Molecular Electrocatalysts for Hydrogen Production: Electrochemical Proton-coupled Electron Transfer

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Theoretical studies of electrochemical proton-coupled electron transfer (PCET) for hydrogen production will be presented. Density functional theory is used to calculate reduction potentials, pK_as, and solute and solvent reorganization energies for the electron and proton transfer steps along the reaction pathways. The heterogeneous rate constants for electron transfer are calculated with Marcus theory. A general theoretical formulation for PCET is utilized to calculate the heterogeneous rate constants of the concerted PCET steps. This theory includes the quantum mechanical effects of the active electrons and transferring proton, as well as the motions of the proton donor-acceptor mode and solvent. Applications to two types of molecular electrocatalysts for hydrogen production will be discussed: cobalt complexes with supporting diglyoxime ligands and nickel complexes with pedant amines to facilitate a proton relay. The thermodynamically favored pathways are identified for each catalyst. The impact of substituents on the mechanisms and rate constants is also examined.

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