plexes does not reveal the existence of any one-electron oxidation processes.

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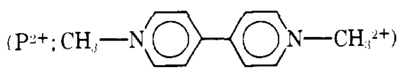
Electron Transfer Quenching of Excited States of Metal Complexes

Sir:

Quenching of the excited states of tris(2,2′-bipyridine)ruthenium(II), $Ru(bpy)_3{}^{2+*}$, by electron transfer has been demonstrated for several electron acceptors.[1-4] Such reactions are potentially of value in energy conversion processes. Likely candidates for a systematic study of such reactions are transition metal complexes because of their often high absorptivity in the visible and their ability to undergo facile electron transfer. Nearly all of the work in this area has utilized the redox properties of $Ru(bpy)_3{}^{2+*}$. Even though the $Ru(bpy)_3{}^{2+}$ system has some remarkable properties, it is clear that fundamental studies need to be carried out on a series of excited states of different orbital origins, and with different lifetimes and absorptivities. We report here a preliminary account of our initial work on the redox quenching of a series of metal complex excited states.

In order to extend the work on $Ru(bpy)_3{}^{2+*}$ we have investigated the reactions between the MLCT (d → π*) excited states of a series of ruthenium(II) chelates and the quenchers paraquat



in 0.10 M $[N(n\text{-}Bu)_4][ClO_4]$–acetonitrile, and $Fe(H_2O)_6{}^{3+}$ in 1.0 M aqueous $HClO_4$. The complexes differ with regard to excited state lifetimes and visible absorption properties (Table I). Flash photolysis studies[3] show that initial excited state quenching is followed by a back-thermal electron transfer reaction (Scheme I). The rate constants for the quenching step were determined by luminescence quenching using Stern–Volmer plots and excited state lifetimes (Table I). Rates for the back-reaction were obtained from flash photolysis by observing the recovery of the bleaching of the Ru(II) chelate (eq 3) following the quenching step (eq 2).

Scheme I

$$Ru(phen)_3{}^{2+} \xrightarrow{h\nu} Ru(phen)_3{}^{2+*} \quad (1)$$

$$Ru(phen)_3{}^{2+*} + Fe(H_2O)_6{}^{3+} \xrightarrow{k_q} Ru(phen)_3{}^{3+} + Fe(H_2O)_6{}^{2+} \quad (2)$$

$$Ru(phen)_3{}^{3+} + Fe(H_2O)_6{}^{2+} \xrightarrow{k_b} Ru(phen)_3{}^{2+} + Fe(H_2O)_6{}^{3+} \quad (3)$$

In all cases the initial quenching step is at, or near, the diffusion-controlled limit. The rates for the back-reaction between $Fe(H_2O)_6{}^{2+}$ and $Ru(phen)_3{}^{3+}$ or $Ru(terpy)(bpy)(NH_3)^{3+}$ are in excellent agreement with values obtained earlier by Cramer and Braddock[5] using the stopped-flow technique.

The f-f excited states of Eu^{3+} and Eu(III) chelates are known to be relatively long lived in solution.[6] They are of interest in terms of redox quenching since they conceivably can act as oxidizing rather than reducing agents, and since electrons must be transferred to relatively deeply buried f levels. Luminescence quenching of the excited states of

Table I. Kinetic and Spectral Data

Complex[a]	Absorption bands Photolyzed λ_{max}, nm (ϵ)[b]	Aqueous (Fe^{3+} as quencher)[c] τ_0 (μs)	k_q ($M^{-1}\,s^{-1}$)	k_b ($M^{-1}\,s^{-1}$)	Nonaqueous (Paraquat as quencher)[d] τ_0 (μs)	k_q ($M^{-1}\,s^{-1}$)	k_b ($M^{-1}\,s^{-1}$)
$Ru(bpy)_3{}^{2+}$[e]	450 (1.38×10^4)	0.624	2.9×10^9	9.5×10^5	0.85	2.4×10^9	8.1×10^9
$Ru(phen)_3{}^{2+}$	422 (1.76×10^4) 447 (1.84×10^4)	0.81	2.5×10^9	8.5×10^5	0.50	2.9×10^9	1.3×10^{10}
$Ru(terpy)(bpy)(NH_3)^{2+}$	462 (8.8×10^3)	0.43	3.1×10^9	1.1×10^4	[f]	[f]	[f]
$Ru(bpy)_2(CN)_2$	445 (9.0×10^3)	0.36	[g]	[g]	0.34	9.2×10^9	2.2×10^{10}
$Eu(phen)_3{}^{3+}$	270 (~5×10^5) 580 (~400)				740	3.7×10^7[h]	6.0×10^8[h]
Pd(OEP)	390 (1.7×10^5) 510 (1.6×10^4) 544 (5.0×10^4)				360	1.5×10^9	1.4×10^9

[a] Key: bpy is 2,2′-bipyridine; phen is 1,10-phenanthroline; terpy is 2,2′,2″-terpyridine; OEP is octaethylporphyrin. [b] In acetonitrile except for Pd(OEP) which is in isobutyronitrile. [c] In 1.0 M $HClO_4$. [d] In 0.1 M $[N(n\text{-}Bu)_4][ClO_4]$ (TBAP)–acetonitrile except for Pd(OEP) which is in isobutyronitrile. [e] Data from ref. 3. [f] Not stable in acetonitrile. [g] Upward curving Stern–Volmer plot indicates a static quenching phenomenon similar to the Cu^{2+}–$Ru(phen)_2(CN)_2$ system reported by J. Demas, *J. Am. Chem. Soc.*, 96, 3663 (1974). [h] NPh_3 as quencher, 0.01 M TBAP. For Stern–Volmer quenching λ_{ex} 580 nm to ensure metal centered excited state. Flash photolysis λ_{ex} 270 nm is necessary because ϵ at 580 nm is not large enough to populate a significant amount of excited state.

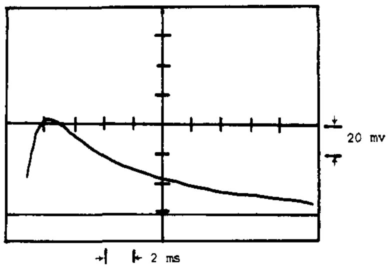


Figure 1. Oscilloscope trace of a solution containing $Eu(Phen)_3{}^{3+}$ and NPh_3 following flash photolysis. The reaction was monitored at λ_{max} for $NPh_3{}^+$ (650 nm) and the trace shows a decrease in transmittance followed by a slow regeneration step which follows equal-concentration, second-order kinetics. Horizontal sweep rate, 2 ms/div; vertical sensitivity 20 mV/division, base line is at 515 mV.

Eu^{3+} and some Eu(III) chelates has been studied,[7] but direct evidence for redox quenching was not obtained. We have investigated redox phenomena in acetonitrile solutions containing $Eu(phen)_3{}^{3+}$ and a series of potential organic reductants including diphenylamine, triphenyllamine, triethylamine, dimethylaniline, and triphenylphosphine using flash photolysis. The systems were studied by excitation of intraligand π-π^* transitions in the uv because they have high absorptivities and intramolecular energy transfer to the emitting f-f states is facile and efficient.[6a] Filter solutions containing the added organic reductant were used; no transient phenomena were observed in the absence of the reductant.

With each organic reductant, quenching of the excited state was accompanied by the appearance of absorption bands attributable to one-electron oxidized radical cations[8] (Scheme II). The $Eu(phen)_3{}^{3+}$-NPh_3 system was studied in detail.

Scheme II

$$Eu(phen)_3{}^{3+} \xrightarrow{h\nu} Eu(phen)_3{}^{3+*} \quad (4)$$

$$Eu(phen)_3{}^{3+*} + NPh_3 \xrightarrow{k_q} Eu(phen)_3{}^{2+} + NPh_3{}^+ \quad (5)$$

$$Eu(phen)_3{}^{2+} + NPh_3{}^+ \xrightarrow{k_b} Eu(phen)_3{}^{3+} + NPh_3 \quad (6)$$

The quenching step (eq 5) is sufficiently slow that it can be followed directly by conventional flash photolysis (Figure 1). The immediately observed product of the quenching is the one-electron oxidation product $NPh_3{}^+$ showing clearly that the quenching mechanism involves electron transfer. The rate constants for the quenching and back-reactions (Table I) were obtained by monitoring the appearance (pseudo-first-order kinetics) and subsequent disappearance (equal-concentration, second-order kinetics[10]) of the absorption due to $NPh_3{}^+$ (Figure 1). Both rate constants are well below the diffusion-controlled limit, but the origin of the relative slowness is unclear in the absence of redox potential[9] and detailed mechanistic information.

Redox quenching of the $\pi \rightarrow \pi^*$ excited states of metalloporphyrins is of importance because of possible analogies with photosynthesis, and because of the high near-uv-visible light absorption of the complexes. The $\pi \rightarrow \pi^*$ excited state of $Pd^{II}OEP$ (OEP is octaethylporphyrin) has a relatively long lifetime (Table I), and undergoes an efficient quenching process with paraquat in isobutyronitrile. Flash photolysis studies show that the initial rapid quenching leads to bleaching of the β band of the porphyrin at 544 nm, and to the appearance of reduced paraquat (λ_{max} 393 and 603 nm). The spectral changes observed are consistent with the formation of the ring oxidized porphyrin[11] (eq 8), followed by rapid, back-electron transfer (eq 9).

Scheme III

$$Pd^{II}OEP \xrightarrow{h\nu} Pd^{II}OEP^* \quad (7)$$

$$Pd^{II}OEP^* + P^{2+} \xrightarrow{k_q} [Pd^{II}(OEP^+)]^+ + P^+ \quad (8)$$

$$[Pd^{II}(OEP^+)]^+ + P^+ \xrightarrow{k_b} Pd^{II}OEP + P^{2+} \quad (9)$$

The results described here show that rapid, bimolecular electron transfer processes can occur based on electron donation to or from the d-π^* (CT), f-f*, and π-π^* excited states of metal complexes. Such reactivity may be a common feature of long-lived excited states, providing that such processes are energetically favorable[12] and kinetic barriers are low.[13] Some of the reactions reported here share with the tris(2,2′-bipyridine)ruthenium(II) system the potentially useful properties of high chemical stability, high absorption in the visible, and the ability to undergo facile electron transfer, and may ultimately find application in energy conversion processes.[14]

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Isotope Effects on Gas Phase Reaction Processes. I. The Determination of Equilibrium Isotope Effects by Ion Cyclotron Resonance Spectroscopy

Sir:

Within the past decade ion cyclotron resonance (ICR) spectroscopy has developed into a formidable tool for the study of the thermodynamic stabilities of ions in the gas phase.[1,2] Of particular importance has been the determination by equilibrium ICR techniques of the acidities and basicities of a wide range of organic molecules.[3] Despite the considerable success which ion cyclotron resonance spectroscopy has entertained with regard to the elucidation of