Book Reviews

Solid State NMR III: Organic Matter. Edited by B. Blümich (Aachen, FRG). Springer-Verlag: New York. 1994. 213 pp. $43.00. ISBN 0-387-57399-2.

This book is edited by a guest editor, B. Blümich, and is published as a third book of the series reviewing solid state NMR. It is Volume 32 of *NMR, Basic Principles and Progress*, Edited by P. Diehl, E. Fluck, H. Günther, R. Kosfeld, and J. Seelig, and consists of four review articles on applications of modern solid state NMR techniques to the study of organic polymeric materials.

In spite of the experimental difficulties, solid state NMR techniques are necessary to obtain NMR-based chemical information on samples that are insoluble in inert NMR solvents or to study effects that are characteristic of the solid state. Nuclear spins in solids are often subject to large orientation-dependent interactions which obscure structural information contained in isotropic chemical shifts and intramolecular spin coupling constants. Such large anisotropic interactions provide not only a challenge experimentally but also an opportunity to study orientation-dependent properties of solid samples. On the one hand, the chemical structural information requires a high-resolution solid state NMR technique to obtain isotropic chemical shift values, and sometimes spin coupling constants. These large anisotropic interactions make the spin relaxation processes sensitively dependent on spin motions. Thus the wide-line solid state NMR technique is uniquely applicable to the study of molecular motions including very slow motions in solids. This book with the combined total of 818 cited references covers both aspects of these solid state NMR techniques which are advancing rapidly. The book is not long enough to comprehensively cover these vast subject areas, but rather contains brief descriptions of the most common and recently developed techniques. Therefore, this is a good reference book and should be available in a science library or in a group that contemplates using the NMR techniques to elucidate molecular properties of solid samples. The book consists of the four review articles that are briefly discussed below.

The first article by G. L. Hoatson and R. L. Vold is entitled ^{2}H-NMR Spectroscopy of Solids and Liquid Crystals (67 pp). The ^{2}H-NMR (DMR for deuteron NMR) is a technique particularly sensitive to the orientational motion of the molecules whose motional correlation times fall in the wide range between 10^{-12} and 100 s covering fast segmental molecular motions as well as some slow motions in solid state samples. (Note that Table 1 erroneously lists inverse correlation times under the correlation time column.) The description of the technique starting from the anisotropic Hamiltonian terms of quadrupolar, dipolar, and chemical shift interactions is simple and easy to follow. Many of the nonconventional DMR methods are briefly discussed. These include cross polarization and zero field NQR, as well as two-dimensional DMR, double quantum DMR, dynamic angle spinning, and double rotation (DOR). Two-dimensional DECODER and VACSY techniques are also discussed. Techniques that give information on molecular dynamics include two-dimensional exchange spectra and a selective inversion recovery method, as well as multiple pulse quadrupolar echo sequence (MQE). Tables of quadrupole coupling constants for methyl, methylene, and aromatic deuterons are provided. Examples include applications of DMR to the analyses of liquid crystal solutions.

The second article by D. Michel and F. Engelke is entitled Cross-Polarization, Relaxation Times and Spin-Diffusion in Rotating Solids (56 pp). Cross-polarization (CP) is the single most important development in enabling high-resolution solid state NMR possible. This article is well organized in explaining how CP works and possible difficulties arising from the Hartman−Hahn mismatch. The thermodynamic model using the lattice and various spin temperature concept is simple to follow. Effects of various spin relaxation processes on the CP efficiency are discussed also. Discussion of effects of sample spinning and newer attempts in minimizing the effect of an imperfect Hartman−Hahn match are included.

The third article by W. S. Veeman and W. E. J. R. Maas is entitled Solid-State NMR Techniques for the Study of Polymer-Polymer Miscibility (35 pp). When experiments are properly designed, NMR should be a valuable technique in studying molecular structures and dynamics of polymer blends and polymer interfaces. This article discusses various NMR methods used for this purpose. The description of these methods are divided into sections of short-range techniques and of long-range techniques that include spin diffusion and dynamic nuclear polarization discussions. These techniques are applied specifically to samples consisting of poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) (PVF_2) blends.

The fourth article by H. W. Beckham and H. W. Siess is entitled Two-Dimensional (2D) Exchange NMR Spectroscopy (46 pp). Although two-dimensional NMR techniques are widely used with liquid samples in solution, they are relative new in solid state applications. The 2D NMR should be particularly useful in studies of slow molecular dynamics in solid samples. Such dynamic processes include spin diffusion, macromolecular motion including chain diffusion, and reorientational motion of molecules below their glass transition temperatures or melting points. These techniques are illustrated with many well-chosen examples involving different polymer samples.

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Advances in Detailed Reaction Mechanisms. Volume 4. Synthetically Useful Reactions. Edited by James M. Coxon (University of Canterbury, New Zealand). JAI Press: Connecticut. 1995. ix + 222 pp. $97.50. ISBN 1-55938-787-4.

This is Volume 4 of the series *Advances in Detailed Reaction Mechanisms*. The present volume presents synthetically useful reactions and is divided into six chapters. The first four chapters can be classified as into the area of organometallics, and the last two chapters are of bioorganic relevance.

The first chapter, by James Rigby and Chris Krueger, deals with mechanisms of synthetically useful cycloaddition reactions mediated by transition metals. This chapter is concise and to the point. It essentially presents a series of typical transformations for each type of cycloaddition followed by a mechanistic discussion. The chapter has a good mix of recent and old examples, and the mechanistic discussions are up to date.

Chapter 2, authored by Yoshinao Tamaru, deals with the chemistry of functionalized organozincs. Eight different reactions of functionalized organozincs with electrophiles are presented and examined. An interesting section on the preparation of organozincs, with useful hints and useful to those who wish to prepare these derivatives for the first time, is also presented. In addition, some catalytic cycles of Pd(O) are discussed, as well as the role of hexamethylphosphoramide (HMPA) in three-component connections. I consider this chapter a must for those who wish to enter the organozinc area, since it clears the fog of the more basic problems normally encountered in these reactions.

Chapter 3, by Naoki Komatsu and Sakae Uemura, discusses the synthetic and mechanistic aspects of asymmetric reactions of organoselenium compounds, in particular, synthesis of chiral selenoxides, asymmetric [2,3]sigmatropic rearrangements, asymmetric selenoxide elimination, and asymmetric selenylation. This chapter starts with a good and short historical background on asymmetric selenoxides. A very good mechanistic discussion on asymmetric selenoxide eliminations is also presented.

Chapter 4, authored by Paul Woodgate, takes as the main theme the application of metal−arene complexes in organic synthesis. It starts with a good introduction, almost textbook, and then concentrates into two particular synthetic problems, i.e., the synthesis of 18-nor-5α-androsta-8,11,13-triene analogues and the functionalization of dibenzo[b,e][1,4]dioxins, important biological compounds. This makes Chapter 4 specific to these two families of compounds.

Chapter 5, by Lyndsay Main, is an abrupt change of topic and discusses mechanisms of cyclization reactions of 2′-hydroxychalcone derivatives, intermediates in the synthesis and biosynthesis of flavonoid compounds. Despite the fact that Chapter 5 is important and quite comprehensive, it is a dramatic change in focus, probably of little appeal to those interested in the first four chapters. It probably could have been better to have stayed focused in the mechanisms of organometallic transformations throughout the book.

The last chapter in the book, by Anna de Raadt, Christian Ekhart, and Arnold Stütz, takes a look at some methods of metal-ion-catalyzed chemical and enzymatic isomerization of free sugars. Chapter 6 should appeal to a broad audience including carbohydrate chemists. The section on metal-ion-catalyzed chemical isomerization of free sugars stays in focus with the organometallic theme developed throughout the first four chapters of this book.

In general, this is a good book to have. It will be particularly welcomed by organometallic chemists.

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Electric Field Applications in Chromatography, Industrial & Chemical Processes. Edited by Takao Tsuda (Nagoya Institute of Technology, Japan). VCH: New York. 1995. xvi + 311 pp. $190.00. ISBN 3-527-28687-X.

Seeking to appeal to the wider community of scientists and engineers and to stimulate discussion between these groups Takao Tsuda has assembled a collection of chapters on topics including separation science, the fabrication of ceramic pieces, dewatering, and rheology and others. The unifying theme throughout this book is the application of electric fields, either for the purposes of solvent displacement (electroosmosis) or for the orientation and/or migration of solutes (electrophoresis). Following a thought-provoking preface by Stellan Hjerten and a helpful introduction and summary chapter are 14 chapters divided into three sections: (1) electrochromatography, (2) applications of electric field for industrial processes, and (3) the application of electric fields for concentration, immunoassay, and molecular orientation. The editor is the author or coauthor for six chapters as well as the introduction and summary section. The remaining eight chapters are the work of 10 other authors or coauthors. References in many chapters appear current through 1994, although this is not consistent for all chapters.

The strength of this book is in the area of electrochromatography, a separation method combining elements of chromatography and electrophoresis introduced by the editor in the early 1980s. The six chapters devoted to this topic are focused on column electrochromatography due to the reliability of column chromatographic methods relative to paper or thin layer chromatographic methods. The material is presented in detail and should serve as a good introduction to this collection of methods as well as a primer for researchers interested in using electrochromatography for the separation of ions, small molecules, and biomolecular analytes. Interlaced throughout this section are a large number of high-quality and informative figures, pictures, and illustrations clearly depicting the underlying principles and the impressive efficiencies which can be attained using electric fields both with and without pressurized or gravity-driven solvent flow. Also interlaced throughout these chapters are numerous references to capillary electrophoretic methods which have become very important during the past 15 years. However, less informed readers would have benefited if early in the first section or in the introduction the distinctions between capillary electrophoresis and electrochromatography were clearly outlined.

The second section of this book is comprised of chapters highlighting some new industrial applications in which electric fields are employed. This diverse collection of topics include electroosmotic dewatering, the electrophoretic formation of ceramic materials, solvent extraction, the resolution of water/oil emulsions, and the development and application of new electroreological fluids. The applied nature of the materials presented in this section is very different from the remainder of the book as is the scale of many of the experiments described within. The inclusion of this section is to stimulate discussion between applied and basic research chemists and to alert the later group to industrial-scale problems seeking new and creative solutions.

The last section of this book returns to a more basic chemical focus with three chapters on dynamic electroconcentration, electric field induced coagulation for immunoassay enhancement, and organized photochemistry. The last of these three chapters is very wide-ranging, discussing photochemical reactions of chromophores interacting with micelles, reverse micelles, vesicles, mono- and multilayered membranes, and inorganic solid surfaces. As in the second section, the diversity of topics serves to illustrate the importance of electric fields in analytical and physical chemistry and the ease with which electric fields can be effectively used.

Overall this book presents a diverse mix of topics from which many readers will find only a few of immediate interest. As this is a book to span many different disciplines the true measure of the success is whether or not the reader's attention is drawn more broadly through the wide range of topics. On this point the editor has made a good attempt. One major reservation I have with regard to this book is that the price will likely keep this book off the shelves of individuals, with libraries as the primary customers. But, if the editor and publisher desire to reach a wider audience of scinetists and engineers, perhaps this is where this book belongs.

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Industrial Inorganic Chemicals: Production and Uses. Edited by R. Thompson. The Royal Society of Chemistry: Cambridge, U.K. 1995. xviii + 408 pp. £39.50. ISBN 0-85404-514-7.

It is encouraging to see the commitment of the editor and authors to improved descriptions of the industrial base utilized to manufacture inorganic chemicals. This book builds on the 1977 Royal Society of Chemistry Publication 31 and a Royal Society Proceedings on Speciality Inorganic Chemicals (SP40) in 1980. The current book objectives are to describe new processes and significant changes in this industry based on markets, environment, and other forces. The editor's strategy is to utilize experts for the separate chapters on inorganic chemicals.

The material in each chapter shares much content with the Kirk−Othmer series and the books by Ullrich; possibly this is just needed to be complete in the current book. However, the Thompson book is much more affordable and targeted than these other large series and is a good recommendation for the reader.

The chapter on environmental aspects is an excellent contribution. The author showed the critical link between concepts of zero tolerance for cadmium, arsenic, and lead and the viability of markets for bulk chemicals. This link is based on natural co-location of such elements and hence the requirement to produce cadmium, arsenic, and lead if desirable metals (often sought as replacements) such as zinc, nickel, and copper are to be manufactured. There is a good concept developed of product recycle as a future secondary materials source.

The chapter on chemical engineering has a good material balance around sodium hydroxide production. The authors' goals for educating chemists regarding production level chemistry are in part met by this chapter.

The remaining chapters cover 11 major inorganic chemicals, mostly those manufactured in bulk quantities (generally greater than 100 000 tonnes per year). The environmental chapter stresses the regulatory requirements for an integrated view of all chemical losses from a manufacturing facility. In the U.K. this is the Integrated Pollution Control concept with emphasis on process efficiency and best available technology. Unfortunately the authors missed a major opportunity to provide even basic industrial estimates of chemical losses from these important industrial processes. This is especially disappointing since the Integrated Pollution Control reports are available. The experts would have been in the best position to write such evaluations, directly from the processes, new and old. The authors do not even provide the most relevant references that would have quantified such process losses. Also there was no description of less frequently occuring wastes from process shutdown, cleaning, maintenance, etc. Also estimates of process equipment lifetimes would have been a valuable contribution.

The areas of thorough coverage in the inorganic chemical chapters are primarily the diversity of products manufactured in closely related facilities such as sulfur products, industrial gases, or boron compounds. Most chapters give a good representation of the manufacturing processes, the markets, and the uses. Some chapters were able to provide costs for the inorganic chemicals products.

In summary, this book has good introductory chapters. Excellent future thinking on the factors affecting the industrial inorganic chemical plants is provided. Moderate quality process descriptions (mostly qualitative) are given, compared to the real need to understand the nature of this industry. The authors have been successful in showing examples

to the chemists of the differences between university education and industrial applications.

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Hydride Generation Atomic Absorption Spectrometry. By Jiri Dedina (Academy of Sciences, Czech Republic) and Dimiter L. Tsalev (University of Sofia, Bulgaria). Wiley: U.K. 1995. xviii + 526 pp. $84.95. ISBN 0-471-95364-4.

The need for improvements in the quantification of elements present in trace concentrations has provided the driving force in analytical research and development for many years. The criteria against which developments may be assessed are varied but include accuracy, precision, sensitivity, detection limit, throughput, and cost. These parameters are not independent and cannot all be maximized simultaneously. It may be considered that a considerable part of modern analytical chemistry research arises from the optimization required to devise methods that meet increasingly stringent values of these performance parameters.

Since the early days of flame atomic absorption and flame atomic emission spectrometries, strenous efforts have been made by almost every researcher in the area of atomic spectrometry to overcome some of the limitations of the flame atomizer and the associated sample introduction system of pneumatic nebulizer (which produces a fine aerosol of sample solution) and spray chamber (which fractionates the droplets so that only those below the critical size of a few micrometers are transported to the flame).

Such sample introduction and atomizer systems convert analyte species in solution to free atoms, capable of absorbing or emitting radiation, by a series of complex physical and chemical processes. Regardless of the element and matrix, the precursors of atoms in the flame are gaseous molecules, usually either the oxide or the halide or some mixed oxide species. As the processes which give rise to the precursors are inefficient (at best 10%), and many oxides are poorly dissociated or reduced by combustion flames, a considerable improvement in atom number density could be achieved if the analyte could be converted to a molecular derivative in solution which was sufficiently volatile and stable to be separated from the solution and transported to an atomizer with high efficiency. This technique of chemical vapor generation has been used for sample introduction in analytical atomic spectrometry for several decades, and it is the use of the derivatization as hydrides that forms the subject matter of Dedina and Tsalev's book. As many of the elements which may be determined by hydride generation (HG) are poorly atomized in the combustion flames typically used in flame spectrometry (air−acetylene and nitrous oxide−acetylene) and as these flames also strongly absorb at the wavelengths used, alternate designs of atomizer are employed in these hydride generation procedures. Devices based on a heated quartz tube are the most widely used, but the atomization efficiency of such atomizers has proved difficult to control from day to day and even the mechanism of atomization has remained unclear for a long time.

Thus, in HG atomic absorption spectrometry, as is the case for many other areas of analytical chemistry, practice runs well ahead of theory and the relevant literature consists of two kinds of papers; those concerned with providing a better understanding of the underlying chemistry and those concerned with obtaining better performance in some real analytical situation. As atomic spectrometry techniques other than atomic absorption also benefit form the use of HG, there is a considerable companion literature concerned with atomic emission, atomic fluorescence, and more recently with plasma source mass spectrometry. Nearly 1600 references from the relevant literature relating to all of these techniques form the basis of this book.

The authors have done a wonderful job in presenting the information contained in this body of original papers. Both authors are extremely well-known, active researchers in this area of analytical atomic spectrometry, and the series editor and publishers are to be congratulated on persuading them to write this long-overdue definitive account of the literature. The text moves smoothly from tutorial introductory material concerned with basic principles of atom formation and spatial distribution in tubular atomizers to atomization mechanisms and then a very important chapter concerned with the mechanisms of the various types of interference that are encountered. The first part of the book concludes with a general overview of hydride generation and a brief survey of other volatile metal compounds that have been used as atom precursors. An appendix to this part deals with some basic atomic absorption theory as it relates to the magnitude of the absorption coefficient.

The second part of the text is devoted to methodology and analytical applications and consists of 10 chapters dealing with the elements antimony, arsenic, bismuth, germanium, indium, lead, selenium, tellurium, thallium, and tin. Each chapter is organized along the same lines and consists of sections on general characteristics, optimization of instrumental and chemical parameters, control of interferences, preconcentration and separation techniques, speciation studies, and the analysis of real samples. This latter section is further subdivided into sections concerned with environmental samples, agricultural samples, food and beverages, biological and clinical samples, geochemical samples, and metallurgical and industrial samples.

The final section of the book is devoted to several appendices which provide lists for several methods of classification of the references. Thus there are lists for technique and analyte (containing no less than 20 different categories), speciation, sample matrix (divided into hydride generation and other volatile derivatives), and finally a list of other relevant key words.

It is tempting to classify the bulk of this text as merely a reference source, but there are occasional critical comments by the authors (for example, the literature relating to the on-line reduction of arsenate to arsenite is summarized as "many of the reported procedures are difficult to repeat"). I am somewhat disappointed that there are not more such evaluative comments, which would give this text the value-added component that could be realized when the authors really are authoritative figures in the field. I would certainly have liked to see some comments on the thorny problem of optimization. Many of the literature reports in this area are characterized by an uncritical use of the single-cycle univariate search procedure or present results of experiments for which it is difficult to discern what optimization procedure has been used. One of the reasons for this, I suspect, is that the day to day reproducibility of the atomization efficiency of quartz tube atomizers is poor and thus long-term optimization studies are doomed. As all commercial quartz tube devices are externally heated tube systems, I would really have liked to have found some definitive comments about procedures for reconditioning quartz tube atomizers, tube lifetime, how to deal with day to day fluctuations in sensitivity, and so on. Another area of obscurity in this field in the mechanism of the transfer of the hydride from the liquid solution to the gas phase (the so-called stripping process) and the role of the design of the gas−liquid separator. It is likely that in continuous flow and flow injection modes of operation (which are increasingly being used compared with batch generation procedures) that stripping and separation are temporally and spatially separated. Again I would have liked to have seen some comments relating to this topic.

A knowledgeable reader will appreciate that there is a body of literature of comparable size to that on which this book is based relating to the determination of mercury as "cold vapor", i.e. the mercury(II) in solution is converted to mercury(0) and stripped by some suitable method prior to transport into a cell for detection by atomic absorption at (or near) room temperature. This topic is not mentioned, even in the chapter on other volatile compounds. It is not clear what the cut-off date for the references is, but it appears that the literature includes a substantial part of the material published in 1992. Thus there is no mention of the recent reports of the determination of cadmium by hydride generation nor of the finding that cadmium, like mercury, can exist as free atoms at room temperature long enough to give a useful atomic absorption signal.

These adverse comments are really only minor, and my strong recommendation is that, if you are involved in the determination of any of the elements listed above by hydride generation, then buy this book. At just under $85, the cost is negligible in comparison with those involved in performing such analyses in the laboratory.

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