

Book Reviews*

Chemical Applications of Density-Functional Theory. Edited by Brian B. Laird (University of Kansas), Richard B. Ross (PPG), and Tom Ziegler (University of Calgary). ACS: Washington, DC. 1996. x + 478 pp. \$126.95. ISBN 0-8412-3403-5.

ACS Symposium Series No. 629. Developed from a symposium sponsored by the Division of Physical Chemistry and the Division of Computers in Chemistry at the 209th National Meeting of the American Chemical Society, Anaheim, CA, April 2–6, 1995. This book combines the two applications of density-functional theory, electronic structure, and statistical mechanics, in one forum. It discusses the density-functional theory used by quantum chemists and solid-state physicists to calculate electronic structures. It presents the use of density-functional theory in the study of phase transition and inhomogeneous fluids by statistical mechanics. It emphasizes both state-of-the-art techniques in areas of application and methodology development.

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Advances in Photochemistry. Volume 21. Edited by Douglas C. Neckers (Bowling Green State University), David H. Volman (University of California-Davis), and Günther von Büнау (Universität Siegen, FRG). Wiley: New York. 1996. ix + 309 pp. \$95.00. ISBN 0-471-14332-4.

Volume 21 offers three chapters on the frontiers of photochemistry written by experts in the field. The book is of general interest to those concerned with the application of photochemistry to the bioorganic, synthetic organic, and spectroscopic fields, and of specific interest to those concerned with any of the chapter topics.

Chapter 1. Photochemistry in Cyclodextrin Cavities. By Pietro Bortolus and Sandra Monti. (119 pp, 371 refs, 42 schemes, 28 tables). The vast cyclodextrin photochemistry literature is summarized and interpreted. Photophysical effects are treated first, followed by photochemistry results. Important concepts such as the use of fluorescence as a probe of host–guest structure, inclusion stoichiometry, and molecular protection are discussed. Lifetime, rate, and binding constant data are presented. The photochemistry section shows how cyclodextrins can act as microvessels to alter unimolecular and bimolecular processes, resulting in rate enhancements, stereo-, regio-, and enantiocontrol, and inhibition of undesirable processes. Product distributions are presented in detail. Photoactive cyclodextrins are treated last. That the reviewer's work is cited is testimony to the thoroughness of the chapter.

Chapter 2. Asymmetric Photoreactions of Conjugated Enones and Esters. By Jean-Pierre Pete. (70 pp, 198 refs, 4 figs, 41 schemes, 4 tables). This chapter concerns photochemistry as a tool for asymmetric induction. Two classes of reactions are treated. The first involves photogenerated reactive intermediates in the presence of a chiral catalyst, and the second involves photoreactions of chiral molecules which result in the production of new centers, including those of molecules with removable chiral appendages. Photodeconjugation of enones via a dienol and subsequent keto–enol tautomerization is discussed first. Using β -amino alcohols as a chiral inducer gives the highest enantiomeric excess for a photochemical transformation. Diastereoselective phototransformations of chiral molecules, mostly involving [2 + 2] cycloadditions, are then discussed. The chiral center(s) can be in many positions, and most of the possible permutations are presented. With esters the chirality is typically in the alcohol portion. Some mention of solid state photoreactions is made, including those from chiral inclusion complexes.

Chapter 3. Photodissociation Dynamics of Hydride Molecules: H Atom Photofragment Translational Spectroscopy. By Michael N. R. Ashfold, David H. Morduant, and Steven H. S. Wilson. (78 pp, 393 refs, 17 figs, 2 tables). The hydrides H₂O, H₂S, H₂O, NH₃, PH₃, CH₄, SiH₄, HCN, and HC≡CH are studied by the relatively new technique of H atom photofragmentation translational spectroscopy, especially the Rydberg excitation method. This technique provides information such as branching ratios, energy and angular momentum disposals, product recoil velocities, rotational alignment, and mutual correlations,

all of which reflect intermolecular forces and therefore the potential energy surface from which fragmentation occurs. The method is described first, and then the data for water are examined in detail and contrasted with previous results. Results with the rest of the hydrides are discussed with reference to the water results.

An index for the current volume is followed by a cumulative index for volumes 1–21.

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Unimolecular Reactions, 2nd Edition. By Kenneth A. Holbrook (University of Hull) and Michael J. Pilling and Struan H. Robertson (University of Leeds). John Wiley & Sons: New York. 1996. xv + 417 pp. \$165.00. ISBN 0-471-92268-4.

At long last, the field of unimolecular reactions has some new books which give justice to the remarkable progress the field has enjoyed since the early 1970s when the two standard books on the subject were published (Robinson and Holbrook in 1972 and Forst in 1973). Three new books have appeared in recent years, namely Gilbert and Smith's *Theory of Unimolecular and Recombination Reactions* (1990), Baer and Hase's *Unimolecular Reaction Dynamics: Theory and Experiments* (1996), and Holbrook, Pilling, and Robertson's *Unimolecular Reactions* (1996). The new Holbrook et al. book is a revision of the 1972 monograph by Robinson and Holbrook. To explain how the new Holbrook monograph fits into these developments, it is necessary to explain how the field of unimolecular reactions has developed. Major advances have come about through the ability to energy select molecules by photoexcitation and to measure direct $k(E)$. These microcanonical topics are covered by the Baer and Hase book. The new volume of Holbrook covers thermal (canonical) systems, in which $k(T)$ is measured and calculated, and in which major strides have been made in our understanding of energy transfer. There is of course some overlap, but on the whole the two books cover very different topics, and together serve as a good reference for the whole field of gas phase unimolecular reactions. On the other hand, Gilbert and Smith cover the same topics as Holbrook, Pilling, and Robertson. Both of these books are excellent but differ considerably in their style, the Holbrook work being much more sedate. Since the Gilbert and Smith book is unfortunately already out of print, the only modern book dealing with thermal unimolecular systems is the new Holbrook volume.

The Holbrook book is divided into 11 chapters plus a number of appendixes. The major topics covered are the basic aspects of the statistical RRKM theory, the evaluation of densities and sums of states, energy transfer, the use of the master equation for collisional energy transfer, and kinetic isotope effects in unimolecular reactions. The book ends with a large chapter on experimental data for numerous reactions. All of these very useful and important topics are treated at a level that can be understood by fourth-year undergraduate and first-year graduate students. The book is similar to the earlier Robinson and Holbrook book except that two important chapters on energy transfer and the master equation are added. These are also part of the Gilbert and Smith book.

Although authored by three individuals, the text is very uniformly written. A minor fault is that it is a bit dry and lacking in excitement. A larger problem is the lack of information about the most recent experimental progress in measuring reaction rates (e.g., H₂CO and NO₂) down to the energetic thresholds. These lovely experiments which provide dramatic support for the transition state theory are not mentioned. Similarly, the most recent work (say up to 1994) on molecular energy transfer using laser methods is not covered. Most of the references here are to work done before 1989. It would also have been helpful if the chapter on molecular energy transfer had covered some of the simple models, such as the Schwartz, Slawsky, and Herzfeld equation or the breathing sphere model. A final detraction of this book is its price of \$165.00, which ensures that this monograph will be bought only by libraries and a few wealthy individuals. In

*Unsigned book reviews are by the Book Review Editor.

spite of these shortcomings, the Holbrook, Pilling, and Robertson book is a valuable and much needed addition to the literature.

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Metals and Ligand Reactivity: An Introduction to the Organic Chemistry of Metal Complexes. By Edwin C. Constable (University of Basel, Switzerland). VCH: New York. 1996. xiv + 308 pp. \$45.00 ISBN 3-527-29277-2.

This revised and expanded second edition serves as an overview of coordination chemistry from the vantage point of the ligand. Organometallic chemistry, as stated in the preface, is not covered. Rather, the focus is upon the influence of metal ions on the chemistry of ligands in heteroatom-metal-bonded systems. The text reviews the effects a metal center may have on the geometry, polarization, and reactivity of coordinated ligands.

The first two chapters include a discourse on the general nature of metal-ligand interactions, and a review of fundamental aspects of crystal-field, molecular-orbital, and ligand-field theory. The remaining eight chapters cover numerous topics which serve to illustrate general principles regarding the reactivity exhibited by labile and nonlabile ligands. Specifically, Chapters 3 and 4 cover Lewis acid-enhanced, nucleophilic attack on coordinated carbonyl and carbonyl-derived compounds. Chapter 5 discusses anionic ligand reactivity and the dual role a metal center may play in modifying this reactivity while stabilizing the product derived from its reaction with an electrophile. Chapter 6 introduces macrocycles. Chapter 7, a new chapter, expands the section on molecular topology appearing in the first edition. This includes an introduction to molecular recognition in the context of metal-template-directed synthesis of cryptands, helical structures, and catenanes. Chapter 8 concerns substitution reactions of coordinated arenes (primarily heteroarenes). Chapter 9 considers redox processes. Lastly, Chapter 10, entitled Envoi, makes some analogies to bioinorganic systems.

Treatment of these topics is introductory, not comprehensive. The array of reactions outline how a metal complex may influence various synthetic aspects of coordinated species. Many examples are provided of reactivity and selectivity patterns not observed in conventional organic synthesis. Additionally, synthesis of products which are inaccessible, or difficult to prepare, using traditional synthetic methods are illustrated.

In general, anyone desiring a primer on the synthetic utility of coordination compounds will be interested in this text. For instance, those wishing to wet their appetite on the sections describing metal-template-assisted ligand design will not be disappointed. However, footnotes to specific reactions are not provided. Rather, the reader is referred to a bibliography of review articles and monographs at the end of each chapter. Updating of these references occurs largely in the chapters treating macrocyclic and supramolecular chemistry.

The convenience of directing the reader to review articles (some of which are relatively dated) presents a risk that the reader may miss important recent advances in the field. For instance, only the "textbook", Criegee-type mechanism (concerted [3+2]-cycloaddition) is presented in the examples of metal oxo-mediated oxidation of alkenes, not the more recent [2+2] mechanistic evidence provided by Sharpless and others. Granted, the text is introductory, and is meant to be as readable as possible. However, providing footnotes would allow even the nonspecialist reader quicker access to the primary literature. Also, although infrequent, not all of the typographical errors (e.g., the pentavalent carbon following the Criegee-like intermediates) have been eliminated.

Notwithstanding these minor criticisms, most readers will find that the author achieves his stated aim of stimulating the reader to "delve deeper into the subject". Moreover, the broad spectrum of topics introduced in the text should provide enough variety to be of general interest to a wide audience.

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Mechanisms of Metallocenter Assembly. Edited by Robert P. Hausinger (Michigan State University), Gunther L. Eichhorn (National Institute on Aging), and Luigi G. Marzilli (Emory University). VCH: New York. 1995. xiv + 267 pp. \$115.00. ISBN 1-56081-920-0.

Metal-containing proteins (or metalloproteins) are ubiquitous in biological systems and thus are the focus of research aimed at defining the roles of the metallocenters in the mechanisms of the respective proteins. These metal sites range from the simple association of a metal with a protein (e.g., Ca^{2+}) to complex, covalently bound assemblages containing both inorganic and organic constituents (e.g., the FeMo cofactor of nitrogenase). The functions of the metallocenters within the proteins are also varied, ranging from simple structural roles, to electron transfer, small molecule sensing, substrate binding, and activation. While much is known about the structures, redox properties, and mechanistic functions for many finished metallocenters in proteins, our understanding of how these metallocenters are biosynthesized, inserted into the target protein, and modified to the final metallocenter has generally only been aggressively studied recently. Not surprisingly, given the range of complexities of the known metallocenters found in proteins, the mechanisms for their assembly range from simple reversible dissociation to a complex series of reactions which can involve many accessory proteins. Understanding the mechanisms of these varied processes in biological metallocenter assembly represents one of the important frontiers in bioinorganic chemistry.

A recent book entitled *Mechanisms of Metallocenter Assembly* brings together, for the first time, a series of reviews on some of the better understood biological systems of metallocenter assembly. This book, published in 1995, is the latest in a series of books published under the general theme of *Advances in Inorganic Biochemistry*. The goal of these volumes is to provide reviews of specific areas of bioinorganic chemistry. *Mechanisms of Metallocenter Assembly* is the latest volume in the series (volume 11). The overall aim of the book is to collect reviews on several systems for metallocenter assembly. This is done in the form of 12 chapters, each covering a different system. The first chapter is written by one of the editors of the book and presents a general overview of the field, with particular emphasis on placing the following chapters into the larger context of the field. Each subsequent chapter, written by experts in their specific fields, presents a series of reviews on the selected systems covered in the book. The areas covered in these subsequent chapters include the assembly of dinuclear iron sites, hemes, cobalt centers, [Fe-S] clusters, and Mo-, Ni-, Cu-, and Zn-containing centers. Each chapter provides an introduction to the area useful for the nonexpert, followed by a thorough coverage of the latest work in the area, usually including new results from the laboratories of the authors. The chapters are generously illustrated with black and white figures. The use of color figures in a few cases would have been a nice addition, but the figures presented are generally very informative. The information presented for each system appears to be relatively current, with the most recent references coming from work published in 1994. Findings since 1994 are obviously not incorporated into the information presented.

The organization of the book into chapters about specific topics of metallocenter assembly provides a general introduction and overview to the systems covered in the book. This format by necessity, however, does not cover some areas related to the overall topic. For example, while the complex events in the biosynthesis of the Mo-containing cofactor of nitrogenase (FeMo cofactor) is covered, the biosynthesis of the other major class of Mo-containing cofactors (Mo cofactor) is not covered. The book is not a comprehensive treatise of all areas in the biological synthesis of metallocenters, but rather is a collection of some of the better studied cases.

In summary, *Mechanisms of Metallocenter Assembly* is an excellent addition in the *Advances in Inorganic Biochemistry* series which provides a totally unique and much needed collection of reviews on several well-studied systems of metallocenter assembly. This book is recommended for the scientist interested in an introduction to the topic of metallocenter assembly and to the specialist working in the area who wants to have what will certainly be the first in a series of books that will appear in the future on this important area of bioinorganic chemistry.

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