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BOOK REVIEWS

Encyclopedia of Electrochemistry, Volume 7b: Inorganic Electrochemistry. Edited by Fritz Scholz (Universität Greifswald, Germany) and Christopher J. Pickett (John Innes Centre, Norwich, UK). Series Edited by Alan J. Bard (University of Texas) and Martin Stratmann (Max-Planck-Institut, Germany). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim. 2006. x + 527 pp. $440.00. ISBN 3-527-31700-7.

This volume constitutes the second part of the *Encyclopedia of Electrochemistry* series in inorganic electrochemistry. The application of electrochemical methods to problems of interest in inorganic chemistry is a rapidly expanding field, and as such, this is a timely contribution. The introduction to basic electrochemical concepts as applied to inorganic chemistry was addressed in the first volume and is not reviewed here. However, this introduction is necessary to appreciate Volume 7b fully, which should be beneficial to those already familiar with this material or used in conjunction with Volume 7a.

The focus of this volume is the electrochemistry of transition metals. The opening chapters primarily emphasize structural motifs of clusters, wherein molybdenum−sulfur systems and related metallo-sulfur clusters as well as oxometalates and polycyanometalates are discussed. The emphasis is on the inorganic structure−property relationships related to redox reactions, and illustrative examples are provided. The authors discuss the ability of electrochemical methods to control electron-transfer reactions and of inorganic systems to provide widely varied redox potentials and the chemical reactions that succeed these electrochemical processes. The relationship of inorganic clusters to biochemical systems for catalysis of redox reactions is highlighted. The chapter on polyoxometalates provides many nice examples of electrochemical data that should give the reader a real appreciation for the complexity of interpreting such data. This work is often presented as cyclic voltammograms instead of tables of data, illustrating the value of such figures and the frequent inadequacy of tabular data. The electrochemical mechanisms invoked in inorganic systems are often very complicated, and thus the illustrative examples provided for this class of polyoxometalates are useful. A shorter section on polycyanometalates completes this section of the volume.

The remaining sections are organized according to the identity of the transition metal being investigated and include chapters on zinc, cadmium, lead, gold, silver, mercury, copper, and the actinides. This is an unusual variation in the grouping of topics but one that works well for this volume. The section on Zn, Cd, and Pb represents a historically important area of inorganic chemistry that has industrial applications in electroplating, metal deposition, corrosion, and batteries and has significance in such areas as surface science, nanoscale characterization, and intermetallic materials. The section on Au, Ag, and Hg focuses on surface characterization, adsorption, and the widely studied self-assembled monolayers of thiols and related systems. Single-crystal electrodes and the interaction and analysis of a variety of analytes and schemes for modifying surfaces are emphasized, and the historically important application of Hg electrodes to aqueous studies, including adsorption on such electrodes, is covered. Far fewer examples of data are given in this section.

The final sections cover Cu electrochemistry and the electrochemical properties of actinides. The first highlights the study of Cu electrodes, electroplating and more historical areas, as well as Cu complex electrochemistry. Large tables of data with redox potentials based on ligand design provide insight into the tuning of redox potentials for Cu complexes, an important topic in many areas of metal complex electrochemistry and redox reactions. The second section is a summary of the electrochemistry of actinides with particular focus on electroplating and the differences seen in aqueous vs nonaqueous electrochemistry and metal speciation.

The book displays some of the characteristic bias of other multiauthor volumes wherein the coverage in a single chapter generally reflects the authors' own interests. However, Volume 7b is a nice complement to 7a, and together they provide a much-needed introduction to modern inorganic electrochemistry as well as information about important historical developments. The up-to-date and detailed literature citations should give the reader ample opportunity to explore concepts in more detail.

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JA069798Y
10.1021/ja069798y

Esterification of Polysaccharides. By Thomas Heinze, Tim Liebert, and Andreas Koschella (Friedrich-Schiller-Universität Jena, Germany). Springer: Berlin, Heidelberg, New York. 2006. xvi + 232 pp. $64.95. ISBN 3-540-32103-9.

It is inevitable that the increasing cost of petroleum-based products will result in polymers based on renewable resources becoming competitive. Among the naturally occurring polymers, polysaccharides are by far the most abundant, and a wide range of structural and functional types can be readily obtained. Formation of esters is a long-established approach to obtain polysaccharide derivatives with modified properties. New methods of preparation and, particularly, new methods for the evaluation of the results of modified procedures have resulted in a resurgence in interest in these materials. Applications of these new methods along with brief outlines of earlier work are summarized in this concise, easily readable book.

After an introduction, the book starts with a chapter on the structures and sources of the commonly available polysaccharides, followed by an up-to-date summary of the methods available for structural analysis of unmodified polysaccharides, ranging from colorimetric methods to 2D and solid-state NMR spectroscopy. The next chapter outlines established procedures

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for the preparation of carboxylic esters and is followed by the longest chapter in the book on new approaches for the preparation of carboxylic acid esters. This last chapter contains a section on the effects of newer media, such as aprotic solvents, salt mixtures, and ionic liquids, on reaction selectivity and efficiency. Applications of a variety of new procedures for esterification, many arising from new methods developed for peptide coupling, such as in situ activation of carboxylic acids, are also described. Two chapters on methods for the direct preparation of sulfonic acid esters and inorganic acid esters are followed by a chapter on methods to analyze the structures of partially esterified polysaccharides. The next chapter outlines techniques for selective deacylation and for protecting primary hydroxyls before esterification. New applications of esterified polysaccharides are then described, including sections on materials for selective separation and for membranes, as well as materials with biological activity, and others. The final chapter contains 65 experimental methods, mostly on the preparation of particular esters, but it also includes procedures for the solubilization of cellulose, the degradation of chitosan, and the determination of the degree of substitution. Surprisingly, no discussion of the commercially important xanthates is included. The book comes with a supplementary disk that contains FTIR, ^{1}H NMR, and ^{13}C NMR spectra of the polysaccharides that are readily available in pure form and of a number of their esters, some with differing degrees of substitution.

The book is clearly written, but there are some typographical errors. The audience for this book will include polymer chemists and those interested in polysaccharides. Although the subject of the book has a long history, many of the references date from within the past 5 years. For the reader, it provides a concise summary of the structures and methods of characterization for the important polysaccharides and their esters as well as an outline of the advances that are being made in the preparation of new materials. The low cost and clear presentation will encourage personal purchase.

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JA069801D

10.1021/ja069801d

HPLC Made to Measure: A Practical Handbook for Optimization. Edited by Stavros Kromidas (Saarbrucken, Germany). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2006. xxxiv + 754 pp. $150.00. ISBN 3-527-31377-X.

This book is a very complete guide to HPLC optimization for what I would call the intermediate- or somewhat advanced-level chromatographer. Beginners can learn much from the thorough coverage also but may get bogged down in the book's 700-plus pages of detailed coverage. Kromidas, the editor and author of many of its chapters, has skillfully woven the various sections of the book together into a logical and practical volume that should find broad acceptance and use among practitioners in the field. The idea that this is a "Handbook" is probably a little misleading since the depth of coverage would preclude one from flipping it open at the bench to look up a parameter in order to conduct an HPLC run. A more likely scenario would be to spend a day or two poring over particular sections to determine the best way to solve a difficult separation problem. Optimization of an analytical method is something that scientists may work toward as necessity dictates, but actually operating at "the optimum" is a luxury few can afford. The preliminary sections of Chapter 1 take analysts through some very pragmatic reasoning to determine exactly what they want or hope to achieve in the optimization process. The book is quite heavy with theoretical information that frames the practical details and puts them completely into context. Although it is unlikely to be adopted as a course textbook, this book will find a host of users in a variety of fields who have the goal of improving their separations with regard to speed, resolution, throughput, sensitivity, or even cost. A valuable text by any estimation, I would recommend it highly for hands-on users or managers directing a group of chromatographers toward more efficient and effective HPLC separations.

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JA0698073

10.1021/ja0698073

Metal Catalyzed Cascade Reactions. Topics in Organometallic Chemistry, 19. Edited by T. J. J. Müller (Universität Heidelberg). Springer: Berlin, Heidelberg, New York. 2006. x + 340 pp. $199.00. ISBN 3-540-32958-7.

This volume, the latest in the *Topics in Organometallic Chemistry* series, features reports from eight research groups active in cascade catalysis. It does not focus on particular reactions or periodic groups but rather offers a broad overview of methods to generate multiple bonds in a given organic molecule with stereo- and regiocontrol. Its mechanistic focus complements a recent review of cascade reactions in the context of total synthesis (*Angew. Chem., Int. Ed.* **2006**, *45*, 7134−7186).

With the important and ubiquitous role of modern Pd-catalysis, it is not surprising that it dominates most, but not all, of this treatise. Negishi et al. and von Zezschwitz and de Meijere, respectively, begin with two chapters focused on Pd-catalyzed C−C bond forming reactions, in which domino Heck reactions, acylpalladium ring closures, formation of aromatic rings, and cyclizations with different combinations of molecular unsaturations are all addressed. The next three chapters build on the Pd-cascade motif, with Patil and Yamamoto reporting on π-allylpalladium additions, Balme et al. on Michael additions involving Pd nucleophiles, and finally Müller on sequential Pd-catalyzed reactions, such as allylic substitution−Suzuki chemistry to form small carbocycles. Müller begins his chapter by briefly differentiating between the terms "cascade", "domino", and "tandem", thereby guiding the reader accustomed to using them interchangeably. Deviation from primarily Pd-focused reactions begins with Pérez-Castells's chapter on cascade Pauson−Khand chemistry, which is necessarily heavy on Co-based methods, followed by a chapter by Malacria and co-workers on polycyclic natural products using a broad selection of metal catalysts and finally by a chapter by Bruneau et al. on Ru-mediated metathesis/hydrogenation or concomitant cyclizations—numerous combinations of cascade/tandem processes are reported here—in addition to organometallic/enzymatic tandem processes.

The material in most chapters is reasonably fresh: ~40% of the references are from the past 5 years. Some minor issues we have with the book include the repetition of numerous subsections in chapters written by different authors and inconsistent grammar or phrasing that causes some chapters to be confusing. The inconsistent appearance of chemical structures also detracts from the book as a whole.

In summary, this book offers several new reactions and approaches to complex molecular synthesis for those considering cascade or domino reactions. Despite several minor quibbles, it effectively accomplishes the goal of compiling several complementary reviews on this burgeoning field. The complexity and number of metal-mediated elementary steps renders this book best suited to the student of synthesis already familiar with organometallic chemistry.

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JA069819O

10.1021/ja069819o

Recent Advances in Actinide Science. Edited by Rebeca Alvarez, Nicholas D. Bryan, and Iain May (The University of Manchester, UK). Royal Society of Chemistry: Cambridge. 2006. XXVI + 810 pp. $249.00. ISBN 0-85404-678-X.

This book is based on the proceedings of the eighth Actinide Conference, “Actinides 2005”, held at the University of Manchester, UK in July 2005. There are 231 contributions, which are organized into six sections: Analysis, the Environment and Biotransformations; Coordination and Organometallic Chemistry; Heavy Elements; Nuclear Fuels, Materials and Waste Forms; Separation and Solution Chemistry; and Spectroscopy and Magnetism. A subject index completes the book.

JA069839Q

10.1021/ja069839q

The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals, 14th ed. Edited by Maryadele J. O’Neil (Editor), Patricia E. Heckelman (Senior Associate Editor), Cherie B. Koch (Associate Editor), and Kristin J. Roman (Assistant Editor). Merck and Co., Inc.: Whitehouse Station, NJ. 2006. 2564 pp. $125.00. ISBN 0-911910-00-X.

This edition of the famous Merck Index provides comprehensive information on significant chemicals, drugs, and biological substances and contains 10,200 short monographs, 32 supplemental tables, and 450 organic name reactions. The typical monograph includes the chemical, common, and generic names of the titled substance, its molecular formula and weight, its CAS Registry number, a description of its activity and importance as well as of its commercial and therapeutic uses, its physical properties, physical data and toxicity, a chemical structure depiction, and up-to-date U.S. regulatory information and literature references. This edition also features a companion CD and more than 700 new or completely revised monographs. Both the supplemental tables and the organic name reactions have also been updated and revised.

JA069838Y

10.1021/ja069838y

Surface-Enhanced Raman Scattering: Physics and Applications. Edited by Katrin Kneipp (Harvard University Medical School, Boston), Martin Moskovits (University of California, Santa Barbara), and Harald Kneipp (Harvard University Medical School). Springer: Berlin, Heidelberg, New York. 2006. xviii + 464 pp. $219.00. ISBN 3-540-33566-8.

Variants of Raman spectroscopy are underused in modern research, but there has been a recent resurgence of interest in them. This collection of 24 articles reveals the major reasons for this renaissance. The editors include both scientists who were critical to the initial understanding of the phenomenon of surface-enhanced Raman scattering (SERS) and scientists who present a fresh perspective on the subject. Likewise, the references include those to the original precedent-setting manuscripts as well as to the extensive recent literature. The articles largely address four critical areas in SERS: the enhancement mechanisms, tip-enhanced Raman scattering, single molecule SERS, and biological applications of SERS.

The six articles that make up the first quarter of this volume provide an explanation of the electromagnetic (EM) enhancement mechanism that is largely responsible for the SERS phenomenon. Upon excitation of the collective oscillation of the conduction electrons in a nanostructured noble metal substrate, EM fields of large magnitude are generated at the nanostructure surface; any molecule within the substantial EM field experiences an increased induced dipole and, thus, generates enhanced Raman scattering. These articles explain the physics behind these EM fields and the resulting enhancement factors as compared to unenhanced Raman scattering. There is a particularly thorough treatment of relevant theoretical simulations, demonstrating that collections of nanoparticles yield significantly higher enhancement factors than individual nanoparticles and even suggesting an optimal array structure to achieve a maximal enhancement factor. The articles also address the generalizable nature of surface-enhanced phenomena by touching on the surface-enhanced mechanisms for infrared absorption, fluorescence, and resonance Raman, as well as nonlinear SERS phenomena. Although only one article addresses the second mechanism, the “chemical” or “electronic” enhancement mechanism, this article is extensive and written by Otto and Futamata, two scientists most expert on this topic. Although SERS experiments classically are performed on Ag, Au, and Cu substrates, Tian and co-workers summarize recent work using transition metal substrates instead. This work is somewhat controversial, but it is of great interest to the SERS community and was discussed vigorously at the 2006 International Conference on Raman Spectroscopy.

Much recent effort in the area of SERS research has been devoted to expanding the type of samples that can be probed with this technique. Classic SERS requires that the molecule of interest reside on or within 10 nm of a noble metal nanostructured surface; however, this is not an ideal constraint. Tip-enhanced Raman scattering circumvents this limitation by bringing a noble metal nanostructure to the sample in a manner similar to noncontact atomic force microscopy. The articles in the next section of this book address the details of tip fabrication, instrumentation challenges, and the tip-enhanced variant of coherent anti-Stokes Raman scattering.

When discovered in 1928, Raman scattering was among the least efficient spectroscopic processes, with scattering cross sections of $\sim 10^{-29}$ cm^2. High-quality SERS experiments yield effective scattering cross sections that are 8 orders of magnitude greater although 6 orders of magnitude smaller than fluorescence cross sections. In 1997, two research groups demonstrated that it is possible to detect single molecules using SERS, yielding enhancement factors of $10^{14}-10^{15}$ over unenhanced Raman scattering. While the mechanism responsible for single-molecule sensitivity is not firmly established, the SERS community generally concurs that this large enhancement occurs when a molecule is positioned between two closely spaced nanostructures. This volume includes several contributions that address the single molecule SERS phenomenon, including how the experiments are done, how the enhancement factors are determined, and the dynamic information that becomes available.

The final third of this volume focuses on the quantitative application of the SERS signal transduction mechanism in bio- and chemosensing motifs. The targets detected include such timely topics as glucose, insulin, ebola, DNA, antigen/antibody pairs, micro-organisms, and chemical warfare agents. These articles are up-to-date and exciting to read and provide ample evidence of the great potential of SERS as an analytical tool for the chemical community while at the same time justifying the intense work that has gone into understanding and optimizing the SERS phenomenon.

Overall, this volume does a good job of balancing fundamental studies with applied ones and new contributors with the experts. It will be a valuable resource for anyone interested in understanding the scope of the SERS field and the great potential of this technique.

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JA069825K

10.1021/ja069835k