

Additions and Corrections

Arriving at an Experimental Estimate of the Intrinsic Activation Barrier of Olefin Insertion into the Zr–C Bond of an Active Metallocene Ziegler Catalyst [*J. Am. Chem. Soc.* **1998**, *120*, 5643–5652]. JÖRN KARL, MARC DAHLMANN, GERHARD ERKER,* AND KLAUS BERGANDER

Page 5649: Equations 9 and 10 should read as follows:

$$\frac{dM_{zA}}{dt} = -\frac{M_{zA} - M_{0A}}{T_{1A}} + \frac{M_{zAinv}}{\tau_{Ainv}} - \frac{M_{zA}}{\tau_A} \quad (9)$$

$$\frac{1}{\tau_A} = k_A = \frac{M_{0A} - M_{zA\infty}}{M_{zA\infty}T_{1A}} \quad (10)$$

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Book Reviews

High-Performance Capillary Electrophoresis: Theory, Techniques, and Applications. Edited by Morteza G. Khaledi (North Carolina State University). Wiley Press: New York. 1998. 1014 pp. \$150.00. ISBN 0-471-14851-2.

Although still considered the “new kid on the block”, high-performance capillary electrophoresis (HPCE) has developed into a sophisticated and truly multidisciplinary technology for the separation and analysis of chemical compounds. The staggering rate of appearance of journal articles recounting new HPCE developments and applications and the technique’s widespread use by scientists in many different fields certainly warrant the publication of this extremely comprehensive treatise on the subject. Khaledi’s compendium of 31 review chapters carefully arranged into five cohesive sections, which constitutes the 146th volume in the J. D. Winefordner (Ed.) Chemical Analysis monograph series on analytical chemistry and its applications, has more than competently accomplished its humbly-stated objective of providing “...an updated comprehensive reference on various aspects of the technique...intended for beginners as well as experienced users.”

Part I is subtitled Theory and Modes of HPCE. This eight-chapter section serves as an excellent primer on the subject, and could almost stand alone as material for an advanced seminar or course to indoctrinate newcomers to the field. In addition to including chapters that provide a general introduction to the technique and to the underlying theory, this section includes chapters on capillary gel electrophoresis, capillary isoelectric focusing, capillary isotachopheresis, and one of the newest HPCE modes, capillary electrochromatography. Due to the editor’s own interest and expertise in the area of micellar electrokinetic chromatography, there are two chapters to be found on this topic in the introductory section of the book.

Part II, Detection Systems in HPCE, is composed of four chapters that clearly document the most commonly encountered and powerful detection methods currently in practice, including chapters about detectors based on light, electrochemical detection, indirect detection, and mass spectrometric detection. In light of the book’s already tremendous size, it seems only reasonable that some less commonly encountered but still noteworthy detection methods, such as refractive index, thermo-optical, radionucleotide, Raman, nuclear magnetic resonance, and single-cell biosensor methods, are given only brief mention in the first chapter of this section.

Six chapters covering various Operational Aspects and Special Techniques in HPCE constitute Part III of this monograph. Two relatively new and particularly exciting areas in HPCE, namely two-dimensional separations and microfabricated devices for separations in HPCE, are well-documented here, along with chapters on sample introduction and stacking, coated capillaries, nonaqueous capillary electrophoresis, and method validation. Collectively, these chapters

serve as a “do-it-yourself” manual for the technique, giving practical advice and useful alternatives for the many instances when simple free solution capillary zone electrophoresis is not sufficient for the task at hand. These chapters are a testament to the ingenuity and fortitude of many researchers in the area who have built HPCE into much more than a simple offshoot of its slab gel predecessor.

The 10 chapters in Part IV, Applications of HPCE, justifiably account for almost one-third of the pages of this book. A listing of the chapter titles reveals the more familiar players, such as—Peptide Analysis by Capillary Electrophoresis, Capillary Electrophoresis of Proteins, Capillary Electrophoresis of Carbohydrates, DNA Sequencing by Multiplexed Capillary Electrophoresis, Chiral Separations by Capillary Electrophoresis, Capillary Electrophoresis of Inorganic Ions, and The Analysis of Pharmaceuticals by Capillary Electrophoresis, along with some less conventional but equally exciting applications, such as On-Line Immunoaffinity Capillary Electrophoresis, Microbioanalysis Using On-Line Microreactors-Capillary Electrophoresis Systems, and Electro-pheretically Mediated Microanalysis. Although some of these chapters understandably include their own versions of materials covered in depth in previous sections of the book, this overlap is kept to a minimum and so does not affect the readability or importance of these later chapters.

The fifth and final section of this book is unique in its isolation of Physicochemical Studies in their own section. Composed of just three chapters (Affinity CE, Determination of Physicochemical Parameters, and Applications of Micellar Electrokinetic Chromatography in Quantitative Structure—Activity Relationship Studies), this section will undoubtedly be important to advanced practitioners and specialists in the field. Decoupling of this material from earlier sections, however, ensures that the more casual reader need not be challenged by its content.

It is no small feat to produce a monograph that is truly up-to-date in a field as rapidly changing as high performance capillary electrophoresis, yet Khaledi has managed to do exactly that. Numerous chapters include sections on recent developments, future directions, or even addenda that provide the most recent possible updates occurring after submission of chapters by individual authors but prior to final publication of the monograph. References to the scientific literature included in most chapters are as recent as 1997 or 1998. Other particularly noteworthy aspects of this book are its extensive index, allowing for casual use of the book for quick reference; its refreshing lack of duplication within chapters written by different authors; and the appearance of work by many of the most well-respected and experienced CE researchers today. Khaledi’s High Performance Capillary Electrophoresis is definitely a worthwhile addition to both private

and institutional CE collections, and can be used as both the starting point and ending point for all HPCE-related questions.

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GC/MS: A Practical User's Guide. By Christopher McMaster and Marvin McMaster (University of Missouri, St. Louis). Wiley: New York. 1998. 167 pp. \$59.95. ISBN 0-471-24826-6.

According to the authors, the purpose of the book is to provide a textbook on practical GC/MS that includes "modern systems and application." The book contains three sections, each composed of four to five chapters.

In the past decade, due to the advent of electrospray ionization, the significance of GC/MS as a versatile tool for analysis of complex mixtures has been overshadowed by HPLC/MS. However, GC/MS is still widely used in both industry and academia with new instrumentation, techniques, and applications still being developed. Field portable GC/MSs for on-site analysis, fast GC/MS using time-of-flight mass spectrometers that detect components of complex mixtures in seconds rather than minutes, sensitive (subfemtomole) derivatization techniques with fast reaction times (a few seconds) for analysis of nonvolatile compounds, and solid phase extraction in conjunction with GC/MS are a few examples. To my complete dismay, however, I found no "modern systems or application." While the book provides some useful information on troubleshooting GC, and on GC/MS analysis of volatile and semivolatile organic compounds, the bulk of material presented is outdated and contains numerous shortcomings, errors, and incorrect information (as listed below) which preclude it from being used a textbook.

(1) Many important and fundamental subjects in GC/MS are not covered. These include: modern derivatization techniques for analysis of non-volatile compounds, different types of injection techniques, types of stationary phases used in modern GC capillary columns, ionization mechanisms of some of the commonly used ionization techniques in GC/MS (such as chemical ionization), and theory of operation of mass analyzers usually used in GC/MS. In addition, important concepts in quantitative GC/MS such as sensitivity, detection limits, and linear dynamic range are omitted.

(2) Only two GC/MS applications (US EPA protocols for volatile and semivolatile organic analyses) are presented. These applications, while useful, are definitely not modern. Applications of GC/MS to the analysis of nonvolatile compounds such as biological samples are ignored.

(3) Outdated technology is presented throughout. A packed column is chosen to explain the effects of GC variables on separation. An outdated mass spectrometer (HP 5972, in which changing from electron ionization to chemical ionization required breaking the vacuum and installing a new source, a 4-h procedure) is used to explain the effect of varying the ion-source components on tuning the MS.

(4) The book contains numerous errors and wrong information, some of which are listed below. CI is introduced as "chemically induced ionization" (p 9), and protonated molecules formed under CI are called "molecular ions" (p 47), rather than protonated molecules. MALDI (matrix-assisted laser desorption and ionization) is listed as "maser-assisted..." (p 134). Page 51 lists the wrong molecular weights for nitrogen and oxygen. Page 32 states that the most common GC column stationary phase is "methyl silicone", though the substance is actually dimethyl polysiloxane. The separation of ions of different m/z by quadrupole mass analyzers is stated to be achieved by "sweeping the frequency of the applied RF signal" (p 9), while it is usually achieved by ramping the applied DC voltage/RF amplitude at a fixed RF frequency. Descriptions of alternative techniques such as HPLC/MS, CZE/MS, and SCF/MS are found to be trivial and useless. The explanation of the operation of quadrupole ion trap mass spectrometers bears several mistakes. For example, page 121 states, "uncharged material from the GC stream enters the trap around the ring electrode, it is ionized, collides with other molecules, fragments, and is stored in stable orbits between the electrodes," incorrectly implying electrons in the ion trap only ionize the molecules, and the fragmentation observed is only due to collision with neutral molecules. In fact, interaction of energetic electrons with neutral molecules both ionizes and fragments

them. Page 122 states, "once in the ion trap, the sample is ionized with 70 V electrons", which is even inconsistent with the author's own schematic (Figure 12.3, p 124). In the commercial ion traps referenced by the author (Finnigan MAT ITD), the kinetic energy of the electrons arises from several sources including the gate electrode (+180 V) and the phase and the amplitude of the RF voltage inside the ion trap when electrons interact with neutrals. According to the Finnigan MAT's ion trap manual, the kinetic energy of the electrons is in the range of 50–80 eV. Another example of incorrect information is the mechanism of ionization that is provided for electrospray ionization (ESI). For example, on page 140 it is stated that in ESI, "the effluent is forced through a capillary out into the source vacuum through a coronal electron discharge operating at 25 kV. The discharge is produced off the sharp tip of a very fine needle. Electrons released at the needle tip form a cloud through which mobile phase stream from a capillary tube explodes into the evacuated interface. These electrons knock other electrons off the sample, producing molecular ions." First, for most ESI sources, the effluent is sprayed at atmospheric pressure, and not "into the source vacuum". Second, the electrospray needle usually operates below the onset of corona discharge and there is no needle operating at 25 kV. Third, the mechanism of electrospray ionization is not as explained above. Briefly, in ESI charged droplets are formed at the tip of the capillary (usually at 2–5 kV), solvent evaporation reduces the size and, therefore, increases the electric field at the surface of these droplets. Once the charge repulsion overcomes the surface tension, droplets disintegrate. Sequential fission leads ultimately to gas-phase ions. Incorrect information is also given for ion spray (p-142) and MALDI (p-134).

(5) Another important shortcoming of this book is its lack of literature citing and up-to-date references. The authors in several locations write, "the literature has reported..." yet no literature is cited. The only place that the authors provide any additional literature is in Appendix D under "GC/MS Selected Reading List" where they list four journals and six books dating from 1971 to 1994, all together ignoring several comprehensive journal reviews and books about GC/MS and other subjects presented in their book.

Overall, this is a scientifically poorly written and poorly edited text, whose errors, mistakes, and shortcomings outweigh its usefulness.

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Chemistry and Biology of Serpins. Edited by Frank C. Church, Dennis D. Cunningham, David Ginsburg, Maureen Hoffman, Stuart R. Stone, and Douglas M. Tollefsen. Plenum Press: New York. 1997. xvii + 358 pp. \$95.00. ISBN 0-306-45698-2.

Serine protease inhibitors, or serpins, represent a large, diverse family of proteins that have evolved over millions of years. Serpins are found in viruses, plants, invertebrates, and vertebrates. Serine proteases and their regulatory serpins are involved in numerous intracellular and extracellular biological processes, including metabolic pathways; cell growth and differentiation; tissue remodeling; inflammatory processes; coagulation, hemostasis, and thrombosis; tumorigenesis and metastasis; and apoptosis. Dozens of reviews presenting aspects of serpins appeared in the literature between 1990 and 1996, the few years preceding the convening of the International Symposium on the Chemistry and Biology of Serpins, held April 1996, at the University of North Carolina at Chapel Hill School of Medicine. These reviews tended to be short, dealing with the mechanism of action of serpins, structural characteristics, or details of a single serpin species. The timing was ripe for a meeting of experts in the field to bring disparate aspects of serpins to the attention of colleagues and ultimately, in the form of this book, to the scientific community. Overall, the book successfully achieved this goal.

The book is, apparently, the compilation of 22 primary presentations at the meeting in a textual format, along with the abstracts of nearly 100 poster presentations. The greatest value of this volume is that it brings together minireviews of specific serpins that function in a broad spectrum of biological activities. The chapters are categorized, sometimes a little arbitrarily, under seven headings: Introduction; Coagulation; Neurobiology and Cancer; Fibrinolysis; Development and Re-

production; Inflammation; and Non-Inhibitor Serpins. There is virtually no cross-referencing of information from one chapter to the next.

The introductory chapters either are without figures or contain unlabeled figures that do not facilitate an understanding of the serpin structure/mode of action for a nonexpert. Individuals who are new to the field would do well to begin their readings with Chapters 10, by D. A. Lawrence, and 20, by R. Carrell, D. Lomas, P. Stein, and J. Whisstock. Both chapters present an excellent overview, with good to well-defined figures, of the rather unique mechanism by which these suicide inhibitors function and their structural modifications during the inhibitory process. The Lawrence chapter uses the plasminogen activator inhibitor-1 as a model serpin, while the Carrell et al. chapter defines structural/functional features common to several serpins with comparisons to natural mutants with altered functions. The references are current and should help both novice and expert.

There are four excellent chapters in the coagulation section dealing with serpins that modulate the serine protease, thrombin. They are clearly presented, most with well-labeled figures, and with good to extensive references that should service workers in the field at all levels. Three of the chapters present structural/functional aspects of specific serpins. In the extensively referenced chapter by I. Bjork and S. T. Olson, the details and mechanism of action of antithrombin in the absence and presence of heparin are well presented. D. M. Tollefsen follows with a discussion of the thrombin inhibitor, heparin cofactor II, and the potential role of dermatan sulfate. S. T. Cooper and F. C. Church present how thrombin may be further regulated by protein C inhibitor. The final chapter in this section, by D. L. Becker, J. C. Fredenburgh, A. R. Stafford, and J. I. Weitz, presents, with both background and data, how thrombin escapes some regulation when complexed with fibrin.

Each chapter in the neurobiology and cancer section discusses very distinct aspects of proteases/protease inhibitors. D. D. Cunningham and F. M. Donovan present data showing that thrombin, most widely recognized as a modulator of coagulation and platelet activation, also regulates neurons and astrocytes. The mitogenic properties of thrombin are regulated by the serpin, protease nexin-1. This clearly presented paper is more a presentation of research data than a review of the field. The chapter on Maspin, a purported tumor-suppressing serpin, is also primarily a research paper with highly speculative conclusions. The final chapter in this section cursorily presents the complex nature of protease/protease inhibitor control of tumor progression. The focus on serpins is brief and underdeveloped.

The section on fibrinolysis contains four papers addressing different aspects of the plasminogen activator enzymes/inhibitors. The first paper, by D. A. Lawrence, has been referred to above as a good presentation of a serpin mechanism. The second paper is primarily an overview of the research, by E. L. Madison, on the structure/function of a tissue type plasminogen activator with no mention of its serpin regulator. A very brief and limited overview of plasminogen activator inhibitor type-2 follows. The final chapter in the section, by D. J. Eitzmann and D. Ginsburg, gives an excellent review of the plasminogen activator inhibitors along with the presentation of data to support an understanding of the biology of these inhibitors. The information in the preceding three chapters would have been better served if this section was presented first.

Two of the three chapters in the section on development and reproduction deal with serpins in nonhuman systems. One concentrates on the sheep uterine serpin, uterine milk protein. Large quantities of this protein accumulate in pregnancy, and while the sequence and some

structural properties have been deduced, the exact function remains to be clarified. The section on insect serpins by M. R. Kanost and H. Jiang is a very interesting presentation of a young field of serpin research that may ultimately give clues to the evolution of these molecules and could yield clinical/laboratory tools that may regulate proteases in unique ways. The last chapter of the section is an excellent discussion of proteases/serpins in the male genital tract. A brief but very clear overview with extensive references is presented of proteases associated with the fertilization of the ovum and their regulatory serpins. Information is also presented about one of the major seminal fluid proteases, prostate-specific antigen (PSA). Physiological and pathological aspects of PSA are presented along with the clinical value of measured serum levels.

G. S. Salvesen introduces a different family of proteases, the caspases, or cysteine-dependent aspartate-specific proteases, in the first of four chapters in the inflammation section. A link between caspases, apoptosis, and serpins is presented. Exciting potentials for future studies emerges from the author's speculations based upon current knowledge. The next chapter in this section, by A. E. Davis III, presents a wonderful review of the C1 inhibitor, whose major function is in the modulation of host defense and vascular permeability. A listing of references encompassing the 1950s to the present affords the reader a good historical perspective of the field. The structure/function of C1 is reinforced by the analysis of naturally occurring mutations. The myxoma virus is a member of the poxvirus family that encodes for a serpin called SERP-1, as described in the next well-presented chapter by P. Nashs, A. Lucas, and G. McFadden. Rabbits are the normal host of the myxoma virus, with the virally induced pathogenesis exacerbated by SERP-1 interfering with the host inflammatory response. Some exciting potential clinical uses of SERP-1 are proposed. The final excellent chapter in this section, by R. Carrell et al., has already been discussed above.

The final two chapters are concerned with non-inhibitor serpins. The chapter by S. P. Becerra is essentially an overview of her research. It demonstrates the neurotrophic activity and properties of the serpin-like protein, pigment epithelium-derived factor (PEDF), which was initially isolated from conditioned media from human fetal retinal pigment epithelial cells. In the final brief chapter, E. H. Ball, N. Jain, and B. D. Sanwal present some data about the non-inhibitory serpin, colligin, found in the endoplasmic reticulum. It appears that colligin binds to procollagen and may serve a chaperone-like role in the complex posttranslational processing of collagen.

None of the chapters in this book are extensive reviews of a specific serpin, and the quality of the presentations is a little spotty, although, in general, they are quite good. The strength of the book is its coverage of numerous species within the serpin family, along with current (up to the time of the meeting) and historical references. This book gives the reader an outstanding appreciation not only of where this relatively young important field has come from, but also of where the field is heading. This is the most recent publication on serpins listed in the Library of Congress, a list that includes only two other books. As such, this book is a valuable resource for established researchers looking for background information on serpins. It is also an excellent compendium of information for workers new to the field.

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