PROTON-COUPLED ELECTRON TRANSFER IN CATALYSIS AND ENERGY CONVERSION

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Proton-coupled electron transfer (PCET) reactions play a vital role in a wide range of catalytic processes. This talk will focus on recent advances in the theory of PCET and applications to enzymes, molecular electrocatalysts, and nanoparticles. The quantum mechanical effects of the active electrons and transferring proton(s), as well as the motions of the proton donor-acceptor mode and solvent or protein environment, are included in a general theoretical formulation.[1] This formulation enables the calculation of rate constants and kinetic isotope effects (KIEs) for comparison to experiment. Studies of the enzyme soybean lipoxygenase provide a physical explanation for the experimental observation of unusually large KIEs of up to 700 for C-H bond activation at room temperature. The calculations also elucidate the substantial impact of distal mutations on the magnitude and temperature dependence of the KIE in this enzyme.[2] A combined experimental and theoretical study of a series of substituted benzimidazole-phenol model systems inspired by the Tyr_Z-His190 redox proton relay found in photosystem II provide insight into the physical principles underlying proton relays.[3] Theory predicts a concerted two-proton transfer process associated with the electrochemical oxidation of the phenol, accompanied by a decrease in the redox potential of the phenol and a small KIE, when the benzimidazole substituents are strong proton acceptors such as primary or tertiary amines. Electrochemical, spectroelectrochemical, and KIE experiments are consistent with these predictions. Recent calculations on photoreduced zinc oxide nanocrystals have elucidated the effects of proton diffusion between sites within the nanocrystals as well as the nature of PCET to the nitroxyl radical TEMPO.[4,5] This wide variety of applications illustrates the diversity and complexity of PCET in catalysis.

References

1) S. Hammes-Schiffer, *J. Am. Chem. Soc.* **2015**, *137*, 8860.
2) A. V. Soudackov, S. Hammes-Schiffer, *Faraday Discuss.* **2016**, *195*, 171.
3) M. T. Huynh, S. J. Mora, M. Villalba, M. E. Tejeda-Ferrari, P. A. Liddell, B. R. Cherry, A.-L. Teillout, C. W. Machan, C. P. Kubiak, D. Gust, T. A. Moore, S. Hammes-Schiffer, and A. L. Moore, *ACS Cent. Sci.* **2017**, *3*, 372.
4) S. Ghosh, J. Castillo-Lora, A. V. Soudackov, J. M. Mayer, and S. Hammes-Schiffer, *Nano Lett.* **2017**, *17*, 5762.
5) S. Ghosh, A. V. Soudackov, and S. Hammes-Schiffer, *ACS Nano* **2017**, 11, 10295.