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Oxygen Quenching of Metal-centered Excited States of Polypyridyl Complexes of Chromium(III)

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Oxygen quenching of the excited triplet states of organic molecules has been extensively investigated [1–4]; in contrast, studies of the interactions between O_2 and the excited states of inorganic complexes have only recently been reported [5–9]. Two important mechanisms [10] are used to account for the quenching of excited states: energy transfer (reaction 1), and oxidative (reaction 2) or reductive (reaction 3) electron transfer. The metal-to-ligand-

$$^{*}M(NN)_3^{n+} + Q \xrightarrow{\text{en. tr.}} M(NN)_3^{n+} + {}^{*}Q \qquad (1)$$

$$^{*}M(NN)_3^{n+} + Q \xrightarrow{\text{oxid.}} M(NN)_3^{(n+1)+} + Q^- \qquad (2)$$

$$^{*}M(NN)_3^{n+} + Q \xrightarrow{\text{red}} M(NN)_3^{(n-1)+} + Q^+ \qquad (3)$$

charge-transfer (MLCT) excited states of $^{*}Ru(NN)_3^{2+}$ and $^{*}Os(NN)_3^{2+}$ (NN = 2,2′-bipyridine, bpy; 1,10-phenanthroline, phen, or their substituted derivatives) are apparently quenched by O_2 via simple energy transfer to give $^1O_2$ with very high efficiencies (0.68–0.85) [6]. However, Sutin and coworkers [8] concluded from their study, corroborated by Hammond and coworkers [9], that O_2-quenching of (MLCT)$Ru(NN)_3^{2+}$ and, by analogy, (MLCT)$Os(NN)_3^{2+}$, proceeds via an electron transfer pathway (reaction 2). Inasmuch as the ^2E states of $Cr(NN)_3^{3+}$ complexes are metal-centred, it is important to examine the effects of the orbital nature of the excited state and ligand substitution for Cr(III) in comparison with those reported for Ru(II) [8].

The $Cr(NN)_3^{3+}$ complexes (Table I) were prepared as ClO_4^- salts by reacting anhydrous $CrCl_2$ with the stiochiometric amount of the ligand in N_2-purged acidic aqueous solutions. Oxidation to Cr(III) was effected with Cl_2 gas. All the complexes gave good elemental analyses [11]. Quenching rate constants, k_q, (Table I) were obtained from phosphorescence ($\lambda \sim 728$–742 nm) intensity measurements (Perkin-Elmer MPF 2A spectrofluorimeter; $\mu = 1.0$ *M* HCl; 25 °C) in N_2-purged, air-equilibrated, and O_2-purged aqueous solutions.

The data in Table I show that for the reaction of O_2 with $(^2E)Cr(NN)_3^{3+}$, the values of k_q are 2–3 orders of magnitude smaller than the diffusion controlled rate and 1–2 orders of magnitude smaller than the values of k_q for organic triplet states ($\sim 3 \times 10^9$ M^{-1} s^{-1} for 10.0 kK $< E_T <$ 15.0 kK; when $E_T >$ 16.0 kK, k_q decreases in value [1]). Presumably, whenever the donor triplet energy exceeds the energy of the acceptor state by ~1.0 kK a diminution in the rate of energy transfer takes place [1, 12]. Inasmuch as the two lowest excited states of O_2 occur at ~12.9 kK ($^1\Sigma_g^+$) and ~7.9 kK ($^1\Delta_g$) [13] and the energy of $(^2E)Cr(NN)_3^{3+}$ is ~13.7 kK, energy transfer to form $^1_1O_2$ is energetically feasible (reaction 4). The data

$$(^2E)Cr(NN)_3^{3+} + {}^3O_2 \rightarrow (^4A_2)Cr(NN)_3^{3+} + {}^1O_2 \qquad (4)$$

also show that k_q is particularly sensitive to small differences in the energies of the ^2E donor states.

TABLE I. Oxygen Quenching Rate Data of $(^2E)Cr(NN)_3^{3+}$ Complexes.

Complex	k_q (10^7 M^{-1} s^{-1})	^2E, kK	ΔE^f, V[a]
$Cr(4,4'\text{-}Ph_2bpy)_3^{3+}$	17	13.4_7	
$Cr(4,4'\text{-}Me_2bpy)_3^{3+}$	3.4	13.6_8	−0.17[b]
$Cr(bpy)_3^{3+}$	1.7	13.7_4	0.02[b]
$Cr(4,7\text{-}Ph_2phen)_3^{3+}$	31	13.4_6	
$Cr(3,4,7,8\text{-}Me_4phen)_3^{3+}$	15	13.5_7	−0.175
$Cr(4,7\text{-}Me_2phen)_3^{3+}$	19	13.6_2	−0.140
$Cr(5\text{-}Clphen)_3^{3+}$	3.7	13.7_4	0.125
$Cr(phen)_3^{3+}$	2.7	13.7_4	0

[a] $E^f[Cr(NN)_3^{3+}/Cr(NN)_3^{2+}] - E^f[Cr(phen)_3^{3+}/Cr(phen)_3^{2+}]$; ref. 24. [b] Ref. 25.

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Consideration of these results suggests that reaction 4 generates $(^1\Delta_g)O_2$. The variations in k_q can neither be attributed to Franck-Condon factors [1], nor solely to the insulating effect of the tight solvation spheres [5] about the highly charged cations. However, the magnitude of k_q, relative to the diffusion controlled limit, may arise from the insulating effect of the solvation spheres which would retard the penetration of O_2 to the distance required for effective quenching [5].

Balzani and Bolletta [14] have recently shown that collisional energy transfer processes can successfully be treated within the Weller and the Marcus concepts of outer-sphere electron transfer processes in excited state reactions [15]. With this approach, k_q is given by eq. 5 [16]

$$k_q = \frac{k_d}{1 + e^{\Delta G/RT} + \dfrac{k_{-d}}{k^o_{en}} e^{\Delta G^{\neq}/RT}} \qquad (5)$$

where [17]

$$\Delta G = -E^{o,o}(*D,D) + E(*Q,Q) + \\ + C(*D,D) + C(Q,*Q) \qquad (6)$$

and $E^{o,o}$ represents the 0,0 spectroscopic excited state energy. The free energy of activation for the energy transfer step may be given by eq. 7 if the Weller model is adopted or by eq. 8 if the Marcus relationship is used in calculating k_q values from eq. 5.

$$\Delta G^{\neq} = \frac{\Delta G}{2} + \left[\left(\frac{\Delta G}{2}\right)^2 + \left(\frac{\lambda}{4}\right)^2\right]^{1/2} \qquad (7)$$

$$\Delta G^{\neq} = \frac{\lambda}{4}\left[1 + \frac{\Delta G}{\lambda}\right]^2 \qquad (8)$$

In both these two relationships, λ is the reorganizational parameter associated with energy transfer. Taking λ as ~6 kcal/mol (the value obtained to curve-fit the experimental k_q values of Table I) various k_q's can be calculated for different ΔG values; these are illustrated in Figure 1. When $\Delta G > -3.0$ kK, both the Weller and the Marcus model predict near-identical behaviour. However, when the driving force for energy transfer becomes more favourable (< -3.0 kK), the Weller relationship suggests that $k_q \approx k_d$ while the Marcus model predicts a dramatic decrease in the values of the quenching constants (the Marcus inverted region). From Figure 1, it is evident that oxygen quenching of these metal-centered $(^2E)Cr(NN)_3^{3+}$ states follows a Marcus inverted behaviour. This behaviour is analogous to the electron transfer quenching of the MLCT states of polypyridine ruthenium(II) by various complexes in which *vestiges* of the inverted Marcus region have been observed [18]. However, the experimental values of k_q were several orders of magnitude larger than those expected from the Marcus model. This type of discrepancy has led several workers to refine the theory or to explore other approaches [19].

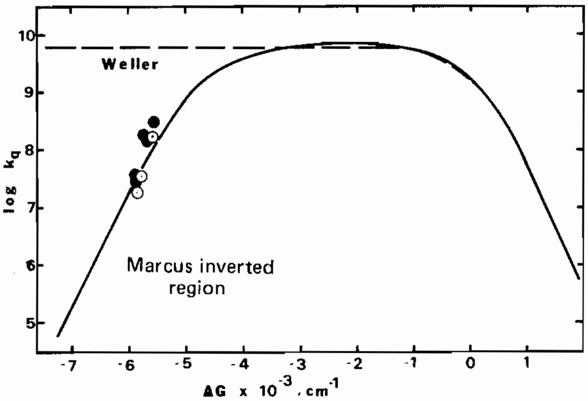

Figure 1. Theoretical plot of log k_q *versus* the free energy change ΔG. Solid circles represent experimental quenching constants for quenching of the phenanthroline complexes; open circles indicate the k_q values for the bipyridyl complexes.

The values of k_q of Table I also exhibit some functionality toward the redox potentials of the complexes. A plot of log k_q for the phenanthroline complexes against ΔE^f [20] (see *e.g.* Table I) reveals a small, but definitive, dependence on redox potentials [11]. Such a dependence has previously been taken as evidence for an electron transfer pathway in the quenching of the MLCT states of $*Ru(NN)_3^{2+}$ by Eu(III) [8] and by Eu(II) [21]. The variations of k_q with ΔE^f do not support reductive quenching (reaction 3) inasmuch as the stronger oxidant, (^2E)-$Cr(5\text{-}Clphen)_3^{3+}$, has one of the smaller quenching rates. In fact, the variations are suggestive of an oxidative electron transfer mode (reaction 2), even though formation of $Cr(NN)_3^{4+}$ and HO_2 radicals is expected to be endoergic ($\Delta G > 0.2$ eV). An oxidative electron transfer mode has recently also been inferred in the quenching of $(^2E)Cr(bpy)_3^{3+}$ by $Fe(CN)_6^{3-}$ [22] and $IrCl_6^{2-}$ [23].

We conclude from the above discussion that the reaction of $(^2E)Cr(NN)_3^{3+}$ with O_2 occurs predominantly via an energy transfer mechanism, in contrast to the behaviour of MLCT states.

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