Communication

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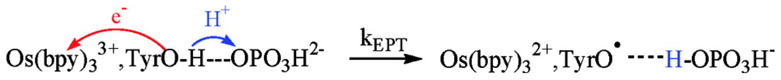

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The Role of Free Energy Change in Coupled Electron−Proton Transfer

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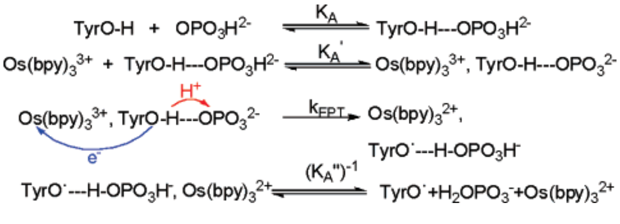
There is increasing recognition in proton-coupled electron transfer (PCET) reactions of the mechanistic importance of elementary steps in which simultaneous electron−proton transfer occurs from different orbitals on the donor to different orbitals on the acceptor (EPT).[1−5] EPT is different from H-atom (HAT) or hydride transfer in which electrons and protons are transferred from the same bond. Although microscopically more complex, and in competition with pathways involving sequential electron transfer followed by proton transfer (ET−PT) or vice versa (PT−ET), EPT pathways are utilized to avoid high energy intermediates. A theoretical basis for understanding EPT is available from the work of Cukier, Hammes-Schiffer, and others. They provide explicit predictions concerning the dependence of rate constants on free energy change (ΔG), temperature, and isotope effects.[2,6,7]

Extensive data are available for testing the influence of enthalpy changes (bond energies), and to a lesser extent ΔG, on k for HAT.[3,8,9] There are limited data on the ΔG dependence of EPT and in some cases interpretation of results has been controversial.[10−17] We report here the results of an extended kinetic study which, for the first time, explores the dependence of driving force ($-\Delta G$) on EPT over an extended range by varying both the electron and proton acceptors.

We recently reported an EPT pathway in the oxidation of tyrosine by $[\mathrm{Os(bpy)_3}]^{3+}$, Scheme 1.[15] In this pathway prior association of tyrosine (TyrOH) occurs with the base form of the $H_2PO_4^-/HPO_4^{2-}$ buffer followed by multiple site-electron proton transfer (MS-EPT) (k_{EPT} in Scheme 1). In the MS-EPT pathway electron transfer occurs to $[\mathrm{Os(bpy)_3}]^{3+}$ and proton transfer to HPO_4^{2-}.[5,15,18] Under the conditions of the reaction MS-EPT is in competition with pathways involving ET−PT and PT−ET. The MS-EPT step was isolated by kinetic analysis (Supporting Information).

Scheme 1



We have extended the earlier electrochemical study which is based on simulation of cyclic voltammograms by exploring the ΔG dependence of EPT over an unprecedented range in ΔG values made possible by varying both the pK_a of the acid form of the base and the redox potential of the oxidant. An important aspect of this study was to assess whether the same ΔG dependence would appear by varying both the electron and proton acceptors for a MS-EPT pathway.

Results are illustrated in Figure 1 as plots of $RT \ln k_{red}$ versus $-\Delta G°'$ in eV: Figure 1a shows the bases (pK_a) acetate (4.7; Ac$^-$), succinate monoanion (5.6; succ), histidine (6.6; his), dibasic phosphate (7.2; HPO_4^{2-}), and tris (8.1; tris) with the common oxidant $[\mathrm{Os(bpy)_3}]^{3+}$ and Figure 1b shows the oxidants $\mathrm{Ru(bpy)_3}^{3+}$ ($E°' = 1.25$ V vs NHE), $\mathrm{Ru(dmb)_3}^{3+}$ (1.10 V, dmb is 4,4′′-dimethyl-2,2′-bipyridine), $\mathrm{Fe(bpy)_3}^{3+}$ (1.05 V), and $\mathrm{Os(bpy)_3}^{3+}$ (0.85 V) with the common base succinate monoanion.

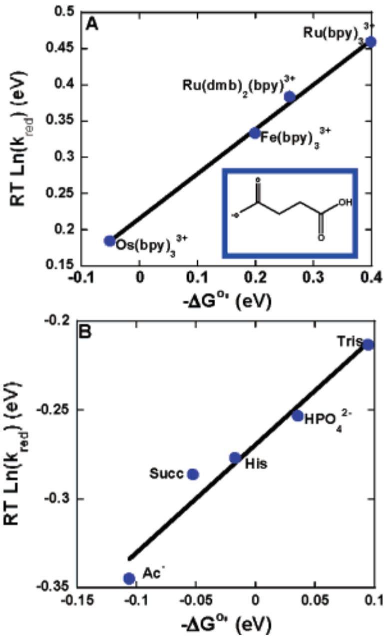


Figure 1. Variation of $RT \ln k_{red}$ with $-\Delta G°'$ in eV at 298 K: (A) by varying $E°'(M^{3+/2+})$ for the oxidant with succinate monoanion as the base (the slope of the drawn line is 0.61) and (B) by varying the pK_a of the acceptor base with $[\mathrm{Os(bpy)_3}]^{2+}$ as the oxidant (the slope is 0.61). Each solution contained 0.8 M NaCl to maintain ionic strength and added buffer for (A) a 0.050 M succinate solution at pH 4.9 with a 15:1 acid to base ratio and (B) 0.050 M buffer solutions with a 10:1 base to acid ratio. The rate constants were evaluated by the kinetic analysis described in the Supporting Information.

Over a range in $\Delta G°'$ values of ~0.5 eV in $E°'$ and ~0.2 eV in pK_a, the ΔG dependence of k_{red} ($= k_{EPT}$) for both sets of reactions is the same within experimental error with $RT \ln k_{red}$ increasing with $-\Delta G°'$ with a slope of ~0.6 regardless of how $\Delta G°'$ was varied. These results are consistent with MS-EPT in the redox step in Scheme 1 with simultaneous transfer of electrons and protons to different acceptors. The $\Delta G°'$ values in Figure 1 are approximate since they neglect differences in ΔG for formation of the association complexes before ($K_A K_A'$ in Scheme 1) and after EPT occurs ($1/K_A''$).

A slope of 0.5 in the variation of $RT \ln k_{red}$ with $-\Delta G°'$ in eV is predicted by the classical Marcus−Hush expression for electron transfer, $\Delta G^* = (\lambda + \Delta G°')^2/4\lambda \approx \lambda/4 + \Delta G°'/2$ ($\lambda \ll \Delta G°'$).[19−21] For EPT the quantum nature of the proton transfer requires application of the sum over vibrational states approach of Hammes-Schiffer et al., eq 1.[2,6] In eq 1, V_{ET} is the electron-transfer matrix element, λ is the sum of the solvent and intramolecular reorganization energies treated classically, and φ_μ and φ_ν are the proton

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vibrational wave functions for the proton before and after EPT occurs. The summations are over initial levels μ in their Boltzmann populations, $P(\mu)$, and from each initial vibrational level μ to final level ν. This equation is valid in the limit of weak vibronic coupling, where the product of V_{ET} and the proton vibrational wavefunction overlap is small, and neglects small variations in λ for the individual vibronic channels.

$$k_{\mathrm{EPT}} = \frac{2\pi}{\hbar} \sum_{\mu} P_{\mu} \sum_{\nu} V_{\mathrm{ET}}{}^{2} \langle \varphi_{\mu} | \varphi_{\nu} \rangle^{2} (4\pi\lambda RT)^{-1/2} \times \exp - \left[\frac{(\lambda + \Delta G^{\circ\prime} + (\mu - \nu)\hbar\omega)^{2}}{4\pi\lambda RT} \right] \quad (1)$$

$$RT \ln(k_{\mathrm{red}}) = RT \ln(k_{\mathrm{o}}) + \frac{\Delta G^{\circ\prime}}{2}\left(1 + \frac{\Delta G^{\circ\prime}}{2\lambda}\right) \quad (2)$$

$$k_{\mathrm{o}} = \frac{2\pi}{\hbar} V_{\mathrm{ET}}{}^{2} \langle \varphi_{\mu=0} | \varphi_{\nu=0} \rangle^{2} (4\pi\lambda RT)^{-1/2} \exp\left(-\frac{\lambda}{4RT}\right) \quad (3)$$

If EPT is dominated by the $\mu = 0 \rightarrow \nu = 0$ v channel, $RT \ln k_{\mathrm{EPT}}$ is predicted to vary with $-\Delta G^{\circ\prime}$ in eV as shown in eq 2. The quantity, $k_0 = 8.9 \times 10^2$ s^{-1}, can be evaluated as the average of k_{red} values at $\Delta G^{\circ\prime} = 0$ eV from the plots in Figure 1. The experimental slopes of ~0.6 in Figure 1 are consistent with contributions from multiple μ acceptor levels with higher overlaps in levels above $\mu = 0$.[2,6]

A plot of $RT \ln k_{\mathrm{red}}$ versus $-\Delta G^{\circ\prime}$ in eV for the complete data set including all oxidants and all bases is shown in Figure 2. An attempted fit to the quadratic expression in eq 2 with $k_0 = 8.9 \times 10^2$ s^{-1} and $\lambda = 0.9$ eV for the related reaction in eq 4[13] is also shown. These data provide direct evidence for participation of vibronic levels above μ, $\nu = 0$ and, perhaps, for a novel "quantum beat" effect at ~3000 cm^{-1} due to the O−H transfer mode.[22]

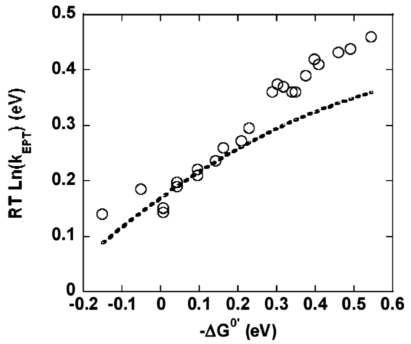

Figure 2. Variation of $RT \ln(k_{\mathrm{red}})$ versus $-\Delta G^{\circ\prime}$ in eV by varying both $E^{\circ\prime}$ for the oxidant and pK_a for the acceptor base, see text. The dashed line is a plot of $RT \ln(k_{\mathrm{red}}) = RT \ln(k_{\mathrm{o}}) + \Delta G^{\circ\prime}/2\ (1 + \Delta G^{\circ\prime}/2\lambda)$ according to eq 2 with $k_{\mathrm{o}} = 8.9 \times 10^2$ s^{-1} from Figure 1 and $\lambda = 0.90$ eV from ref 13 for the reaction in eq 4.

These results are important in demonstrating that a systematic dependence on ΔG exists for EPT independent of whether ΔG is varied through the electron or proton acceptor. The variation observed is qualitatively consistent with the underlying theory for EPT and is relevant to the role of ΔG in related biological reactions such as oxidation of tyrosine Y_Z by oxidized chlorophyll $P_{680}{}^{+}$ in the reaction center of Photosystem II.[5,23−25]

A pH dependence has been reported for intramolecular electron transfer from tyrosine to Ru^{III} and Re^{II} in complexes such as the one shown in eq 4 (bpy-$CH_2C_6H_4OH$ is 4-[2,2′]bipyridinyl-4-ylmethyl phenol). It has been attributed to MS-EPT with proton transfer to the surrounding medium with the pH dependence arising from the ΔG change for the overall PCET reaction.[10−14]

$$[\mathrm{Ru^{III}(bpy)_2(bpy{-}CH_2C_6H_4OH)}]^{3+} \rightarrow [\mathrm{Ru^{II}(bpy)_2(bpy{-}CH_2C_6H_4O^{\bullet})}]^{+} + \mathrm{H^{+}(pH)} \quad (4)$$

In our study an apparent pH dependence exists because of the specific participation of the base form of the buffer as a proton acceptor. Rate constants for MS-EPT depend on the pK_a of the acid form of the base and $E^{\circ\prime}$ of the oxidant not on the pH. In agreement with earlier predictions[16,17] and a recent theoretical analysis,[26] this is understandable since at the microscopic level there is no basis for coupling a local gain or loss of protons in an elementary step to the surrounding ensemble of solvent, protons, buffer, etc. that define the final equilibrium state including the pH.

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Supporting Information Available: Experimental information and the kinetic analysis and data used in constructing Figures 1 and 2. This material is available free of charge via the Internet at http://pubs.acs.org.

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