JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Book Review

Book Review of Asymmetric Phase Transfer Catalysis

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J. Am. Chem. Soc., **2008**, 130 (37), 12547-12547 • DOI: 10.1021/ja805398n • Publication Date (Web): 02 August 2008

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Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

Asymmetric Phase Transfer Catalysis. Edited by Keiji Maruoka (Kyoto University, Japan). Wiley VCH Verlag GmbH & Co. KGaA: Weinheim. 2008. xiv + 214 pp. $145. ISBN 978-3-527-31842-1.

The book covers recent developments in asymmetric phase-transfer catalysis (PTC) since the milestone work of the Merck Group (1984) and O'Donnell and co-workers (1989). Although the last authoritative review on PTC by E. V. Dehmlow and S. S. Dehmlow (1993) views enantioselective PTC reactions quite critically because of the often observed instability of quininium and quinidinium salts and the obscure source of chiral impurities, the present book nicely outlines the magnificent progress during the past decade. Its cover is somewhat misleading in the sense that it implies an emphasis on mechanistic aspects of nonstereoselective PTC (no chiral catalyst is depicted!), for which the editor refers the reader to other monographs and reviews in the Preface. The nine independent chapters guide the reader through the concepts and applications of asymmetric catalysts to phase-transfer reactions.

The first chapter is a short introduction to PTC that includes a brief description of its principles and mechanisms. Chapter 2 concerns the application of PTC to amino acid synthesis using cinchona alkaloid-derived phase-transfer catalysts. In the following chapter, the applications of cinchona derivatives to a variety of asymmetric reactions to form new carbon−carbon, carbon−oxygen, carbon−nitrogen, and carbon−fluorine bonds are reviewed. The fourth chapter addresses oligomeric cinchona alkaloid derivatives for asymmetric synthesis, in which the straightforward synthesis and variation of catalyst design are discussed and their applications to phase-transfer reactions are described. Mechanistic suggestions are also presented. The next chapter covers the synthesis and application of binaphthyl- and biphenyl-modified C_2-symmetric spiro phase-transfer catalysts that have emerged as a particularly effective new class of catalysts. Designs and applications of chiral two-center phase-transfer catalysts derived from tartaric acid and BINOL are summarized in the sixth chapter. Other asymmetric phase-transfer catalysts that contain C_2-symmetric guanidinium salts, C_3-symmetric ammonium salts, and L-menthol-derived ammonium salts as well as others are presented in Chapter 7, and the use of chiral crown ethers, Taddol, Nobin, and metal(salen) complexes as catalysts for asymmetric phase-transfer reactions is reviewed in Chapter 8. Chiral quaternary ammonium fluorides are presented in the final chapter in which the development of the catalytic properties of such salts in asymmetric PTC for carbon−carbon bond formation is discussed.

The authors not only present the widely investigated asymmetric alkylation of Schiff base esters to functionalize amino acids but also include, inter alia, epoxidation, hydroxylation, aldol reactions, Michael addition, Darzens' reaction, and the fascinating fluorination with $(PhSO_2)_2NF$. The illustrations of some transition states in several chapters are not easy to visualize because the three-dimensional drawings are unclear, and the formatting of some schemes and illustrations is inconsistent.

The book is compact and easy to read, and the references are current up to early 2007. The chapters are independent in content, although several introductions overlap in content, which is not undesirable. The reader learns about the versatility of PTC and principles of catalyst design. Overall, the book offers a welcome introduction to asymmetric phase-transfer catalysis and can be highly recommended as an addition to chemical libraries.

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JA805398N
10.1021/ja805398n

Origin of Life: Chemical Approach. Edited by Piet Herdewijn (Katholike Universiteit Leuven, Belgium) and M. Volkan Kisakürek (Verlag Helvetica Chimica Acta, Zürich, Switzerland). VHCA: Zürich and Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim. 2008. xii + 418 pp. $190.00. ISBN 978-3-906390-50-5.

This book is a compilation of articles of "explorative chemistry" on a wide range of theories to address "What is the origin of life?". As the Editors state, chemistry is defined here in the broadest sense in the attempt to explore this fundamental and complex question. The articles originally appeared in the journal *Chemistry & Biodiversity* and were written by "eminent players in the field". A sampling of the chapters includes "Reactions of the HCN-Tetramer with Aldehydes" by Koch, Schweizer, and Eschenmoser; "Intractable Mixtures and the Origin of Life" by Schwartz; and "Conformational and Chiral Selection of Oligonucleotides" by Froeyen et al. A subject index completes the book.

JA805583Q
10.1021/ja805583q

Atom Resolved Surface Reactions: Nanocatalysis. By P. R. Davies and M. W. Roberts (Cardiff University, U.K.). Royal Society of Chemistry: Cambridge. 2008. xviii + 222 pp. $189.00. ISBN 978-0-85404-269-2.

The authors of this book do an outstanding job showing how the use of scanning tunneling microscopy (STM) has advanced surface chemistry and heterogeneous catalysis. In the first three chapters, they introduce the field and discuss the fundamentals of scanning tunneling microscopy and important related experimental methods. Readers who are not familiar with instrumental techniques of surface analysis will gain some knowledge of the weaknesses and strengths of several techniques other than STM but will have to consult other references to understand those methods. In the main section of the book, the authors discuss surfaces and surface reactions of increasing complexity, not only focusing on chemical aspects but also introducing more experimental techniques of relevance. Whereas earlier chapters

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deal with chemisorption of small inorganic molecules and catalytic oxidations on pristine single crystal surfaces under ultrahigh vacuum conditions, later ones address even more complex systems, such as high-pressure environments, chemisorption of organic molecules, chemical reactivity on clusters and nanoparticles, and industrially relevant catalytic reactions such as hydrogenation and desulphurization. The book ends with a chapter on surface engineering at the nanoscale using bottom-up approaches.

Importantly, the authors do not simply summarize the work that has been performed but rather evaluate it critically, giving it the unique perspective of those who have been working for a long time in this field. Many of the chapters start out with an outline of heterogeneous catalysis before STM was available. Often, this historical perspective contains references to specific conferences and reveals specific challenges of the day, which will make this book of interest to chemistry historians. However, documenting history is not a goal of the authors; instead, they use this perspective to show the important contributions made possible by different methods of surface analysis. This is followed in each chapter by a critical up-to-date discussion of recent advances made possible by the use of STM. These sections are illustrated with a large number of well-chosen figures, many of them impressive STM images of the highest quality. Every chapter also contains a summary that reflects on the specific contributions of STM and makes important cross-references to other chapters. Finally, as a unique feature of this book, each chapter has a section with sources for further reading in addition to the usual list of references.

In summary, this insightful scholarly contribution gives a unique and timely overview of the atomic-level understanding of heterogeneous catalysis to which STM has contributed so much. Not only is it a fascinating introduction to heterogeneous catalysis for those new to the area, but also its individual chapters give excellent reviews on specific subtopics of the field. If there was one aspect of the book that I would have liked to have seen better developed, it would have been the index—a minor detail indeed.

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JA805420F

10.1021/ja805420f

Molecular Modeling of Proteins. Methods in Molecular Biology, 443. Edited by Andreas Kukol (University of Hertfordshire, U.K.). Humana Press: Totowa. 2008. xii + 390 pp. $99.50. ISBN978-1-58829-864-5.

This book covers many different aspects of protein modeling and is just one volume in an extremely large series (over 500 volumes published or planned). It contains 19 chapters, which are organized into six parts: (I) Methodology, (II) Free Energy Calculations, (III) Molecular Modeling of Membrane Proteins, (IV) Protein Structure Determination, (V) Conformational Change, and (VI) Applications to Drug Design. The main weakness of the book, as is frequently true for such edited volumes, is that the quality of the individual chapters is quite uneven. Some aspects of molecular modeling of proteins are quite well covered, whereas others are covered too briefly, with many important aspects being completely absent.

The first two chapters on molecular dynamics (MD) and Monte Carlo simulation techniques are useful but extremely short. The third chapter on computation of kinetic isotope effects using hybrid quantum and classical methods, a specific problem that in comparison with the previous topics has a much smaller audience includes almost as many pages as the first two chapters. The chapter on the comparison of protein force fields for MD simulations provides a useful summary of the topic. The chapter on normal modes and essential dynamics is also particularly useful. It contains, in addition to standard normal-mode analysis, a review of principal components analysis and elastic network methods, although several newer methods such as the anisotropic network model and hierarchical or mixed coarse-grained models are not mentioned. Part I on methodology, and indeed the whole book, lacks a chapter on coarse-grained structures, their interactions, and utility, although these approaches are highly popular in protein modeling. Part II, "Free Energy Calculations", contains a chapter on calculations of absolute protein−ligand binding constants and one on free energy calculations for membrane proteins. These two chapters might have been better placed into Parts III and IV, instead of forming a section of their own. Part III on molecular modeling of membrane proteins contains three rather useful chapters, although there is significant overlap among them since they all cover MD simulations of membrane proteins. Part IV, "Protein Structure Determination" (Why the term "determination" instead of "prediction"?), is made up of three chapters: a general one on comparative modeling of proteins and two more specific ones on modeling of transmembrane proteins using high-throughput MD simulations with experimental constraints and NMR-based modeling and refinement of proteins and their complexes. This part of the book lacks chapters on fold recognition methods, such as threading and techniques for the prediction of novel folds. Part V, "Conformational Change", contains three different chapters that cover conformational changes in protein function, folding, and unfolding by all-atom MD simulations, and modeling of protein misfolding in the context of prion disease. The final part on applications to drug design comprises three slightly overlapping chapters on the identification of putative drug targets and potential drug leads, receptor flexibility for large-scale ligand screens, and molecular docking.

This book might be useful as an overview of the various techniques and methods used for the molecular modeling of proteins. Since the editor specializes in molecular dynamics simulations of membrane proteins, both MD simulations techniques and modeling of membrane proteins are emphasized in the book, although this narrower range of covered topics is not indicated by the title. Protein modeling based on coarse-grained representations and their contact potentials and Monte Carlo and stochastic simulations based on coarse-grained models are useful subjects that were not covered well; such approaches are especially important for studying biological processes slower than the time scales accessible by atomic molecular dynamics. In many places, there are specific details given for the use of specific computer programs, which detracted from the book's generality and its long-term value, but may on the other hand be appealing for some novices. Overall, the range of topics covered by the book is somewhat limited, with many of the fundamental details inadequately covered.

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JA805842D

10.1021/ja805842d

Hazardous Chemicals Desk Reference, 6th ed. By Richard J. Lewis, Sr. (formerly at the National Institute for Occupational Health and Safety). John Wiley & Sons, Inc.: Hoboken, NJ. 2008. xx + 1954 pp. $175. ISBN 978-0-470-18024-2.

This latest edition of *Hazardous Chemicals* includes updates to two-thirds of the more than 5800 entries as well as 500 new ones, most of which were selected because they are on the EPA TSCA Inventory. Each entry includes a description of the physical and chemical properties of the material in question, its various synonyms, and the hazards associated with it. Government agency standards and recommendations for handling the chemical are also given. There are also three cross-indices to aid the reader in finding a chemical: the CAS Number Cross-Index, Synonym Cross-Index, and DOT Guide Cross-Index.

JA805584M

10.1021/ja805584m

Electrodeposition from Ionic Liquids. Edited by Frank Endres (Clausthal University of Technology, Clausthal-Zellerfeld, Germany), Andrew Abbott (University of Leicester, U.K.), and Douglas MacFarlane (Monash University, Clayton, Australia). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim. 2008. xxii + 388 pp. $200. ISBN 978-3-527-31565-9.

The literature dealing with room temperature ionic liquids (RTILs) has grown exponentially in recent years, stimulating interest in using RTILs for electrochemical applications. A good, if rather brief, overview of the field was given in Hiroyuki Ohno's book *Electrochemical Aspects of Ionic Liquids*, published by Wiley in 2005. However, as Ken Seddon points out in the Preface to the present book, Ohno's excellent little book devotes only 20 pages to electrodeposition. Endres and his colleagues have addressed the need for an up-to-date and authoritative book on electrodeposition in RTILs by assembling a strong team of coauthors to cover a very wide array of relevant topics, ranging from basic physical and electrochemical properties to electrodeposition of metals, alloys, and semiconductors. Often such multiauthor books suffer from lack of coherence, but in this case the editors have managed to bring all the contributions together to make an excellent integrated reference text that provides an up-to-date review of the literature (up to mid-2007) while at the same time combining fundamental aspects with practical tips and an overview of technological applications. The book will be useful to those beginning fundamental work in the area as well as to others wishing to assess the potential of RTILs for practical applications, such as electroplating and surface finishing. The authors have adopted a realistic and down-to-earth style, as illustrated by a section on "troublesome aspects"—not something one normally finds in books of this type. Issues such as costs, environmental impact, and recycling are also assessed in an honest way. In their conclusion to the book, the editors highlight the relatively small number of research groups engaged in work on electrodeposition in RTILs. It remains to be seen if RTILs fulfill their early promise as stable, water-free media for deposition of reactive materials, but this book should stimulate new research in this relatively new area, where much remains to be discovered.

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JA8057937

10.1021/ja8057937

Tailor-Made Polymers: Via Immobilization of Alpha-Olefin Polymerization Catalysts. Edited by John R. Severn (Borealis Polymer Oy, Porvoo, Finland) and John C. Chadwick (Eindhoven University of Technology, The Netherlands). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim. 2008. xxii + 352 pp. $200.00. ISBN 978-3-527-31782-0.

Single-site polyolefin catalysts are among the most actively studied compounds in chemistry and chemical engineering. Although the molecular nature of these catalysts may suggest otherwise, the polymerization of olefins by single-site catalysts is rarely, if ever, carried out homogeneously in industry. The restrictions placed on commercial polyolefin catalysts, such as stability, nonadherence to reactor surfaces, and the need for compatibility with existing industrial facilities, make heterogenized catalysts a necessity. Of course, the process of immobilization should not interfere with any of the carefully imparted chemical properties, e.g., activity and selectivity, of the molecular catalysts.

Only a multidisciplinary approach drawing from chemistry, chemical engineering, and polymer science can successfully address a problem of such complexity. The varied backgrounds of the 31 authors who contributed to this book, with approximately equal numbers from industry and academia, attest to this fact. Although most academic research on heterogenized catalysts is published in peer-reviewed journals, the findings of many important industrial studies are scattered across patents and technical reports and thus are not readily accessible. Reviews on the various aspects of heterogenized polyolefin catalysts are salted throughout the open literature, but recent progress in this area has been so spectacular that a comprehensive monograph was long overdue.

Both the title and subtitle of this book reflect that this is not only just a book on the heterogenization of polyolefin catalysts—although that is the main subject—but also one on modern polyolefin catalysis in general. The editors and contributors have done a superb job in organizing the contents in a logical fashion. Chapters 1 and 2, for example, provide excellent introductions to modern homogeneous and heterogeneous polyolefin catalysis, respectively. Chapter 3 is concerned with the fundamentals of polymer-particle growth and engineering aspects of polymerization. The most commonly used cocatalysts, namely MAO and perfluoroarylborates, and their manners of heterogenization are the topics of Chapters 4 and 5, respectively. Two materials familiar to heterogeneous catalysis, namely magnesium chloride (Chapter 6) and solid super acids (Chapter 7), are also shown to be highly useful supports or cocatalysts, respectively, for heterogenized polyolefin catalysis. Chapter 8 is a modern treatment of the well-known concept of multicomponent catalysis in the context of heterogenization, and the tethering of olefin polymerization catalysts to inorganic oxides is covered in Chapter 9. More esoteric aspects, like the polymerization of olefins in mesoporous materials and polymerically supported catalysts, are discussed in Chapters 10 and 11, respectively. The next chapter introduces the reader to the novel topic of self-immobilizing catalysts, i.e., catalysts that make their own support.

Naturally, the book is primarily addressed to industrial and academic chemists with a professional interest in polyolefin catalysis. The reader-friendly layout and the lucid writing, however, are bound to make this book attractive to a wider audience of chemists and chemical engineers. Nearly 1000 recent literature references guide the interested reader to pertinent sources in the primary literature and thus further augment the eminent usefulness of the text.

Anybody wanting to learn more about heterogenized, single-site polyolefin catalysts and the prospects and challenges these materials offer could hardly do better than to read this thoroughly comprehensive and up-to-date book on the subject.

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JA805981T

10.1021/ja805981t