

The Influence of Electronic Coupling on the Free Energy and Barriers for Electron Transfer

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Molecular approaches to solar energy conversion often utilize a bridge (B) to link an electron acceptor (A) to an electron donor (D). Fundamental studies of A-B-D compounds where the bridge was fixed and the Gibbs free energy, ΔG° , was tuned have provided kinetic data that served as test of electron transfer theory. A notable advance from such studies was the experimental validation of Marcus kinetic normal, activationless, and inverted electron transfer reactions that continue to be exploited in artificial photosynthetic assemblies. On the other hand, much less is known about electron transfer dynamics when ΔG° is fixed and the electronic coupling (H_{DA}) mediated by the bridge is tuned. In order to quantify the influence of H_{DA} , a series of A-B-D compounds capable of photoinduced electron transfer were synthesized with bridge units that provided either strong (adiabatic) or weak (non-adiabatic) electronic coupling by a phenyl or xylyl bridge, Figure 1.¹⁻³ The redox equilibrium shown will be the focus of this presentation.

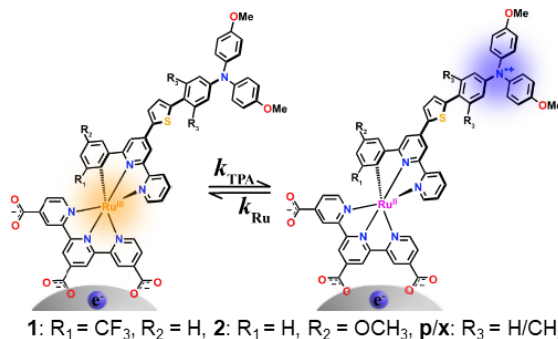


Figure 1. The A-B-D compounds utilized to test how electronic coupling influences electron transfer reactivity. Pulsed light excitation results in rapid excited state injection and the subsequent redox equilibrium was quantified.

Electron transfer theories predict that an increase in the quantum mechanical mixing of electron donor and acceptor wavefunctions at the instance of electron transfer will lower the absolute value of the Gibbs free energy change. Figure 2 provides a quantitative description of adiabatic and non-adiabatic electron transfer in an A-B-D compound. Marcus taught that the many-fold potential surfaces for electron-transfer can be reduced to parabolic Gibbs free energy surfaces (GESs) that are a function of a single reaction coordinate with fixed force constants for the A-B-D ‘reactants’ and the A^- -B- D^+ ‘products’. When the bridge allows the D and A to retain their original identities, the difference in formal reduction potentials, ΔE° , accurately predicts equilibrium concentrations and non-adiabatic electron transfer occurs by hopping from the reactant to the product GES. At an opposite extreme (not shown), strong electronic coupling mixes the D and A wavefunctions such that a single minimum ground-state GES results. The

far more interesting intermediate H_{DA} case that is common to electron transfer in solar energy conversion. Kinetic measurements enabled the influence of coupling on the free energy to be quantified and the expected $|\Delta G_{ad}^0| < |\Delta G^0|$ was realized.¹

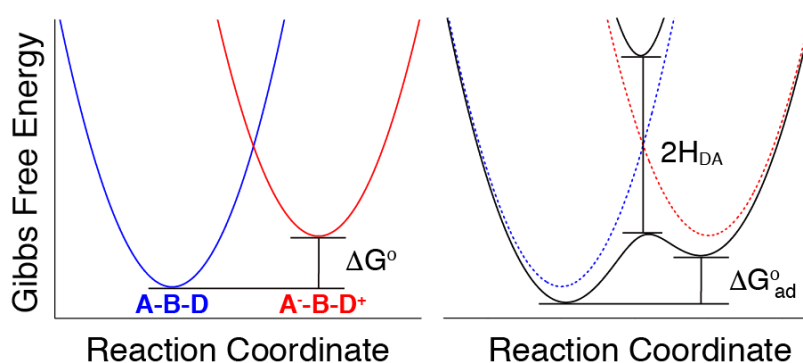


Figure 2. Gibbs free energy surfaces that represent a redox equilibrium between A-B-D (blue) and A-B-D⁺ (red) as the electronic coupling matrix element (H_{DA}) is increased from 0 (non-adiabatic) to over 1000 cm^{-1} (adiabatic). Emphasis is placed herein on the Gibbs free energy change that accompanies electron transfer.

Figure 2 indicates that the adiabatic electron transfer barrier is smaller than that for non-adiabatic transfer. To test this expectation, the kinetics for electron transfer were measured as a function of temperature and analyzed with Eyring and Marcus continuum theories.⁴ The data indicate that even though coupling accelerates the electron transfer by allowing a rapid approach to the transition state, a substantial entropic penalty is imposed despite smaller enthalpy of activation for thermodynamically uphill reactions. Interestingly, the free energy barriers were found to be independent of the coupling, despite the theoretical expectation that H_{DA} reduces the barrier. Entropies of activation were dissected into nuclear and electronic components and the degree of (non-) adiabaticity was accounted for through the transmission coefficient (κ_{el} , Eyring) or Jortner adiabaticity parameter, (κ_a , Marcus). Indeed, the entropy of activation was found to be a significant contributor to the barrier for adiabatic transfer.⁴ The work presented here provides an early example of explicit characterization of thermal electron transfer reactions that lie in extreme regimes of electron transfer theory and which are relevant to energy conversion schemes.

1. **Kinetics Teach That Equilibrium Constants Shift Toward Unity with Increased Electronic Coupling.** Sampaio, R.N.; Piechota, E.J.; Troian-Gautier, L.; Maurer, A.B.; Berlinguette, C.P., Meyer, G.J. *Proc. Nat. Acad. Sci. USA* **2018**, *115*, 7248-7253.
2. **Optical Intramolecular Electron Transfer in Opposite Directions through the Same Bridge That Follows Different Pathways.** Piechota, E.J.; Sampaio, R.N.; Troian-Gautier, L.; Meyer, G.J. *J. Am. Chem. Soc.* **2018**, *140*, 7176-7186.
3. **A Kinetic Pathway for Interfacial Electron Transfer from a Semiconductor to a Molecule.** Hu, K.; Blair, A.D.; Piechota, E.J.; Schauer, P.A.; Sampaio, R.N.; Meyer, G.J.; Berlinguette, C.P. *Nature Chem.* **2016**, *8*, 853-859.
4. **Entropic Barriers Determine Adiabatic Electron Transfer Equilibria.** Sampaio, R.N.; Piechota, E.J.; Troian-Gautier, L.; Maurer, A.B.; Berlinguette, C.P., Meyer, G.J. DOI: 10.1021/acs.jpcc.8b11815, *in press*.