Quantum Yield of Formation of the Lowest Excited State of Ru(bpy)$_3^{2+}$ and Ru(phen)$_3^{2+}$

F. BOLLETTA*, A. JURIS, M. MAESTRI and D. SANDRINI

Istituto Chimico 'G. Ciamiciani' dell'Università, Bologna, Italy

Received October 26, 1979

Fig. 1. Dependence of the reciprocal quantum yield of oxidation of Ru(bpy)$_3^{2+}$ to Ru(bpy)$_3^{3+}$ upon $1/[S_2O_8^{2-}]$ in 1 N H$_2$SO$_4$. The line has an intercept of 0.5 ± 0.05 corresponding to a limiting quantum yield of 2.0 ± 0.2.

In the last few years it has been found that transition metal complexes containing aromatic molecules such as 2,2′-bipyridine or 1,10-phenanthroline as ligands are very interesting photochemical and photophysical systems [1]. These complexes have large extinction coefficients in the visible, are generally stable towards photodissociation and are able to emit luminescence even in fluid solution at room temperature. Moreover, the emitting excited state has usually long enough lifetime to be involved in bimolecular processes such as electron transfer [1] and energy transfer [2]. The electron transfer reactions of these complexes are particularly interesting because they can provide a basis for the design of artificial systems to be used in the splitting of water by solar energy [3–5]. The best known among these complexes are the tris-bipyridine and the tris-phenanthroline Ru(II) complexes, Ru(bpy)$_3^{2+}$ and Ru(phen)$_3^{2+}$, whose lowest excited states, which may formally be considered a triplet metal-to-ligand charge transfer state (^{3}CT), have been extensively used for both electron and energy transfer processes.

The convenience of using an excited state in bimolecular processes is of course related to the quantum yield of formation of such an excited state. The quantum yield of formation of Ru(bpy)$_3^{2+}$, hereafter indicated as Φ_T, was suggested to be unitary by Demas and Crosby [6]. Later, experimental results have cast some doubts on this value. Bensasson *et al.* [7], using flash-photolysis techniques, suggested a lower limit value of 0.5 for Ru(bpy)$_3^{2+}$, but more recently they have found evidence for Φ_T = 1 [8]. On the other hand, from energy transfer experiments we have obtained a Φ_T value $\cong$1 for Ru(bpy)$_3^{2+}$ and $\cong$0.6 for Ru(phen)$_3^{2+}$ [9]. Thus we thought it worthwhile using another technique to try to evaluate Φ_T for Ru(bpy)$_3^{2+}$ and Ru(phen)$_3^{2+}$. Such a technique is based on electron transfer experiments involving the excited states of the complexes and S$_2$O$_8^{2-}$ ions as oxidizing agents.

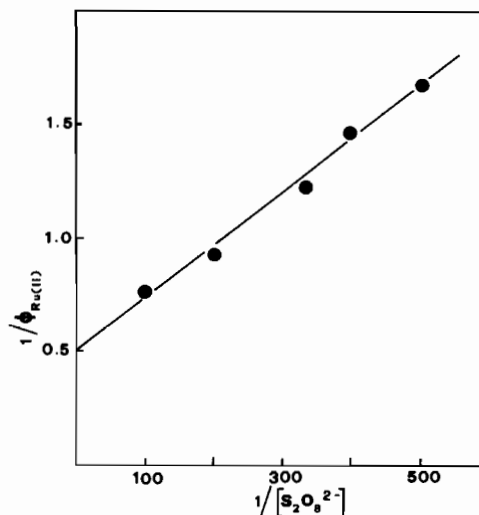The phosphorescence emission of the two complexes was quenched by S$_2$O$_8^{2-}$ ions; bimolecular

quenching constants of 5.33 × 10^8 M^{-1} s^{-1} and 5.63 × 10^8 M^{-1} s^{-1} were obtained from Stern–Volmer plots for Ru(bpy)$_3^{2+}$ and Ru(phen)$_3^{2+}$, respectively.

Acid solutions (1 N H$_2$SO$_4$) containing 10^{-4} M Ru(bpy)$_3^{2+}$ or Ru(phen)$_3^{2+}$ and S$_2$O$_8^{2-}$ up to 0.1 M were spectrophotometrically stable (within 3%) at 20 °C in the dark for at least 20 minutes. Irradiation of these solutions with 445 nm light (which was totally absorbed by the metal complex) caused a decrease in the optical density of the solution at 450 nm. The spectral variations were in agreement with conversion of the Ru(II) complex into the corresponding Ru(III) species. This conversion, which was complete for irradiation periods longer than 20 minutes, is supported by the fact that it was possible to completely regenerate the absorbance due to Ru(II) species by reducing the irradiated solutions with Na$_2$SO$_3$. The optical density at 450 nm decreased linearly with time for short irradiation periods ($\leqslant$60 s) so that it was possible to calculate the quantum yield of loss of Ru(II), $\Phi_{Ru(II)}$. The $\Phi_{Ru(II)}$ value strongly depended on S$_2$O$_8^{2-}$ concentration and specifically it increased with increasing [S$_2$O$_8^{2-}$]. As is shown in Fig. 1 for the Ru(bpy)$_3^{2+}$– S$_2$O$_8^{2-}$ system, a plot of $1/\Phi_{Ru(II)}$ *vs.* $1/[S_2O_8^{2-}]$ is linear with intercept 0.5 ± 0.05; the same intercept value was obtained for Ru(phen)$_3^{2+}$.

This behavior can be explained by a mechanism which implies a monoelectronic oxidation of excited Ru(II) complexes with formation of a SO$_4^{2-}$ ion and a SO$_4^-$ radical. This radical is known to be a highly oxidizing agent [10], and may be able to oxidize a
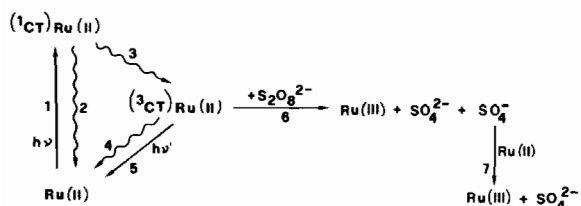
---

*Author to whom correspondence should be addressed.

$(^1CT)_{Ru(II)}$

Fig. 2. Reaction scheme for the photooxidation of $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ by $S_2O_8^{2-}$ ions.

ground state Ru(II) complex to the corresponding Ru(III) species*.

A general, although simplified, reaction scheme is reported in Fig. 2. This scheme holds for both $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ complexes. Irradiation of Ru(II) species in their charge transfer band leads to the singlet charge transfer state (step 1) which either deactivates to the ground state (step 2) or undergoes intersystem crossing to the triplet charge transfer state (step 3). In the absence of $S_2O_8^{2-}$ ions the (^{3}CT) state thermally deactivates to the ground state (step 4) or gives phosphorescence emission (step 5). When $S_2O_8^{2-}$ ions are present, the (^{3}CT) state may deactivate by electron transfer reaction leading to Ru(III) species (step 6). Moreover, the SO_4^- radicals formed can oxidize the Ru(II) complexes (step 7).

A steady-state treatment of the reaction scheme of Fig. 2 leads to the following equation for $\Phi_{Ru(II)}$:

$$\Phi_{Ru(II)} = \frac{k_3}{k_3 + k_2} \cdot \frac{2k_6[S_2O_8^{2-}]}{k_4 + k_5 + k_6[S_2O_8^{2-}]} =$$

$$\Phi_T \cdot \frac{2k_6[S_2O_8^{2-}]}{k_4 + k_5 + k_6[S_2O_8^{2-}]}$$

This equation holds if (i) the electron transfer is the only quenching mechanism of (^{3}CT)Ru(II) by S_2-O_8^{2-} ions and (ii) the electron transfer reaction is irreversible. Our choice of $S_2O_8^{2-}$ ion as oxidizing agent completely meets the above conditions. An

energy transfer mechanism, which represents an alternative quenching mode, can in fact be ruled out on energetic grounds. Moreover back electron transfer reaction is unlikely**. Thus, in our case, when $[S_2O_8^{2-}]$ is sufficiently high that $k_6[S_2O_8^{2-}]$ is the only deactivation path for the triplet, $\Phi_{Ru(II)} = 2 \times \Phi_T$. The extrapolated value obtained for $\Phi_{Ru(II)}$ from the plot of Fig. 1 leads to the conclusion that for both $Ru(bpy)_3^{2+}$ and $Ru(phen)_3^{2+}$ the quantum yield of formation of the lowest excited state is unity.

Acknowledgements

References

1 V. Balzani, F. Bolletta, M. T. Gandolfi and M. Maestri, *Topics Curr. Chem.*, *75*, 1 (1978).
2 V. Balzani, L. Moggi, M. F. Manfrin, F. Bolletta and G. S. Laurence, *Coord. Chem. Rev.*, *15*, 321 (1975).
3 J. M. Lehn and J. P. Sauvage, *Nouv. J. Chim.*, *1*, 449 (1977).
4 A. Moradpour. E. Amouyal, P. Keller and H. Kagan, *Nouv. J. Chim.*, *2*, 545 (1978).
5 K. Kalayanasundaram, J. Kiwi and M. Gratzel, *Helv. Chim. Acta*, *61*, 2720 (1978).
6 N. J. Demas and G. A. Crosby, *J. Am. Chem. Soc.*, *93*, 2841 (1971).
7 R. Bensasson, C. Salet and V. Balzani, *J. Am. Chem. Soc.*, *98*, 3722 (1976).
8 R. Bensasson, C. Salet and V. Balzani, *C.R. Acad. Sci. Ser. C*, in press.
9 F. Bolletta, M. Maestri and V. Balzani, *J. Phys. Chem.*, *80*, 2499 (1976).
10 R. Memming, *J Electrochem. Soc.*, *116*, 785 (1969).
11 R. W. Matthews and T. J. Sworski, *J. Phys. Chem.*, *79*, 684 (1975).

---

*This mechanism is similar to that proposed by Matthews and Sworski [11] in the photooxidation of Ce(III) ions by $S_2O_8^{2-}$. Note that the reduction potential of the involved species are: $E^\circ_{Ru(III)/(^3CT)Ru(II)} = -0.86$ V [1], and -0.92 V [1]; $E^\circ_{Ru(III)/Ru(II)} = 1.26$ V [1], and 1.26 V [1], for the bipyridine and phenanthroline complexes, respectively; $E^\circ_{S_2O_8^{2-}/SO_4^{2-}} + SO_4^- \leqslant 0.6$ V [10]; $E^\circ_{SO_4^-/SO_4^{2-}} \geqslant 3.4$ V [10].

**Although the back reaction is thermodynamically allowed, its occurrence seems implausible on the basis of concentration and order considerations. In any case it cannot compete with the reduction of SO_4^- by $Ru(bpy)_3^{2+}$.