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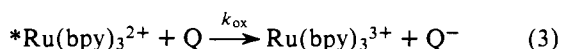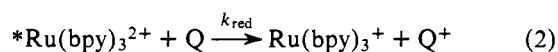
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Figure 1. Stern–Volmer plots for the quenching of the $*Ru(bpy)_3^{2+}$ luminescence by cyanide complexes (see Table I).

Electron and Energy Transfer Mechanisms in the Quenching of the Tris(2,2'-bipyridine)ruthenium(II) Luminescence by Cyanide Complexes

Sir:

Efficient quenching of electronically excited coordination compounds can take place by either energy or electron transfer.[1,2] In the case of the emitting state of tris(2,2'-bipyridine)ruthenium(II), $*Ru(bpy)_3^{2+}$, the following potentially efficient quenching processes may thus be expected:

$$*Ru(bpy)_3^{2+} + Q \xrightarrow{k_{en.t.}} Ru(bpy)_3^{2+} + *Q \qquad (1)$$

$$*Ru(bpy)_3^{2+} + Q \xrightarrow{k_{red}} Ru(bpy)_3^{+} + Q^{+} \qquad (2)$$

$$*Ru(bpy)_3^{2+} + Q \xrightarrow{k_{ox}} Ru(bpy)_3^{3+} + Q^{-} \qquad (3)$$

The "thermodynamic" barriers for these reactions may be evaluated knowing that the energy difference between $*Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{2+}$ is 17.1 kK (2.12 eV),[3] and that the reduction potentials of the $*Ru(bpy)_3^{2+}$-$Ru(bpy)_3^{+}$ and $Ru(bpy)_3^{3+}$-$*Ru(bpy)_3^{2+}$ couples are +0.84 V[4] and −0.83 V,[4-7] respectively, vs. the NHE. Kinetic ("intrinsic") barriers are also known to be important

in both energy[1,8] and electron[6,9,10] transfer reactions. Quenching of $*Ru(bpy)_3^{2+}$ by energy transfer (reaction 1) has been demonstrated for several acceptors.[1] Oxidative quenching (reaction 3) has been shown to occur with various oxidants,[6,11-13] whereas only indirect evidence has so far been obtained for the reductive quenching (reaction 2), using $S_2O_4^{2-}$, $Ru(NH_3)_6^{2+}$, and $Fe(CN)_6^{4-}$ as quenchers.[4] We describe here the results obtained from the quenching of $*Ru(bpy)_3^{2+}$ by several cyanide complexes which were chosen because they span a wide range of excited-state energies and redox potentials (Table I), and we report definite evidence for the occurrence of reaction 2.

Quenching of the $*Ru(bpy)_3^{2+}$ luminescence (intensity and lifetime) and the photochemical experiments were carried out in aerated aqueous solutions at pH 4, $\mu = 0.50$ (NaCl), and 23°. The Stern–Volmer quenching plots are shown in Figure 1. The quenching rate constants, calculated using $\tau^0 = 400$ ns, are collected in Table I together with some values obtained by other authors.

Solutions containing the highest concentration of $Mo(CN)_8^{4-}$, $Os(CN)_6^{4-}$, and $Ni(CN)_4^{2-}$ used in the quenching experiments were irradiated in a conventional photochemical apparatus with 464-nm light. For the $Ru(bpy)_3^{2+}$-$Mo(CN)_8^{4-}$ system, irradiation caused an increase in pH while the absorption spectrum decreased at λ <255 nm and increased at about 270 and 390 nm, indicat-

Table I. Quenching of $*Ru(bpy)_3^{2+}$ by Various Cyanide Complexes[a]

Quencher Q	$E(*Q)$,[b] kK	$E^0(Q^+/Q)$,[c] V	$E^0(Q/Q^-)$,[c] V	k_q,[d] $M^{-1} s^{-1}$	Reaction[e]
$Mo(CN)_8^{4-}$	19.6[f]	+0.73[g]	(<-1.8)[h]	3.4×10^8	2
$Cr(CN)_6^{3-}$	12.4[i]	—	-1.28[j]	7.5×10^8 [k]	1
$Fe(CN)_6^{4-}$	23.7[l]	+0.36[j]	(<-1.7)[l]	3.3×10^9 [m]	2
$Fe(CN)_6^{3-}$	23.5[l]	$(> +0.75)$[n]	+0.36[j]	6.5×10^9 [o]	3
$Co(CN)_6^{3-}$	26.0[p]	—	-0.83[j]	$<10^6$	—
$Os(CN)_6^{4-}$	47[l]	+0.75[j]	—	1.2×10^9	2
$Ni(CN)_4^{2-}$	23[q]	$(> +1.0)$[n]	-1.35[r]	5.6×10^9	1 or 2
$Pd(CN)_4^{2-}$	22.7[i,s]	$(> +1.0)$[n]	(< -1.8)[h]	$<10^6$	—
$Pt(CN)_4^{2-}$	23.0[i,s]	—	—	$<10^6$	—

[a] $E(*Ru(bpy)_3^{2+}) = 17.1$ kK, E^0 $(*Ru(bpy)_3^{2+}$-$Ru(bpy)_3^{+}) = +0.84$ V, E^0 $(Ru(bpy)_3^{3+}$-$*Ru(bpy)_3^{2+}) = -0.83$ V. [b] Lowest energy absorption feature, unless otherwise noted. [c] Reduction potential at 25° and $\mu = 0$, unless otherwise noted. [d] 23°, $\mu = 0.50$. [e] Reaction responsible for the quenching (see text). [f] From ref 14. [g] "Stability Constants of Metal-Ion Complexes", *Chem. Soc., Spec. Publ.*, **No. 17** (1964). [h] Electroinactive up to the indicated potential at the mercury electrode in deaerated 0.50 M NaCl solution, 25°. [i] P. D. Fleischauer and P. Fleischauer, *Chem. Rev.*, **70**, 199 (1970). [j] D. A. Buckingham and A. M. Sargeson in "Chelating Agents and Metal Chelates", F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N.Y., 1964, p 237. [k] F. Bolletta, M. Maestri, and L. Moggi, *J. Phys. Chem.*, **77**, 861 (1973). [l] From ref 18. [m] This value is in agreement with that reported in ref 4. [n] Electroinactive up to the indicated potential at the platinum electrode in deaerated 0.50 M NaCl solution, 25°. [o] 25°, ref 4. [p] H. Kataoka, *Bull. Chem. Soc. Jpn.*, **46**, 2078 (1973); K. W. Hipps and G. A. Crosby, *Inorg. Chem.*, **13**, 1543 (1974). [q] From ref 14 and 25. [r] Half-wave potential vs. the SCE, from A. A. Vlček, *Collect. Czech. Chem. Commun.*, **22**, 948 (1957). [s] Energy of the lowest excited state from emission spectra. [t] A. N. Frumkin, *Trans. Faraday Soc.*, **55**, 156 (1959).
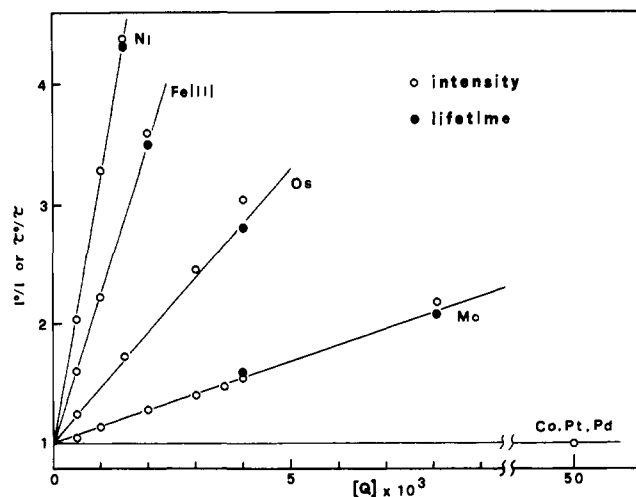
ing the formation of $Mo(CN)_8^{3-}$.[14] The very high optical density of the solution prevented quantitative measurements. The quantum yield of proton uptake, $\Phi(H^+)$, increased with increasing $Mo(CN)_8^{4-}$ concentration. The plot of $1/\Phi(H^+)$ vs. $1/[Mo(CN)_8^{4-}]$ was linear with $\Phi(H^+)_{lim} = 0.05 \pm 0.01$ and $K_{SV} = 170 \pm 50$ M^{-1}, in agreement with the value obtained from the quenching experiments (140 M^{-1}, Figure 1). The reaction was not suppressed by 0.1 M HCN, which prevented CN^- release from directly excited $Mo(CN)_8^{4-}$ (see also ref 15). As the quantum yield of the direct $Mo(CN)_8^{4-}$ aquation was 0.8 under our experimental conditions, the quenching of $*Ru(bpy)_3^{2+}$ cannot occur by energy transfer to a *reactive* $Mo(CN)_8^{4-}$ level.[16] For the $Ru(bpy)_3^{2+}$-$Os(CN)_6^{4-}$ system, irradiation caused an increase in pH and the appearance of four bands at 306, 330, 405, and 414 nm, which are characteristic of $Os(CN)_6^{3-}$.[18] For short irradiation periods, the apparent quantum yield of $Os(CN)_6^{3-}$ formation was of the order of 0.005. After long irradiation periods, both the pH and spectrum reached constant values. No spectral change was ever observed in the 450-nm region where $Ru(bpy)_3^{2+}$ exhibits a very intense absorption band. The final $Os(CN)_6^{3-}$ concentration was $\sim 1 \times 10^{-4}$ M, i.e., $\sim 2.5\%$ of the initial $Os(CN)_6^{4-}$ concentration and $\sim 150\%$ of the $Ru(bpy)_3^{2+}$ concentration. For the $Ru(bpy)_3^{2+}$-$Ni(CN)_4^{2-}$ system, neither the pH nor the spectrum showed any change upon irradiation.

The results obtained with $Mo(CN)_8^{4-}$ and $Os(CN)_6^{4-}$ show that a reductive quenching (reaction 2) takes place and that a fraction of $Mo(CN)_8^{3-}$ and $Os(CN)_6^{3-}$ escapes the back-reduction by $Ru(bpy)_3^+$. The quantum yield values show that this fraction is very small. As no $Ru(bpy)_3^{2+}$ is lost, an alternative reoxidation path for $Ru(bpy)_3^+$ must be present. The most probable is the reaction with O_2, whose rate constant is reported to be 1.8×10^9 M^{-1} s^{-1}.[19] The observed H^+ uptake is presumably due to a subsequent reaction of O_2^- with H^+,[20] although direct oxidation of $Ru(bpy)_3^+$ by H^+ cannot be ruled out. For both $Mo(CN)_8^{4-}$ and $Os(CN)_6^{4-}$, quenching by energy transfer is not thermodynamically favorable (Table I) and oxidative quenching is rather implausible, so that the *only* important quenching mechanism is presumably reaction 2.[22] For the same reasons, there is little doubt that the only quenching mechanism for $Fe(CN)_6^{4-}$ is reaction 2 (see also ref 4).

The data gathered in Table I merit some further comments. With $Cr(CN)_6^{3-}$, oxidative quenching is not thermodynamically favorable, while reductive quenching is presumably even less favorable since it should lead to a $Cr(IV)$ cyanide complex. Energy transfer appears thus to be the only possible quenching mechanism, as already shown by sensitized luminescence experiments.[24] With $Fe(CN)_6^{3-}$, energy transfer is not allowed and reductive quenching is completely implausible, so that only oxidative quenching is expected to occur. The lack of quenching by $Co(CN)_6^{3-}$ can be explained since (i) energy transfer is not allowed, (ii) reductive quenching is implausible because it would lead to a $Co(IV)$ complex, and (iii) oxidative quenching, even if thermodynamically not unfavorable, is expected to involve a high intrinsic barrier.[9,10] In the case of $Ni(CN)_4^{2-}$, oxidative quenching does not seem thermodynamically favorable, whereas reductive quenching may be possible since the electroinactivity up to $+1.0$ V could be due to "kinetic" factors. On the other hand, quenching by energy transfer to the lowest $Ni(CN)_4^{2-}$ triplet cannot be ruled out since the lowest energy shoulder in the absorption spectrum (~ 23 kK) has been attributed to either the second[14] or the third[25] excited triplet. The complex is photochemically inert[26] and thus the observed lack of sensitized aquation does not rule out ener-

gy transfer. The strong distortion[27] of the d-d excited states of this complex may be a further argument in favor of an energy transfer mechanism. Finally, the lack of quenching by $Pd(CN)_4^{2-}$ and $Pt(CN)_4^{2-}$, for which energy transfer can safely be ruled out, indicates that both reductive and oxidative quenching cannot take place because of unfavorable thermodynamic and/or intrinsic barriers.

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Intramolecular 1,1-Cycloaddition Reactions of Nitrile Ylides[1]

Sir:

Nitrile ylides are a long known and thoroughly investigated class of 1,3-dipoles.[2-4] Access to this group of dipoles can be realized by (a) treatment of imidoyl halides with base,[5] (b) thermal or photochemical elimination of phosphoric acid ester from 4,5-dihydro-1,3,5-oxazaphospholes,[6] and (c) photolysis of 1-azirines.[7,8] The greatest opportunity for structural variation is offered by the latter route. Among the possible resonance forms of a nitrile ylide, a car-