$^4T_2 \rightsquigarrow {}^2E$ Intersystem-crossing Efficiency in the $Cr(bpy)_3{}^{3+}$ and $Cr(phen)_3{}^{3+}$ Ions in Aqueous Media

By Nick Serpone* and Mary A. Jamieson
(*Department of Chemistry, Concordia University, Montreal, Quebec, Canada* H3G-1M8)
and Morton Z. Hoffman
(*Department of Chemistry, Boston University, Boston, Massachusetts* 02215)

Summary Comparison of the photoaquation quantum yields of $Cr(bpy)_3{}^{3+}$ and $Cr(phen)_3{}^{3+}$ complexes in alkaline aqueous media, from direct irradiation into the spin-allowed $^4T_2$ manifold and into the spin-forbidden $^2T_1/^2E$ states, indicates that the $^4T_2 \rightsquigarrow {}^2E$ intersystem-crossing (isc) yields are identical for the two complexes (η_{isc} *ca.* 1).

The photochemistry and photophysics of polypyridyl chromium(III) complexes, $Cr(NN)_3{}^{3+}$, have been the object of many recent investigations.[1–3] Detailed studies on $Cr(bpy)_3{}^{3+}$ (bpy = 2,2′-bipyridine) have demonstrated that excitation into the spin-allowed quartet manifolds (see Figure) results in the rapid formation of the lowest excited-quartet state, $^4T_2$, (lifetime $\leqslant 1$ ns)[4] which undergoes non-radiative (nr) decay ($^4k_{nr}$) to the $^4A_2$ ground state, in competition with intersystem crossing (isc) ($^4k_{isc}$) into the doublet manifolds $^2T_1/^2E$ and reaction with the solvent ($^4k_{rx}$); no fluorescence has been observed from $^4T_2$ in aqueous solution. The thermally equilibrated $^2T_1/^2E$ states undergo non-radiative ($^2k_{nr}$) and radiative ($^2k_{rad}$) return to the ground state and react (*via* $^2T_1$)[5] with the solvent ($^2k_{rx}$) to form a 7-co-ordinate intermediate which is the direct precursor of the final aquated product.[3] Back intersystem-crossing from $^2T_1/^2E$ to $^4T_2$ has been ruled out on experimental and theoretical grounds.[3,6]

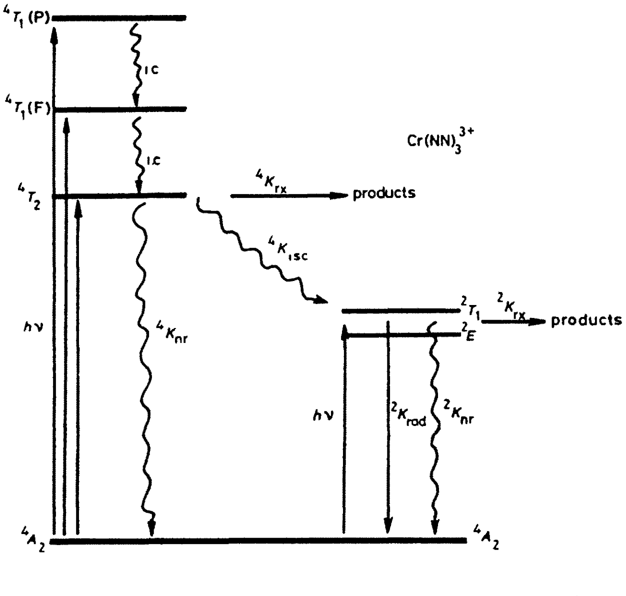

Figure. Simplified energy-state diagram for polypyridyl-chromium(III) complexes (i.c. = internal conversion).

The identity of the reactive excited-state in the photochemical activity of chromium(III) complexes, however, continues to be a controversial issue. It is generally accepted, for example, that part of the photochemistry quenched in parallel with the luminescence from $^2T_1/^2E$ states must take place from these states. What is too often not clear, however, is whether this quenched photoreaction occurs directly from the doublet manifolds or from the quartet manifold subsequent to back intersystem-crossing. One crucial parameter in elucidating the photochemical mechanism of polypyridylchromium(III) complexes is the intersystem-crossing yield [equation (1)]. Therefore it is not

$$^4\eta_{isc} = {}^4k_{isc}/({}^4k_{isc} + {}^4k_{nr} + {}^4k_{rx}) \qquad (1)$$

surprising that various studies have been directed at evaluating η_{isc}. Bolletta *et al.*[7] evaluated $^4\eta_{isc}$ for $Cr(bpy)_3{}^{3+}$ to be *ca.* 1; the corresponding value for $Cr(phen)_3{}^{3+}$ (phen = 1,10-phenanthroline) in 1:3 (v/v) H_2O-DMF (DMF = dimethylformamide) solution was reported to be *ca.* 0·2. This latter value has been questioned[6] in the light of the photophysical and photochemical similarities between the two complexes. We have also shown that $^4\eta_{isc}$ is dependent on the solvent medium[8] and recent studies[9] have revealed that $Cr(bpy)_3{}^{3+}$ exhibits unusual photochemical behaviour in DMF–H_2O solutions. It becomes imperative that $^4\eta_{isc}$ be determined under the same conditions of solution medium in which the photochemistry is investigated.[3,5]

In alkaline solution, the quantum yield (Φ_{rx}) for the photoaquation reaction [equation(2)] reflects the population of the

$$Cr(NN)_3{}^{3+} \xrightarrow[OH^-{-}H_2O]{h\nu} Cr(NN)_2(OH)_2{}^{+} + NN \qquad (2)$$

$^2T_1/^2E$ states and the other competitive modes. For example, if excitation were directly into the doublet manifolds, $^2\Phi_{rx} = {}^2k_{rx}{}^2\tau$, where $^2\tau = 1/({}^2k_{rx} + {}^2k_{nr} + {}^2k_{rad} + {}^2k_g[Cr^{III}] + {}^2k_q[Q])$; ^2k_g is the rate constant for the quenching of $^2T_1/^2E$ by the ground-state substrate and ^2k_q represents the rate constants of all the other steps that quench $^2T_1/^2E$. For excitation into the quartet manifolds, $^{4\rightarrow 2}\Phi_{rx} = {}^4\eta_{isc}{}^2k_{rx}{}^2\tau$; inasmuch as $^4\Phi_{rx}$, the quantum yield of reaction directly from $^4T_2$, is $<10\%$ of $^{4\rightarrow 2}\Phi_{rx}$, its contribution can be ignored. Therefore, $^{4\rightarrow 2}\Phi_{rx} = {}^2\Phi_{rx}{}^4\eta_{isc}$. Equation (3) may be used for

$$\left(\frac{^{4\rightarrow 2}\Phi^{p}_{rx}}{^{4\rightarrow 2}\Phi^{b}_{rx}}\right) = \left(\frac{^{2}\Phi^{p}_{rx}}{^{2}\Phi^{b}_{rx}}\right)\left(\frac{^{4}\eta^{p}_{isc}}{^{4}\eta^{b}_{isc}}\right) \qquad (3)$$

a comparison between $Cr(bpy)_3{}^{3+}$ (b) and $Cr(phen)_3{}^{3+}$ (p), where $^{4\rightarrow 2}\Phi^{p}_{rx}$ 0·010,[10] $^{4\rightarrow 2}\Phi^{b}_{rx}$ 0·18,[5] and $^4\eta_{isc}$ *ca.* 1.[7] Determination of $({}^2\Phi^{p}_{rx}/{}^2\Phi^{b}_{rx})$ under identical photochemical and solution medium conditions to those used to determine $^{4\rightarrow 2}\Phi^{p}_{rx}$ and $^{4\rightarrow 2}\Phi^{b}_{rx}$ would give an estimation of $^4\eta^{p}_{isc}$.

Argon-purged solutions of the title complexes ($1{\cdot}0 \times 10^{-3}$ M) (at pH 9·26) and 1 M NaCl in 0·008 M Britton–Robinson buffer were flashed at 22 °C under identical conditions with 0·3 μs pulses [λ_{exc} (max) 692 nm with oxazine 720 dye] from a Phase-R Corp. DL-2100C tunable dye laser which delivers 1—1·3 J pulse^{-1}. The concentration of free bpy or phen released from the photoreaction was determined with the same extraction procedure previously used to evaluate $^{4\to2}\Phi_{\text{rx}}$;[1,3] the limit of detection of free bpy or phen by this spectrophotometric method is *ca.* 3×10^{-7} M. Identical samples were also kept in the dark in order to assess and account for the thermal component of the observed photoreaction.

Under the conditions of the experiments, the concentration of free bpy from the photolysis (100 pulses) of $\text{Cr(bpy)}_3{}^{3+}$ was 4×10^{-6} M; no free phen ($<3 \times 10^{-7}$ M) was observed from the identical photolysis of $\text{Cr(phen)}_3{}^{3+}$. Inasmuch as $^{2}\Phi_{\text{rx}}$ is defined as $(\Delta[\text{NN}]/\Delta t)(I_{\text{a}})^{-1}$ and for the same concentrations of weakly absorbing $\text{Cr(bpy)}_3{}^{3+}$ and $\text{Cr(phen)}_3{}^{3+}$ in cuvettes of the same path length, equation (4) can easily be derived. Since the ϵ_λ values of $\text{Cr(phen)}_3{}^{3+}$ at 695 and 727 nm are approximately twice those of $\text{Cr(bpy)}_3{}^{3+}$[11] and from the values of the other parameters, we predict that if $^4\eta^{\text{p}}_{\text{isc}}$ *ca.* 1, Δ[phen] is *ca.* 4×10^{-7} M, while if $^4\eta^{\text{p}}_{\text{isc}}$ *ca.* 0·2, Δ[phen] is *ca.* 2×10^{-6} M.

$$\left(\frac{^{4\to2}\Phi^{\text{p}}_{\text{rx}}}{^{4\to2}\Phi^{\text{b}}_{\text{rx}}}\right) = \left(\frac{^4\eta^{\text{p}}_{\text{isc}}}{^4\eta^{\text{b}}_{\text{isc}}}\right)\left(\frac{\Delta[\text{phen}]}{\Delta[\text{bpy}]}\right)\left(\frac{\epsilon_\lambda}{\epsilon^{\text{p}}_\lambda}\right) \qquad (4)$$

To the extent that we observe no free phen in the photolysed $\text{Cr(phen)}_3{}^{3+}$ solution, we conclude that $^4\eta^{\text{p}}_{\text{isc}} \simeq {}^4\eta^{\text{b}}_{\text{isc}} \simeq 1$. This result is in accord with the value of 0·95 suggested by Kane-Maguire and Langford[12] from O_2-quenching studies of the photoracemization of optically acitve $\text{Cr(phen)}_3{}^{3+}$. It is also interesting to note that $^{4\to2}\Phi^{\text{p}}_{\text{rx}}$ *ca.* $0{\cdot}05\,{}^{4\to2}\Phi^{\text{b}}_{\text{rx}}$. Two main factors may account for this difference: (a) ground-state quenching in the phen complex in 1 M Cl^- media[13] and (b) the greater rigidity of the phen *vis-à-vis* the bpy ligand framework.[10]

Support of this work by N.S.E.R.C. (Canada), F.C.A.C. (Quebec), N.S.F. (USA), and NATO is gratefully acknowledged.

(*Received*, 14*th May* 1980; *Com.* 527.)

---

[1] N. Serpone, M. A. Jamieson, M. S. Henry, M. Z. Hoffman, F. Bolletta, and M. Maestri, *J. Am. Chem. Soc.*, 1979, **101**, 2907, and references therein.

[2] B. Brunschwig and N. Sutin, *J. Am. Chem. Soc.*, 1978, **100**, 7568.

[3] M. Maestri, F. Bolletta, L. Moggi, V. Balzani, M. S. Henry, and M. Z. Hoffman, *J. Am. Chem. Soc.*, 1978, **100**, 2694.

[4] A. D. Kirk, P. E. Hoggard, G. B. Porter, M. G. Rockley, and M. Windsor, *Chem. Phys. Lett.*, 1976, **37**, 199.

[5] M. A. Jamieson, N. Serpone, M. S. Henry, and M. Z. Hoffman, *Inorg. Chem.*, 1979, **18**, 214.

[6] C. H. Langford and R. Sasseville, *Inorg. Chem.*, 1980, **19**, 2850.

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

[8] R. Sriram, M. Z. Hoffman, and N. Serpone, *J. Am. Chem. Soc.*, submitted for publication.

[9] G. B. Porter and J. VanHouten, *Inorg. Chem.*, submitted for publication; *Inorg. Chem.*, 1979, **18**, 2053.

[10] M. A. Jamieson, N. Serpone, R. Sriram, and M. Z. Hoffman, *Inorg. Chem.*, submitted for publication.

[11] E. König and S. Herzog, *J. Inorg. Nucl. Chem.*, 1970, **32**, 585; C. H. Langford, personal communication.

[12] N. A. P. Kane-Maguire and C. H. Langford, *Inorg. Chem.*, 1976, **15**, 464.

[13] R. Sriram, M. Z. Hoffman, M. A. Jamieson, and N. Serpone, *J. Am. Chem. Soc.*, 1980, **102**, 1754.