Introduction: Proton-Coupled Electron Transfer

Sharon Hammes-Schiffer received her B.A. in 1988 from Princeton University and her Ph.D. in Chemistry at Stanford University in 1993. She was a postdoc at AT&T Bell Laboratories and was appointed the Clare Boothe Luce Assistant Professor of Chemistry and Biochemistry at the University of Notre Dame in 1995. She has been at Pennsylvania State University since 2000, when she was appointed the Shaffer Associate Professor of Chemistry and subsequently appointed the Eberly Professor of Biotechnology in 2006. She is a Senior Editor for *The Journal of Physical Chemistry* and *The Journal of Physical Chemistry Letters*. Dr. Hammes-Schiffer's current research centers on the investigation of proton, electron, and proton-coupled electron transfer reactions in chemical, biological, and interfacial processes. Her work encompasses the development of analytical theories and computational methods, as well as applications to a wide range of experimentally relevant systems. She has been a recipient of the National Science Foundation CAREER Award (1996), an Alfred P. Sloan Research Fellowship (1998), the Camille Dreyfus Teacher-Scholar Award (1999), the Iota Sigma Pi Agnes Fay Morgan Research Award (2005), the International Academy of Quantum Molecular Science Medal (2005), and the American Chemical Society Akron Section Award (2008).

The coupling of electron and proton transfer reactions is essential for a broad range of biological and chemical processes. The title of this special issue, "Proton-Coupled Electron Transfer", was designed to encompass all processes in which electron and proton transfer reactions are coupled. As in most active areas of research, the terminology in this field has evolved over the years. Initially, proton-coupled electron transfer (PCET) was defined as a specific type of reaction in which an electron and proton transfer in a single kinetic step. More recently, PCET has been used to denote a much broader class of processes, as in the title of this issue. In this context, the concerted mechanism, which has been denoted CPET, CEP, or EPT, is defined to be the simultaneous transfer of the electron and proton in a single step without a stable intermediate. The sequential mechanism involves a stable intermediate, where either the proton transfers prior to the electron, denoted PT-ET, or the electron transfers prior to the proton, denoted ET-PT. The distinction between concerted and sequential mechanisms is not always possible, particularly in ultrafast processes, where the definition of a stable intermediate is unclear. Furthermore, some PCET processes involve multiple electron and proton transfers, leading to a combination of concerted and sequential mechanisms within a single process.

In general, the electron and proton may transfer in the same direction or in different directions. The transfer of an electron and proton to or from different species, often in different directions, has been denoted separated CPET, orthogonal PCET, bidirectional PCET, and multiple-site electron−proton transfer (MS-EPT) in the literature. The transfer of an electron and a proton in the same direction from a single donor to a single acceptor has been denoted collinear PCET or hydrogen atom transfer (HAT). Numerous other definitions of HAT have been proposed in the literature. For example, HAT has been defined to correspond to reactions in which the transferring electron and proton come from and end up in the same bonds or the same molecular orbitals. Many of these definitions are not rigorous because of the quantum mechanical behavior and associated delocalization of the electrons and transferring protons. HAT has also been defined to correspond to PCET reactions in which the proton transfer is electronically adiabatic (i.e., the electrons respond instantaneously to the proton motion).

A variety of different rate constant expressions that are valid in different regimes have been derived for PCET processes. When the electrons and transferring protons are treated quantum mechanically, a concerted PCET reaction can be viewed in terms of electron−proton vibronic states. In the regime where the electron−proton vibronic coupling between the reactant and product states is much greater than the thermal energy, the electron−proton subsystem responds instantaneously to the solvent and protein motions, and the process is vibronically adiabatic. In this regime, the system remains in the ground electron−proton vibronic state, and the rate constant has the general form of multidimensional transition state theory. In the more typical regime, the electron−proton vibronic coupling between the reactant and product states is much less than the thermal energy, and the process is vibronically nonadiabatic. In this regime, the process is viewed in terms of nonadiabatic transitions between reactant and product electron−proton vibronic states, and the nonadiabatic rate constant can be derived with the golden rule formalism.

Other distinguishing characteristics lead to further variations in rate constant expressions for concerted PCET reactions. PCET processes involving substantial charge redistribution with a large solvent reorganization energy may be described in terms of collective solvent coordinates (i.e., a Marcus theory treatment), but processes with small solvent reorganization energy (i.e., typical HAT reactions) may require the explicit dynamical treatment of intramolecular solute modes. The form of the vibronic coupling differs for electronically adiabatic and nondadiabatic proton transfer (i.e., depending on the relative time scales of the electrons and transferring protons). Furthermore, the proton donor−acceptor motion has been shown to play an important role in PCET and has been included in the rate constant expressions in various regimes.

The form of the rate constant expression for a sequential PCET process depends on the relative time scales of the individual steps. Moreover, processes involving proton transport along proton relays require consideration of the formation of the hydrogen-bonded network and the possibility of intermediate proton states in the proton-conducting channel. Finally, photoinduced ultrafast PCET processes exhibit nonequilibrium effects that can be described by nonadiabatic molecular dynamics methods. Thus, a single theoretical treatment does not apply to all PCET processes.

10.1021/cr100367q

Similarly, a wide range of experimental techniques is required to probe the detailed mechanisms of these diverse reactions.

In 2007, Huynh and Meyer published a landmark review in *Chemical Reviews* on PCET that is linked to this current special issue. Significant progress has been made in this field over the past several years. This special issue highlights this progress and spans both theoretical and experimental studies of PCET in solution, DNA, and proteins, as well as electrochemical and ultrafast interfacial PCET. The first two contributions in the special issue focus on general aspects of PCET. The fundamental theoretical concepts of coupled electron and proton transfer processes, including both concerted and sequential mechanisms, as well as electron transfer coupled to proton translocation, are reviewed by Hammes-Schiffer and Stuchebrukhov. The thermochemistry of a range of PCET reagents is presented by Warren, Tronic, and Mayer in a number of useful tables. This review also discusses the mechanistic implications of these thermochemical data.

Another set of contributions in this special issue focus on PCET in biological systems. Kumar and Sevilla cover the important topic of PCET in DNA, with particular focus on ion radical formation. Dempsey, Winkler, and Gray review PCET in protein redox machines, including photosystem II and ribonucleotide reductase, as well as tyrosine model systems. Siegbahn and Blomberg discuss quantum chemical studies of PCET in metalloenzymes, including cytochrome *c* oxidase, photosystem II, and ribonucleotide reductase. In these studies, density functional theory is used to examine the energetics on the electronic ground state with a classical treatment of the transferring hydrogen nuclei. In another contribution, the detailed mechanism of cytochrome *c* oxidase, including electron tunneling and proton pumping, is reviewed by Kaila, Verkhovsky, and Wikström. In a review linked to this special issue, Stubbe, Nocera, Yee, and Chang provided a detailed account of radical initiation and long-range PCET in ribonucleotide reductase. In a Perennial Review, Nagel and Klinman cover the significant topic of tunneling and dynamics in enzymatic hydride transfer.

The final two contributions in this special issue center on interfacial PCET. In a Perennial Review, Costentin, Robert, and Savéant review the electrochemical approach to the mechanistic study of PCET. The electrochemical approach is highly suitable for this purpose because the PCET reaction can be controlled through the electrode potential, and the current density can be measured with high precision. Petek and Zhao cover the significant topic of ultrafast interfacial PCET, with detailed accounts of methane on Pt(111) surfaces and water or methanol on titanium dioxide (TiO_2) surfaces. The coupling between electronic and nuclear motions in these interfacial systems plays a vital role in the activation of bonds containing hydrogen atoms, which is important for the development of alternative renewable energy sources such as solar fuel cells.

As is clear from the contributions to this special issue, PCET processes exhibit remarkable diversity and complexity. The coupling between electrons and protons plays a critical role throughout chemistry and biology, and these processes have been studied with a broad spectrum of theoretical and experimental methods. I would like to thank all of the authors for their outstanding contributions to this special issue. In addition, I would like to recognize that several important contributors to the field were unable to participate in this special issue for various reasons. I would also like to emphasize that the PCET field is still relatively young, and these reviews do not constitute the final word on these topics. Hopefully this special issue will provide the foundation and impetus for further progress in addressing the theoretical and experimental challenges associated with coupled electron and proton transfer reactions.

Sharon Hammes-Schiffer
Department of Chemistry, Pennsylvania State University,
University Park, Pennsylvania 16802, USA

CR100367Q