Remsen Lecture
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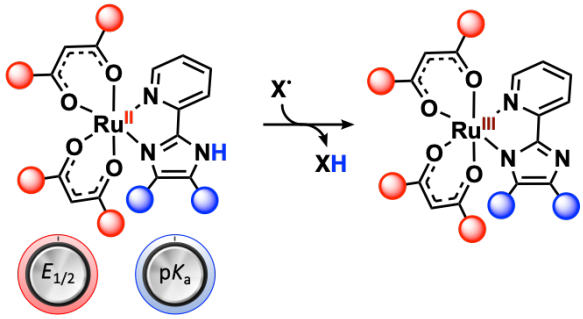
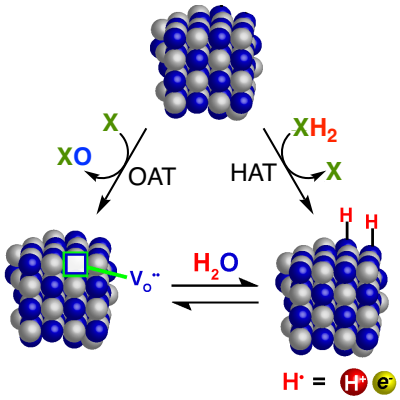
Proton-Coupled Electron Transfer from Molecules to Material Interfaces

Chemical oxidation and reduction (redox) reactions are often described as the transfer of electrons, but protons frequently play an equally important role. Such proton-coupled electron transfer (PCET) reactions are central to many chemical processes, from catalysis in fuel cells to the biological 'electron' transport chain. Fundamental studies of single PCET reaction steps are needed to understand reactions that range from H-atom transfer (HAT), a reaction studied by organic and physical chemists for over a century, to reactions in which the e^- and H^+ are quite separated. Two of the systems to be discussed are illustrated below. Understanding the rate constants for these reactions starts with the reaction driving force $\Delta G°_{PCET}$, the difference between the donor and acceptor bond dissociation free energies (BDFEs or $BDFE_{effective}$). This presentation will discuss contributions to k_{PCET} other than the $\Delta G°_{PCET}$, including possible imbalance of the PCET process and variation of the intrinsic barriers.

Similar PCET principles also broadly apply to reactions at solid/solution interfaces, from metal to oxide surfaces, and from thermal and electrochemical catalysis to corrosion and supercapacitors. These can all be considered to involve surface H atoms. However, the surface–H BDFE for a given material is not a single value (as in a molecule) but often varies with the surface coverage. These are called non-ideal H-binding isotherms. The talk will describe measurements of these isotherms in a number of systems, and the implications of the non-ideality. Strong connections and interesting contrasts between molecular and interfacial PCET will be discussed.



Changing red and blue substituents vary the $E°$ and pK_a mostly independently, probing imbalance by decoupling the $\Delta G°_{ET}$ and $\Delta G°_{PT}$ components of $\Delta G°_{HAT}$.



Oxygen-atom transfer (OAT) and H-atom transfer (HAT) at iridium dioxide nanoparticles