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Adventures in Proton-Coupled Electron Transfer: from Hydrogen Atom Transfer to Electrocatalysis to Nanocrystals

James M. Mayer
Department of Chemistry, Yale University, james.mayer@yale.edu

A wide range of chemical processes proceed by proton-coupled electron transfer (PCET), from combustion to fuel cells to redox processes of minerals. This presentation will begin with fundamental studies of single reaction steps that involve transfer of one proton and one electron. Some of these reactions 'look like' transfer of a hydrogen atom, while in other reactions the electron and proton are quite separated in the reactants or products, as in the drawing below left. The rate constants for many of these reactions can be understood using a version of Marcus Theory, which shows the commonality of organic and transition metal H-atom transfer reactions. These PCET concepts are being used to development and understand new electrocatalysts for the oxygen reduction reaction. Our studies of iron porphyrin electrocatalyst have shown very high turnover frequencies for some catalysts, but also show that these TOFs typically correlate with the electrochemical overpotentials (Figure below right). The origin of this effective 'scaling relationship' will be discussed. The breadth of importance of PCET ideas will be illustrated by examples in the redox reactivity of oxide nanoparticles.



