Book Reviews

The Enzymes, Vol. XX; Mechanisms of Catalysis (3rd Edition). Edited by David S. Sigman. Academic Press, Inc., San Diego, CA. 1992. ix + 546 pp. 16 × 23 cm. ISBN 0-12-122720-0. $99.00.

This volume continues in the outstanding tradition of the series edited by Paul Boyer and Edwin Krebs. Volume XX is the second in a two-part miniseries on "Mechanisms of Catalysis"; volume XIX focused on the general principles, and volume XX focuses on specific reaction types. The only shortcoming of this volume is the limited scope of topics; however, although the topics are relatively few, they have been chosen so that a variety of reaction types could be covered in any one area. For example, in the chapter on carboxylation and decarboxylation O'Leary discusses several kinds of carboxylases including biotin-dependent ones, a variety of β-keto acid decarboxylases not requiring cofactors as well as metal-dependent decarboxylases, thiamin-dependent decarboxylases, pyridoxal phosphate-dependent decarboxylases, and pyruvate-dependent decarboxylases. Therefore, many more classes of enzymes are covered than what may appear from the 10 chapters that comprise the volume. The apparent goal of this volume, as determined by the selection of authors of the various chapters, was to present the latest in enzyme *chemistry*, and this goal was beautifully met. The chapter authors and reference authors comprise a list of Who's Who in mechanistic enzymology. Each author presents literature and personal insights into the particular enzyme-catalyzed reactions he discusses.

Transient-State Kinetic Analysis of Enzyme Reaction Pathways by K. A. Johnson gives a very nice overview of the rationale, methods, analysis, and interpretation of transient-state kinetics. Several examples of explicit solutions for two-step reactions are given and experiments are described for the measurement of reaction rates at enzyme active sites. Methods of data fitting also are included.

Metal Ions at Enzyme Active Sites by J. J. Villafranca and T. Nowak focuses on metal ions as electrophilic catalysts. Properties of metal ion–ligand complexes, methods to study metal ion environments in proteins, and nine different metal ion-assisted phosphoryl transfer reactions are discussed.

Phosphate Ester Hydrolysis by J. A. Gerlt describes syntheses and configurational analyses of oxygen chiral phosphate and thiophosphate esters by NMR methods, nonenzymic phosphate ester hydrolysis, and six examples of enzyme phosphate ester hydrolysis.

In the chapter Nucleotidyltransferases and Phosphotransferases: Stereochemistry and Covalent Intermediates, P. A. Frey gives a scholarly discussion of theory and experiments used to differentiate mechanism and stereochemistry in these reactions and to identify covalent intermediates.

Glycosidases and Glycosyltransferases by Gregory Mooser includes approaches to the elucidation of the mechanisms for various enzymes in this class. A nice discussion of the differentiation of S_N1 and S_N2 mechanisms for these reactions is presented.

In Carboxylation and Decarboxylation M. H. O'Leary compares these two processes, which usually are discussed as separate reaction types, in terms of their similarities in reaction mechanisms and transition states, and the chemical bases for how the various enzymes catalyze these reactions and the kinds of experiments used to characterize the mechanisms. Selected examples from each category of enzymes that catalyze these reactions are discussed in detail.

In R. Kluger's chapter on the Mechanisms of Enzymic C–C Bond Formation and Cleavage, a broad diversity of enzyme reactions also is discussed. The generalities of these reactions from a physical organic point of view and the experiments used to differentiate these mechanisms are clearly presented. More detailed discussions of biotin-, pyridoxal phosphate-, tetrahydrofolate-, and thiamin pyrophosphate-dependent enzymes that catalyze these reactions are included.

A particularly important chapter (from the reviewer's standpoint), Enzymic Free Radical Mechanisms by E. J. Brush and J. W. Kozarich, also is included. This chapter discusses eight radical-producing enzymes from a mechanistic point of view and shows the importance and relevance of radicals in enzymology.

The chapter entitled Molecular Mechanism of Oxygen Activation by P-450 by Y. Watanabe and J. T. Groves emphasizes the nonenzymic model chemistry to support various mechanisms of cytochrome P-450-catalyzed reactions.

N. J. Oppenheimer and A. L. Handlon cover key features in Mechanism of NAD^+-Dependent Enzymes from the theoretical to the experimental with regards to a variety of dehydrogenases and enzymes that cleave the nicotinamide-glycosyl bond of NAD^+.

In summary, this book is an important addition to the personal library of anyone interested in getting a start at understanding enzyme mechanisms from a chemical point of view or for the practitioner interested in reading about the latest advances in this field.

Richard B. Silverman

Department of Chemistry
Northwestern University
2145 Sheridan Road
Evanston, Illinois 60208-3113

0022-2623/93/1836-0633$04.00/0