Photochemistry and Photophysics of Tris(2,2′-bipyridine)chromium(III)

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Summary Phosphorescence intensity and lifetime and doublet absorption of $[Cr(bpy)_3]^{3+}$ (bpy = 2,2′-bipyridine) do not depend on pH (1·0—9·6), whereas the photoaquation quantum yield increases from $\leqslant 10^{-3}$ at pH 4 to *ca.* 0·1 at pH 9; complete quenching of the phosphorescence by I^- ions causes at least 95% quenching of the photoreaction.

THE $[Cr(bpy)_3]^{3+}$ ion (bpy = 2,2′-bipyridine) is currently used in energy and electron transfer processes,[1,2] but the photochemistry and photophysics of the complex itself have not been fully investigated. We report here preliminary results of emission intensity and lifetime, and flash and continuous photolysis experiments carried out on this complex in solution under various conditions.

Experiments were performed using apparatus and techniques previously described.[3] Aqueous solutions were used unless otherwise noted. The $^4T_2 \rightsquigarrow {}^2E$ intersystem crossing efficiency is close to unity.[2] The luminescence spectrum of the complex consists of two narrow peaks at 695 and 727 nm attributed[4] to phosphorescence from the thermally equilibrated $^2T_1$ and ^2E levels.† The phosphorescence quantum yield ($<10^{-3}$) is independent of excitation wavelength (350—450 nm) and pH (1·0—9·6). The phosphorescence lifetime is 60 μs in deaerated aqueous solution at 22 °C, independent of pH (1·0—9·6). The phosphorescence intensity at 727 nm decreases with increasing temperature ($\Delta E = 38{\cdot}1$ kJ mol^{-1}).[5] The phosphorescence is quenched by O_2 (k_q *ca.* 2×10^7 l mol^{-1} s^{-1}) and I^- ions ($k_q = 1{\cdot}1 \times 10^9$ l mol^{-1} s^{-1}).

Upon flash excitation of O_2-free aqueous solutions of $[Cr(bpy)_3]^{3+}$, a transient is observed which exhibits absorption bands at 390, 445, and 590 nm, and shoulders at 475 and 650 nm. The entire spectrum decays by first order kinetics, with $k = 1{\cdot}6 \times 10^4$ s^{-1} at 22 °C, independent of pH in the range $-0{\cdot}4$ to 13·1. The temperature dependence of the decay rate constant corresponds to an activation energy of 34·7 kJ mol^{-1}. The transient is quenched by oxygen ($k_q = 1{\cdot}7 \times 10^7$ l mol^{-1} s^{-1}) and I^- ions ($k_q = 1{\cdot}2 \times 10^9$ l mol^{-1} s^{-1}). These results indicate that the transient absorption is due to the same excited state which is responsible for the phosphorescence emission.

In continuous irradiation experiments, a net photochemical reaction is obtained which is stoicheiometrically identical to the thermal reaction (1),[6] where P is $[Cr(bpy)_2(OH)_2]^+$, $[Cr(bpy)_2(H_2O)(OH)]^{2+}$,

$$[Cr(bpy)_3]^{3+} \xrightarrow[H_2O]{h\nu} P + bpy \qquad (1)$$

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† Hereafter these two levels will be considered as a single level and called ^2E.

or $[Cr(bpy)_2(H_2O)_2]^{3+}$ depending on the pH of the solution. The quantum yield at 11 °C depends on pH exactly in the same way as does the rate constant of the thermal reaction.[6] The 'plateau' values are $\phi \leqslant 10^{-3}$ (pH 4) and ϕ *ca.* 0·1 (pH 9·6). At pH 9·6, the quantum yield is independent of the excitation wavelength (313—465 nm). The photoreaction is quenched by oxygen and iodide ions to nearly the same extent as the phosphorescence. With I^- ions as quencher, a plot of ϕ/ϕ° *vs.* I/I°[7] at pH 9·6 and 11 °C shows that at least 95% of the reaction is quenched upon complete quenching of the phosphorescence emission. Therefore, the quantum yield of the prompt photoreaction from $^4T_2$ is, at most, 5% of the total quantum yield, and at least 95% of the reacting molecules pass through the emitting state, ^2E. For the quenchable part of the photoreaction there are two possible origins:[7] (i) direct reaction from ^2E and (ii) reaction from $^4T_2$ by molecules which have passed through ^2E ('delayed' photoreaction).

Kane-Maguire, *et al.*[4] observed a broad structureless emission band at 570 nm upon excitation of Me_2SO solutions of $[Cr(bpy)_3]^{3+}$ with Raman laser equipment, and assigned this band to $^4T_2 \rightarrow {}^4A_2$ fluorescence. In Me_2SO solution we have obtained the following results: (i) with a Raman laser apparatus equipped with a R446 photomultiplier, a broad emission band is observed at 570 nm which is more intense than the 727 nm phosphorescence band; with a conventional spectrofluorimeter equipped with the same photomultiplier, however, the phosphorescence band at 727 nm is clearly observable but no emission is present at 570 nm, and (ii) continuous irradiation with the laser equipment causes an increase in the 570 nm emission and a decrease in the 727 nm emission. These results seem to indicate that the 570 nm emission is due to some product which is formed along the laser beam rather than to $^4T_2 \rightarrow {}^4A_2$ fluorescence.

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[1] F. Bolletta, M. Maestri, L. Moggi, and V. Balzani, *J.C.S. Chem. Comm.*, 1975, 901; R. Ballardini, G. Varani, F. Scandola, and V. Balzani, *J. Amer. Chem. Soc.*, 1976, **98**, 7432; S. C. Pyke and J. F. Endicott, personal communication.

[2] F. Bolletta, M. Maestri, and V. Balzani, *J. Phys. Chem.*, 1976, **80**, 2499.

[3] R. Ballardini, G. Varani, L. Moggi, V. Balzani, K. R. Olson, F. Scandola, and M. Z. Hoffman, *J. Amer. Chem. Soc.*, 1975, **97**, 728.

[4] N. A. P. Kane-Maguire, J. Conway, and C. H. Langford, *J.C.S. Chem. Comm.*, 1974, 801.

[5] See also: N. A. P. Kane-Maguire and C. H. Langford, *Chem. Comm.*, 1971, 895.

[6] M. Maestri, F. Bolletta, N. Serpone, L. Moggi, and V. Balzani, *Inorg. Chem.*, 1976, **15**, 2048.

[7] R. Ballardini, G. Varani, H. F. Wasgestian, L. Moggi, and V. Balzani, *J. Phys. Chem.*, 1973, **77**, 2947.