Proton-Coupled Electron Transfer

The topic of proton-coupled electron transfer (PCET) has attracted an exceptionally high level of attention from a wide variety of scientists during the last decade. Spectroscopists, biologists, chemists, and theoreticians are combining their efforts to understand one of the most important and intriguing phenomena that occurs during catalytic processes in both biological and chemical systems. A research community has already emerged, and the first international meeting on this topic was held in the Loire Valley, France (PCET 2011). This research theme is fuelled by the fact that all the processes of the main energy transfer pathways in biology (respiration and photosynthesis) involve PCET. Therefore, unraveling the details of the functioning of metalloenzymes such as hydrogenases, cytochrome c oxidase, and the oxygen-evolving complex might help chemists to replicate these events in synthetic models. This book will be especially welcomed by scientists who are already familiar with the different aspects of PCET that are treated within it, and it will also be very useful for newcomers.

The book is organized in five chapters. The first chapter opens with an explanation of the historical connection between the well-known Pourbaix diagram and proton-coupled electron transfer, and also refers to the present messy situation about the proper terminology for the movement of the proton in relation to the electron. Despite the current semantic confusion, the authors present a clear description of the different processes in this chapter, which focuses on the application of the Marcus theory and the interpretation of hydrogen atom transfer (HAT) reactions. The concise introduction to the Marcus theory lays the basis for the description of the different examples of HAT reactions in purely organic systems and in reactions where transition metal complexes are involved. With the help of a well-chosen set of examples, the authors show that a good kinetic model has been developed for HAT reactions based on the Marcus relationship. Although this simplified model omits some important theoretical aspects, it stands as a good conceptual and predictive tool to study a wide range of HAT reactions in solution.

Chapter 2 introduces a theoretical approach to the transition-state picture of proton-coupled electron transfers. The author describes the application of the interacting/intersecting state model (ISM) to atom and proton transfer reactions, while treating the electron transfer reactions by the same model. The aim is to demonstrate a clear relationship between reactivity and molecular parameters. Textbook examples of HAT, PCET, and CPET are discussed within the same theoretical framework.

Chapter 3 is concerned with experimental approaches towards PCET reactions in biological systems. As in the first two chapters, the authors again point to the inconsistency in the definitions and terminology for PCET reactions. The different mechanisms of electron and proton transfers in biological systems are mentioned together with thermodynamic aspects. The kinetic aspects of PCET are discussed, starting with the original mathematical treatment by Marcus, while also pointing to more elaborate theoretical treatments such as the Hammes-Schiffer and Klinman models. This chapter also contains an excellent section on the experimental kinetic approaches to the analysis of PCET reactions, followed by a case study of nitrite reductase.

Chapter 4 discusses the roles of metal-ion-coupled and proton-coupled electron transfer in the catalytic reduction of dioxygen. The introduction explains how protons or metal ions can facilitate uphill electron transfer reactions that would otherwise be thermodynamically impossible. This chapter focuses on the two- and four-electron reduction of O_2 in synthetic models, either electrochemically or chemically. The authors give valuable insights into how PCET and MCET (metal-ion-coupled electron transfer) can play substantial roles in the design of functioning models for the activation and reduction of O_2.

The last chapter discusses the importance of PCET processes in relation to the link from natural photosynthesis to artificial photosynthesis. The chapter reviews experimental evidence for the involvement of PCET processes in the 4-electron/4-proton water oxidation reaction that occurs at the heart of Photosystem II. Recent developments in the design of functional models for the oxidation of water are also presented. The authors point to the great challenges in developing a chemical modular approach for light capture, charge separation, and multi-electron/proton catalysis. While the main emphasis is on the water oxidation reaction, the reactions involving proton and CO_2 reduction are also briefly addressed.

In general, the book gives a good insight into current research on a vibrant topic. It is to be expected that it will be the first in a long upcoming list of publications, given the importance of PCET processes such as the activation of water, production of H_2, reduction of CO_2, and reduction of N_2.

Ally Aukauloo
ICMMO, Université Paris-Sud
Paris (France)

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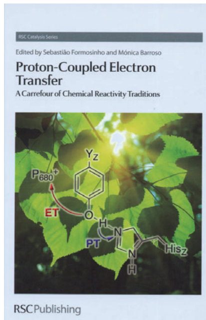

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