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Excited-State Quenching by Proton-Coupled Electron Transfer

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In proton-coupled electron transfer (PCET) reactions, proton transfer accompanies electron transfer. Pathways for PCET have been identified in which simultaneous electron–proton transfer (EPT) occurs.[1] An example is illustrated in eq 2 for reduction of $^3C_{60}$ by phenols with added base, B (eq 1).[2] These reactions are more complex than sequential electron transfer (ET) followed by proton transfer (PT) or vice versa but avoid high energy intermediates such as ArOH[•+]. In the pathway in eq 2, separate sites act as electron ($^3C_{60}$) and proton (B) acceptors. This is an example of multiple site EPT (MS-EPT).[3]
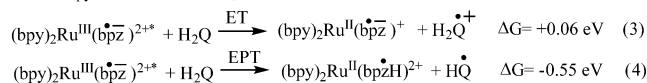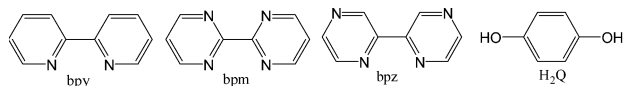
$$^3C_{60} + ArOH-B \rightarrow C_{60}{}^{\bullet-} + ArO^{\bullet} + BH^+ \qquad (1)$$
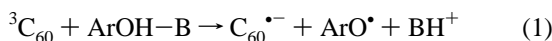
The importance of PCET and EPT in chemistry and biology is

$$^3C_{60}, ArO-H^{\cdots\cdots}B \rightarrow \;^3C_{60}{}^{\bullet-}, ArO^{\bullet\cdots\cdots+}H-B \qquad (2)$$
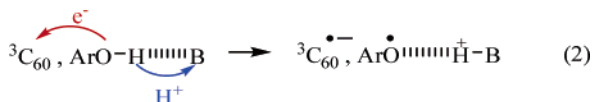
becoming increasingly apparent.[4–9] Here we report a novel example of PCET reductive quenching of an excited state that appears to occur by EPT, mimics related events in Photosystem II, and may have important implications for photochemical energy conversion.

Hoffman et al. have characterized metal-to-ligand charge transfer (MLCT) excited state and ground state pK_a's and redox potentials for the mixed ligand complexes $[Ru(bpy)_{3-m-z}(bpm)_m(bpz)_z]^{2+}$ (bpy is 2,2′-bipyridine; bpm is 2,2′-bipyrimidine; bpz is 2,2′-bipyrazine; m, $z = 0-3$; $m + z \leq 3$).[10–12] For the MLCT excited state $[(bpy)_2Ru^{III}(bpz^{\bullet-})]^{2+*}$, ΔG for reductive quenching by 1,4-hydroquinone (H_2Q) by electron transfer (ET), eq 3, is $+0.06$ eV and for EPT it is -0.55 eV, eq 4. Similarly, ΔG for initial proton transfer is $+0.32$ eV. This comparison demonstrates the value of EPT quenching in avoiding high energy ET or PT intermediates such as $H_2Q^{\bullet+}$ ($E^{0'}(H_2Q^{\bullet+}/H_2Q) = 1.10$ V) and $[(bpy)_2Ru^{II}(bpz^{\bullet-})]^+$ ($E^{0'}([Ru^{III}(bpz^{\bullet-})]^{2+*}/[Ru^{II}(bpz^{\bullet-})]^+) = 1.16$ V).

$$(bpy)_2Ru^{III}(bpz^{\bullet-})^{2+*} + H_2Q \xrightarrow{ET} (bpy)_2Ru^{II}(bpz^{\bullet-})^+ + H_2Q^{\bullet+} \quad \Delta G = +0.06\text{ eV} \quad (3)$$

$$(bpy)_2Ru^{III}(bpz^{\bullet-})^{2+*} + H_2Q \xrightarrow{EPT} (bpy)_2Ru^{II}(bpzH^{\bullet})^{2+} + H\dot{Q}^{\bullet} \quad \Delta G = -0.55\text{ eV} \quad (4)$$

We have used transient absorption (TA), CW and time-resolved emission, and time-resolved electron paramagnetic resonance (TR-EPR) measurements to establish the quenching mechanism shown in Scheme 1. Following 355 nm laser flash excitation of solutions containing H_2Q and $[Ru(bpy)_2(bpz)](PF_6)_2$, at 298 K in argon-deaerated 1:1 CH_3CN/H_2O (0.1 M KPF_6), evidence for transients appears in TA and TR-EPR spectra. Spectral changes are consistent with the reactions in Scheme 1 with kinetic parameters determined

Scheme 1. Mechanism for Reductive Quenching of $[(bpy)_2Ru^{III}(bpz^{\bullet-})]^{2+*}$
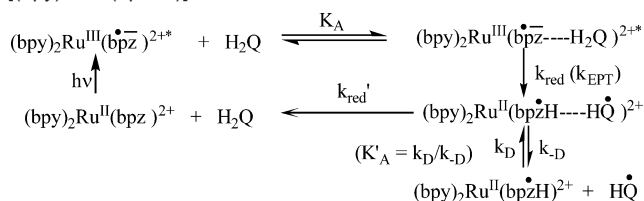
by a combination of static and dynamic quenching measurements with $[H_2Q]$ varied from 0 to 1.51 M (Supporting Information).

In Scheme 1, K_A (10.8 ± 0.1 M^{-1}) is the equilibrium constant for formation of a, presumably, hydrogen-bonded adduct between H_2Q and the excited state, $[(bpy)_2Ru^{III}(bpz^{\bullet-})^{2+*}-H_2Q]$, and k_{red} $[(4.5 \pm 0.1) \times 10^6$ $s^{-1}]$ is the quenching rate constant.

The results of TA and TR-EPR measurements are consistent with PCET in the quenching step with $k_{red} = k_{EPT}$ in Scheme 1. Figure 1 shows the absorption spectrum of a solution acquired 900 ns after laser flash photolysis. The spectrum shown in open circles ($[(bpy)_2Ru^{II}(bpzH^{\bullet})]^{2+} + HQ^{\bullet}$) was constructed by adding the ground state spectrum to the TA difference spectrum (closed circles). The contribution from the latter was determined by the absorbance change at 530 nm and the known $\Delta\epsilon$ difference between $[(bpy)_2Ru^{II}(bpzH^{\bullet})]^{2+}$ and the ground state ($\Delta\epsilon = 3700 - 1240 = 2460$ $M^{-1}cm^{-1}$) at that wavelength.[10] An additional absorption for semiquinone radical, $HQ^{\bullet}$, appears in the spectrum in Figure 1 at $\lambda_{max} = 410$ nm.[13]

The transient spectra show that the electron and proton are transferred concurrently in the quenching step. Similarly, TR-EPR measurements (Figure 2) demonstrate the appearance of $HQ^{\bullet}$ (Supporting Information).[14]

A kinetic isotope effect (KIE) of $k(H_2O)/k(D_2O) = 1.81 \pm 0.06$ was observed for $k_{red} = k_{EPT}$ in Scheme 1. This value is consistent with EPT quenching with nearly symmetrical H-bonding and a short proton-transfer distance in the association complex. For the pre-equilibrium, $K_A(H_2O)/K_A(D_2O) = 1.0 \pm 0.1$ M^{-1}. Stepwise ET-PT or PT-ET within the H-bonded precursor complex would give the same products but would appear to be unlikely on energetic grounds,[15] although they cannot be ruled out definitively.

On the basis of absorption changes following laser flash excitation, and the reactions in Scheme 1, the separation efficiency following EPT quenching is $\eta_{sep} = k_{-D}/(k_{-D} + k_{red}') \sim 0.29$ (Supporting Information). Back reaction between $[(bpy)_2Ru^{II}(bpzH^{\bullet})]^{2+}$ and $HQ^{\bullet}$ ($\Delta G_{EPT} = -1.40$ eV; $\Delta G_{ET} = -0.73$ eV) follows second-order equal-concentration kinetics (Supporting Information) consistent with Scheme 1 with $k(H_2O) = (1.14 \pm 0.06) \times 10^9$ M^{-1} s^{-1}, $k(D_2O) = (9.8 \pm 0.1) \times 10^8$ M^{-1} s^{-1}, and $k(H_2O)/k(D_2O) = 1.19 \pm 0.07$ at 298 K in argon-deaerated 1:1 CH_3CN/H_2O (0.1 M KPF_6) for $k(H_2O)$ and 1:1 CH_3CN/D_2O (0.1 M KPF_6) for $k(D_2O)$. Back reaction in this case presumably occurs by ET followed by PT.
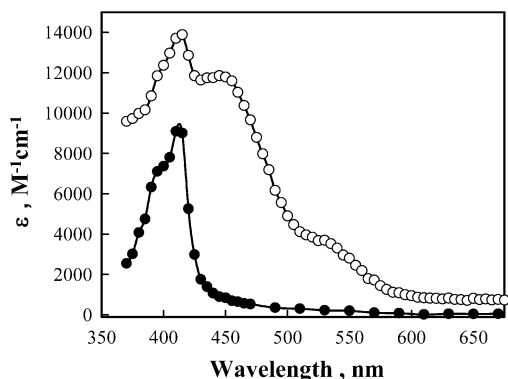
Figure 1. The closed circles (●) depict the absorption spectrum of HQ• generated as described in the text. The open circles (○) represent the absorption spectrum of [(bpy)$_2$Ru^{II}(bpz•H)]$^{2+}$ and HQ• calculated from the transient absorption difference spectrum. The difference spectra were obtained at 298 K, 900 ns after excitation of a solution containing 57 μM [Ru(bpy)$_2$bpz] (PF$_6$)$_2$, 0.1 M KPF$_6$, and 0.47 M H$_2$Q in 1:1 CH$_3$CN/H$_2$O with (●) and without (○) 5 mM Q, respectively.
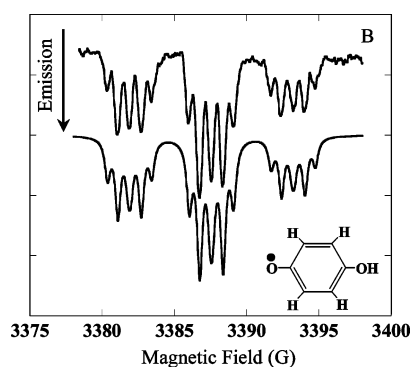

Figure 2. Experimental (top black line) and simulated (bottom gray line) EPR spectra of semiquinone radical (HQ•) obtained following 355 nm flash photolysis of [Ru(bpy)$_2$(bpz)]$^{2+}$ and H$_2$Q in anhydrous CH$_3$CN. The parameters used in the simulation were as follows: hyperfine coupling constants (A(2H(o-**H**)) = 5.66 G, A(**OH**) = 1.62 G, A(2H(m-**H**)) = 0.72 G, g factor = 2.00463, line width = 0.34 G.

The reduced complex reacts with added quinone (Q, 5 mM) by PCET (eq 5), with $k_{red} = (8.5 \pm 0.1) \times 10^8$ M^{-1} s^{-1}, leaving HQ• as the only absorbing species (Figure 1). On a longer time scale, the absorbance at 410 nm disappears with second-order equal-concentration kinetics with $k = (2.9 \pm 0.1) \times 10^5$ M^{-1} s^{-1}, consistent with the disproportionation reaction in eq 6.

$$[(bpy)_2Ru^{II}(bpzH•)]^{2+} +$$
$$Q \rightarrow [(bpy)_2Ru^{II}(bpz)]^{2+} + HQ• \quad (5)$$

$$2HQ• \rightarrow H_2Q + Q \quad (6)$$
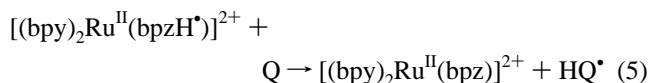
The reaction with Q has potentially important implications for net photochemistry and energy conversion. Reactivity toward Q is shared by other substrates. Benzaldehyde is reduced by [(bpy)$_2$Ru^{II}-(bpzH•)]$^{2+}$ with k(H$_2$O) = (2.2 $\pm$ 0.3) $\times$ 10^6 M^{-1} s^{-1}. Experiments are currently being undertaken to explore possible use of this net H-atom transfer reactivity in photochemical conversion.

Our observations are important in delineating a new type of excited state reactivity that may be present, but previously unidentified, in related excited state reactions.[16,17] The appearance of EPT quenching is a consequence of its favorable driving force compared to ET or PT. From initial experiments, oxidative quenching of [Ru^{III}(4,4′-(OH)$_2$bpy)$_3$]$^{2+*}$(4,4′-(OH)$_2$bpy is 4,4′-dihydroxy-2,2′-bipyridine) by quinone and reductive quenching of [(bpy)$_2$-Ru^{III}(phendione•$^-$)]$^{2+*}$ (phendione is 1,10-phenanthroline-5,6-dione) by tetrachlorohydroquinone also occur by EPT. It appears to be a general pathway for redox quenching of metal complex excited states when accessible and sufficiently favored thermodynamically.
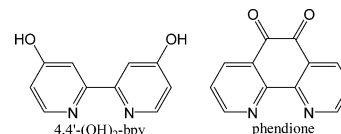
Water oxidation in Photosystem II in green plants is triggered by sensitized excitation and oxidative quenching of the excited state of chlorophyll P$_{680}$. It has been suggested that multiple site EPT (initially described as "H-atom abstraction")[4] occurs[5] in a subsequent step as in eq 2 with P$_{680}$$^+$ as the electron acceptor and histidine190 as the proton acceptor. By contrast, in excited state EPT in eq 7, the excited state functions directly as *both* electron and proton acceptor in a single concerted step.

$$\{(bpy)_2Ru^{III}(bpz•---H-QH)^{2+*}\} \longrightarrow \{(bpy)_2Ru^{III}(bpz•-H--Q•H)^{2+}\} \quad (7)$$
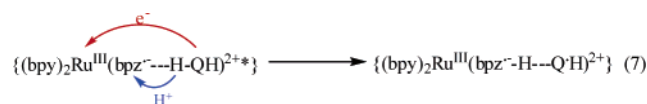
Supporting Information Available: Determination of association constants, additional TA, TR-EPR, and kinetic studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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