fact that, in the quenching of $^*Ru(bpy)_3{}^{2+}$ with dioxygen, protonation to $O_2{}^{\bar{\cdot}}$ slows down the back reaction of $Ru(bpy)_3{}^{3+}$.

Scheme 1.

$$\begin{aligned}
Ru(bpy)_3{}^{2+} &\xrightarrow{h\nu} {}^*Ru(bpy)_3{}^{2+} && (1)\\
{}^*Ru(bpy)_3{}^{2+} &\xrightarrow{k_1} Ru(bpy)_3{}^{2+} + h\nu && (2)\\
{}^*Ru(bpy)_3{}^{2+} &\xrightarrow{k_2} Ru(bpy)_3{}^{2+} + \text{heat} && (3)\\
{}^*Ru(bpy)_3{}^{2+} + BrCH_2NO_2 &\xrightarrow{k_3} Ru(bpy)_3{}^{3+} + Br^- + \cdot CH_2NO_2 && (4)\\
Ru(bpy)_3{}^{3+}\ (\cdot CH_2NO_2 + H^+) &\xrightarrow{e} Ru(bpy)_3{}^{2+}\ (CH_3NO_2) && (5)
\end{aligned}$$

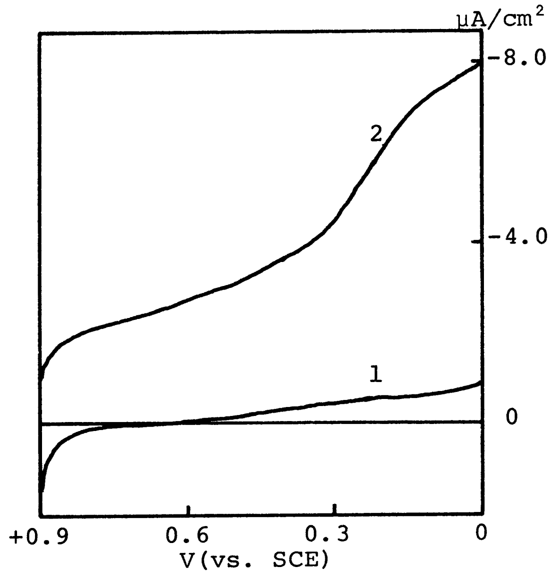


Fig. 1. Current-voltage curves
1: without illumination; 2: under illumination.

It has been reported that $BrCH_2NO_2$ shows one polarographic wave for two electron transfer at around 0 V, because $\cdot CH_2NO_2$ given by the one-electron reduction of $BrCH_2NO_2$ is reduced at those potentials:$^{7)}$

$$BrCH_2NO_2 \xrightarrow{e} Br^- + \cdot CH_2NO_2 \xrightarrow{e,H^+} CH_3NO_2$$

Cathodic photocurrents at around 0 V, therefore, are due to both $Ru(bpy)_3{}^{3+}$ and $\cdot CH_2NO_2$, and the wave in curve 2 is likely to suggest that $\cdot CH_2NO_2$ can not be reduced at an electrode potential more positive than +0.4 V.

The Stern-Volmer relations for the quenching of $^*Ru(bpy)_3{}^{2+}$ emission and for cathodic photocurrents are derived by using the usual stationary state approximation with Scheme 1:

$$\frac{P_0}{P} = 1 + Ksv\{BrCH_2NO_2\} \qquad \text{(emission quenching)} \qquad (6)$$

$$\frac{F}{i} = \frac{1}{I} + \frac{1}{IKsv}\cdot\frac{1}{\{BrCH_2NO_2\}} \qquad \text{(photocurrent)} \qquad (7)$$

where P and P_0 are the emission intensities of $*Ru(bpy)_3{}^{2+}$ in the presence and the absence of $BrCH_2NO_2$, respectively; F is the Faraday constant; i is a photocurrent; I is an effective light intensity; and $Ksv = k_3/(k_1+k_2)$ is a Stern-Volmer constant. Since the Ksv of equation 7 is given by dividing the intercept by the slope, it does not depend upon whether photocurrents contain reduction currents for $\cdot CH_2NO_2$. The Stern-Volmer constants yielded from the least-squares lines are given in Table 1, including those for $Co(NH_3)_5Cl^{2+}$, which is known to deactivate $*Ru(bpy)_3{}^{2+}$ by electron transfer quenching[8,9]:

$$*Ru(bpy)_3{}^{2+} + Co(NH_3)_5Cl^{2+} \longrightarrow Ru(bpy)_3{}^{3+} + Co^{2+} + 5NH_3 + Cl^-$$

The Stern-Volmer constants determined by the two independent methods show a fair agreement with each other. It is, therefore, concluded that the photocurrent arises as a consequence of the electron transfer quenching of $*Ru(bpy)_3{}^{2+}$.

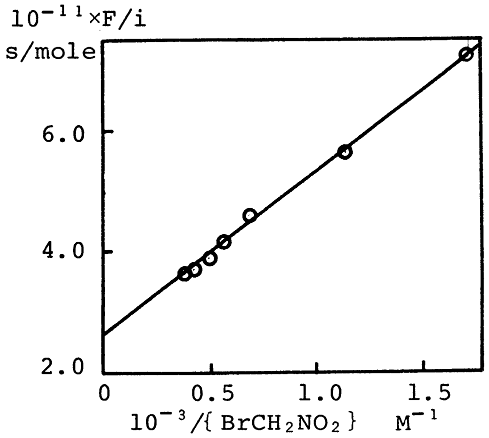


Fig. 2. Stern-Volmer plots for cathodic photocurrents at +0.5 V.

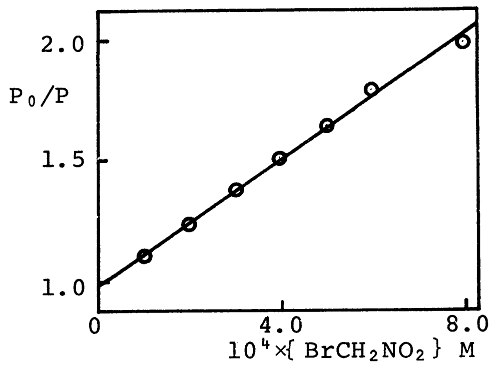


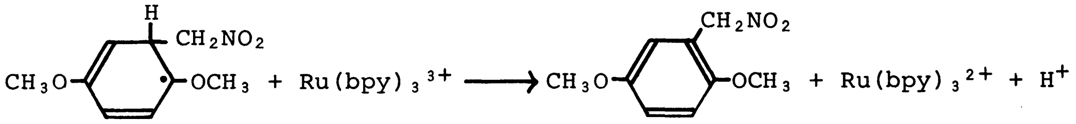
Fig. 3. Stern-Volmer plots for the quenching of $*Ru(bpy)_3{}^{2+}$ emission.

Quencher Method	$BrCH_2NO_2$	$Co(NH_3)_5Cl^{2+}$
Emission quenching[a]	1040 M^{-1}	350[c] M^{-1}
Photocurrent[b]	970	260

Table 1. Stern-Volmer constants for the quenching of $*Ru(bpy)_3{}^{2+}$.
[a] Determined for 0.67 mM $Ru(bpy)_3{}^{2+}$ and 0.1-0.8 mM quencher in 0.1 N sulfuric acid.
[b] Determined for 0.1 mM $Ru(bpy)_3{}^{2+}$ and 0.5-2.1 mM quencher in 0.1 N sulfuric acid.
[c] 100 and 560 have been reported in ref. 8 and 9, respectively.

In order to trap $\cdot CH_2NO_2$ produced from reaction 4, a photoreaction was tried in the presence of 1,4-dimethoxybenzene. In a typical run, 1,4-dimethoxybenzene (696 mg), $BrCH_2NO_2$ (702 mg), and $Ru(bpy)_3Cl_2$ (18 mg) in 2 N hydrochloric acid (2.5 ml), water (20.5 ml), and acetonitrile (27 ml) were irradiated for 4 hours with a 650 W projector equipped with a glass filter (λ > 406 nm) under nitrogen.

The reaction mixture was extracted with dichloromethane, and the extract was dried over anhydrous magnesium sulfate. After evaporation of the solvent under reduced pressure, the residue was chromatographed on silica gel being eluted with chloroform to recover 1,4-dimethoxybenzene (426 mg), and 1,4-dimethoxy-2-nitromethylbenzene[10) (282 mg) was isolated in 73 % yield based on the 1,4-dimethoxybenzene consumed. No reaction proceeded, of course, in the absence of $Ru(bpy)_3Cl_2$. It is reasonable to suppose that the nitromethylation is photo-catalyzed by $Ru(bpy)_3^{2+}$ which is regenerated by the following reaction:



Thus, it was found that each $Ru(bpy)_3^{2+}$ induced the photo-catalytic cycle about 51 times in the above experiment.

Bromomalononitrile also quenched the emission of $^*Ru(bpy)_3^{2+}$ and produced cathodic photocurrents at an SnO_2 electrode. In general, electron deficient oranic halogen compounds may function as a new type of organic quenchers which deactivate excited states by electron transfer quenching accompanied by irreversible decomposition.

References and Notes

(1) C. R. Bock, T. J. Meyer, and D. G. Whitten, J. Amer. Chem. Soc., 96, 4710 (1974).
(2) C. R. Bock, T. J. Meyer, and D. G. Whitten, ibid., 97, 2909 (1975).
(3) S. O. Kobayashi, N. Furuta, and O. Simamura, Chem. Lett., 503 (1976).
(4) All potentials refer to SCE.
(5) G. N. Lewis and M. Kasha, J. Amer. Chem. Soc., 66, 2100 (1944).
(6) J. N. Demas and G. A. Crosby, ibid., 93, 2841 (1971).
(7) J. Armand, Bull. Soc. Chim. Fr., 543 (1966).
(8) H. D. Gafney and A. W. Adamson, J. Amer. Chem. Soc., 94, 8238 (1972).
(9) G. Navon and N. Sutin, Inorg. Chem., 13, 2159 (1974).
(10) PMR($CDCl_3$) δ 3.78(s,3H), 3.80(s,3H), 5.45(s,2H), around 6.9(m,3H); IR(neat) 1560 and 1375 cm^{-1} (nitro group); MS m/e 197(M^+); Found: C, 54.60; H, 5.43; N, 7.01 %. Calcd. for $C_9H_{11}NO_4$: C, 54.82; H, 5.62; N, 7.10 %.

(Received November 4, 1977)