J|A|C|S
BOOK REVIEWS

Elements of Molecular and Biomolecular Electrochemistry: An Electrochemical Approach to Electron Transfer Chemistry. By Jean-Michel Savéant (Université de Paris 7, Denis Diderot). J. Wiley & Sons, Inc.: Hoboken, NJ. 2006. xviii + 486 pp. $135. ISBN 0-471-44573-8.
April 24, 2006

For over 40 years the author has made seminal contributions to the general area of electrochemical techniques and their use in studying reactions of importance in physical organic chemistry. It is indeed fortunate that he was invited to give the Baker lectures in 2002 on this work, which led to this complete and authoritative treatment of the field.

The book starts with an overview of electrochemical approaches to studying electrode reactions, mostly cyclic voltammetric (CV) ones, and a detailed discussion of electron transfer (ET) theory (Marcus−Hush). All of the basics are covered in 77 pages, but it will probably be tough going for the novice in electrochemistry. It continues with the electrochemical study of coupled homogeneous chemical reactions. This field, pioneered by the author, allows for the study of complex reaction schemes involving short-lived reactants, since such species can be generated electrochemically and then studied quantitatively over a wide window of time. Studies of this kind have now attained a high degree of sophistication, and this chapter is probably the best source for learning about this area, better than earlier electrochemical texts and reviews. The chapter includes not only a CV study of the usual array of coupled reactions (EC, ECE, etc.) but also techniques like laser flash injection methods and photomodulation voltammetry. It also covers the more complex reaction schemes, like redox catalysis. Injection, or removal, of an electron often triggers bond breakage, e.g., with alkyl halides, or bond formation, e.g., with olefins, and this field is discussed thoroughly. Topics include dissociative reactions and whether these occur in a concerted or stepwise way, and how factors like molecular structure, solvation, and driving force control the mechanism. This is followed by a discussion of homogeneous catalysis of reactions, including reactions in thin films on electrode surfaces, i.e., supported molecular catalysts. Redox catalysis, e.g., ET from radical anions to vicinal dibromides, is contrasted with chemical catalysis where an intermediate adduct is formed, e.g., reduction of alkyl halides by cobalamins. Finally these are taken a step further in a consideration of homogeneous and immobilized enzymes as electrocatalysts, a large field with many practical applications, e.g., in electrochemical sensors. The discussions here are largely limited to the author's research in this area, but the work described is clearly relevant to much of the research in this area, and useful reviews are referenced. The chapter also includes a discussion of biomolecular recognition of enzyme-linked molecules.

One reading this book has to be prepared for a goodly dose of math. A large fraction of it (121 pages) is devoted to appendices that deal with the mathematical details of the treatments in the preceding chapters. These contain reviews of important concepts like the Laplace transform approach to solving the partial differential equation for diffusion, normalization of variables, and other needed concepts and are an excellent place for someone interested in the CV of coupled chemical reactions to learn about this approach, although familiarity with this kind of mathematics will be necessary here. Knowledge of the more analytical mathematics in this area is rapidly giving way to software packages for computer simulation of these kinds of systems, which are merely mentioned in the book. Thus, it is nice to have the mathematical basis that has driven the field for many years documented so completely in these appendices.

This is probably not a book one sits down to read cover-to-cover, but as a road map to the field and a source of key information, background, and general philosophy, it is invaluable. Its beauty is that the author is expert in electrochemistry (including the mathematical aspects of complex systems and instrumentation), physical organic chemistry, and the theoretical aspects of electron transfer and reaction kinetics and can seamlessly integrate all of these concepts in a single place as few others, certainly not in a multiauthor work, could do. We are indeed fortunate that he was invited to lecture in this area and has prepared what is certain to be the definitive treatment for years to come.

Allen J. Bard, *University of Texas at Austin*

JA069754P

10.1021/ja069754p