Additions and Corrections

***cis*-Hydroxyplatination of Diethyl Maleate: Modeling the Intermediates in a Catalytic Alkene-Hydration Cycle with Organoplatinum(II)−Hydroxo Complexes** [*J. Am. Chem. Soc.* **1995**, *117*, 8335−8340]. MARTIN A. BENNETT,* HONG JIN, SIHAI LI, LOUIS M. RENDINA, AND ANTHONY C. WILLIS

The designation of *cis*-(*R**,*R**)-PtMe{CH(CO_2Me)CH(OH)(CO_2Me)}(PPh_3)$_2$ (**6**) as having a *threo*-configuration is incorrect.

Page 8339, column 2, paragraph 2, line 5 should read as follows: If the Pt−OH group undergoes *syn* addition to dimethyl maleate, the product will be the *erythro* (*R**,*R**)- or (*S**,*S**)-complex, whereas *anti* addition will give the *threo* isomer (Figure 2). The X-ray structure of **6** shows that the PtCH(CO_2Me)CH(OH)CO_2Me) group has the (*R**,*R**)-configuration, i.e. it is priority reflective,[31] corresponding to the *erythro* complex.

The labels *threo* and *erythro* in Figure 2 should be interchanged. The incorrect nomenclature used originally does not affect the assignment of relative absolute configuration or the conclusion about the stereochemistry of addition of the Pt−OH group to dimethyl maleate.

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Book Reviews *

Particle-Induced X-Ray Emission Spectrometry (PIXE). Edited by Sven A. E. Johansson (Sweden), John L. Campbell (Canada), and Klas G. Malmqvist (Sweden). Wiley & Sons: New York. 1995. xxiii + 451 pp. $79.95. ISBN 0-471-58944-6.

Particle-Induced X-Ray Emission Spectrometry (PIXE) is Volume 133 in *Chemical Analysis: A Series of Monographs on Analytical Chemistry and Its Applications*. The book consists of eight chapters. One of the authors, Dr. Johansson, is considered the father of PIXE, whose acryonym is widely known as Proton-Induced X-Ray Emission. Unfortunately, Dr. Johansson passed away before completing the book, and the other coauthors have dedicated the book to his memory. Dr. Johansson and Dr. Campbell coauthored the book *PIXE: A Novel Technique for Elemental Analysis* in 1988 that was also published by Wiley and Sons. The book reviewed here contains figures, tables, equations, and material that were identical to those published in the 1988 book.

Chapter 1 traces the history of PIXE and shows why the technique was developed. In addition, basic principles of the technique are described with simple but informative diagrams of how the X-rays are produced. Minimum detection limits are described as a function of the energy of the proton beam and a "typical" PIXE spectrum is shown to illustrate the multielemental nature of PIXE.

Chapter 2 describes PIXE instrumentation, X-ray detectors, fundamentals, and quantification and is written by Dr. John L. Campbell, whose expertise is on PIXE computer code development for elemental quantification. The chapter begins with details on PIXE instrumentation and shows a diagram of a typical PIXE beam-line. Numerous diagrams and equations illustrate the basic principles PIXE. The chapter is supplemented with a tabulation of elemental contamination of various polymer films used for sample support ofr PIXE. This table is very valuable because it allows the PIXE practitioner to choose the best backing material for sample analysis. Although PIXE is a complicated technique involving a knowledge of physics, Dr. Campbell does a skillful job of explaining the technique without losing the reader.

Section 2.5 of Chapter 2 is one of the most important sections of the book. It describes in detail how elemental quantification is obtained. The section is detailed with complex equations and concepts needed to do quantitative PIXE analysis without using standards. Particular differences between quantification of thin targets and thick targets are also described. Chapter 2 concludes with an in-depth discussion on limit of detection (LOD), accuracy, and precision of PIXE analysis. Data from the analysis of "real" samples and standard reference materials (SRMs) show that PIXE has reasonable accuracy and precision.

Chapter 3 describes in detail micro-PIXE. This chapter seemed out of place for this book and focused on scanning transmission ion microscopy (STIM). This chapter could have been included in the micro-PIXE applications of Chapter 4. The author seemed to vary all over the place with different topics. The chapter also included Rutherford backscatter spectrometry (RBS). The chapter does however contain some unique applications of micro-PIXE with numerous images of various biological and environmental samples that highlight an otherwise boring chapter.

Chapter 4, Biological and Medical Applications, was the most exciting chapter in the book. It was written by Dr. Malmqvist, who has extensive expertise with the analysis of many different types of samples. Here the focus is on biological and medical applications. The chapter begins by discussing the importance of sample collection and preparation. Detailed procedures for reducing sample matrixes to that of the elements of interest are described. The references in this chapter describe several applications of PIXE in medicine. Several results are reported for samples that have not been previously analyzed. Several SRMs were analyzed and results reported for several elements that are not certified in the SRMs. These uncertified elements can be used by other analytical techniques for comparison of accuracy.

The chapter describes methods for sample preconcentrations and methods to eliminate matrix elements (Na, K, Ca, and Mg) from biological fluids (urine and blood). There were several demonstrations on the uniqueness of micro-PIXE in the analysis of single biological cells. The study was done to determine the affects of *cis*-platin (a cancer drug) on Pt distribution in a cell. Several "elemental maps" of different cells were shown. The chapter also demonstrates the use of PIXE for multielemental analysis of samples such as bone, skin, hair, and teeth. The chapter concluded with applications in botany and zoology. Finally, this chapter is intended not only for the PIXE practitioner but for all those interested in all aspects of biological sample analyses. The chapter is rich in references and in elemental concentration values

*Unsigned book reviews are by the Book Review Editor.

for several biological samples whose elemental concentrations have not been reported previously.

Chapter 5, Compositional Analysis of Atmospheric Aerosols, was written by Dr. Thomas Cahill, who has extensive use of PIXE in aerosol analyses. When PIXE was first developed, one first application of this new technique was that in air pollution studies. This chapter describes in detail the process needed to collect and analyze atmospheric aerosols and samples. X-ray spectra of aerosols are shown that allow the reader to observe the multielemental nature of PIXE. The chapter also has a section on the interpretation of aerosol data using multivariate statistics. The combination of PIXE with proton elastic scattering analysis (PESA) showed that total mass analysis of the aerosols collected on the filters can be determined. With this information, it was demonstrated that different molecules such as H_2SO_4 could be detected in aerosols.

Geologists will greatly appreciate Chapter 6, Applications in Earth Sciences. Dr. Campbell again describes the details of PIXE for multielemental analysis of geological samples. The chapter is highlighted with information on the analysis of single grains and crystallites in minerals. The chapter also has a section on multielemental analysis of extraterrestrial samples and applications in mineralogy, petrology, and fluid inclusions.

Museum curators, art collectors, and artifact hunters will appreciate Chapter 7, Applications in Art and Archaeology. Again, Dr. Malmqvist provides an excellent description of the applications of PIXE. Here again we see the uniqueness of PIXE for multielemental and nondestructive analysis of precious samples. One application cited was the use of PIXE to analyze individual letters of the Gutenberg Bible. Additional artifacts such as pottery, jewelry, and alloys were analyzed to determine origin and authenticity.

PIXE has had an extensive hand in the analysis of archaeological samples. Because PIXE is multielemental, provenance studies of potsherds could easily be determined. There were detailed descriptions on the analysis of "paper-like" materials such as postage samples to determine authenticity. Additional applications using proton-induced γ emission (PIGE) and PIXE for the characterization of pigments in oil paintings were also shown.

The final chapter of the book, Chapter 8, Comparison With Other Methods: Future Prospects, puts PIXE in prospective with other current established analytical methods such as NAA, AA, ICPAES, XRF, and ICPMS. Comparison and advantages over X-ray fluorescence (XRF) were demonstrated using specific samples as examples. What was pleasant about this chapter is that it told the truth about the total picture about the advantages and disadvantages of PIXE as compared to XRF. One important factor brought in this chapter was the cost of PIXE system as compared to an XRF system.

In conclusion, PIXE is a book well worth having in your library. It is not only recommended for the PIXE practitioner, but other analytical practitioners will find the book handy. It contains excellent and current references (to 1993), tables on concentrations of elements in various samples, and detailed information on sample handling. The only missing topic in the book is a section on where to purchase the various components (accelerator, detectors, and PIXE code) of a PIXE system and the cost of maintaining a PIXE facility. This information would assist those contemplating constructing a PIXE system.

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Pesticide Properties in the Environment. By Arthur G. Hornsby (University of Florida), R. Don Wauchope (USDA-ARS), and Albert E. Herner (USDA-ARS). Springer: New York. 1995. viii + 227 pp. $49.00. ISBN 0-387-94353-6.

This book and software package, which includes a $3^1/_2$ in. DOS diskette, provides a database of hundreds of pesticides, including theircommon, commercial, and scientific names, their chemical formulas, and their environmental properties, including water solubility, field half-life, sorption coefficient, and vapor pressure. All data are cited to original references and are presented both in printed form and as an electronic database.

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Electron Transfer and Radical Processes in Transition-Metal Chemistry. By Didier Astruc (University of Bordeaux). VCH: New York. 1995. xxi + 630 pp. $140.00. ISBN 1-56081-642-2.

Electron transfer of transition-metal complexes in solution has evolved from two historical perspectives. In the earliest (inorganic) phase, electron transfer was delineated in terms of outer-sphere and inner-sphere mechanisms in wholly inorganic complexes, as originally conceived by H. Taube (who incidentally wrote the forward to this book). The ensuing theoretical constructs by Marcus, Hush, Levich and others, have focused on predicting the interchange kinetics between a neighboring pair of stable (valence) species, *e.g.*, Fe^{II}/Fe^{III}, Cr^{III}/Cr^{II}, etc. Further chemical changes attendant upon electron transfer were (consequently) minimal and not of prime consideration. In the later (organometallic) phase, electron transfer has been largely delineated as a pre-equilibrium interchange between a stable 18-electron (18e) precursor and its metastable radical identified as either a 17e or 19e transient species following oxidation or reduction (and/or ligand loss). As a result, its various followup reactions have introduced a critical new dimension to the electron-transfer phenomenon. Owing to the explosive development of organometallic chemistry over the past 20 years, a rich menu of interesting chemical transformations are now associated with electron transfer in organotransition-metal complexes.

Although electron-transfer in inorganic systems has been extensively monographed, there is no comprehensive treatment of organometallic electron transfer. This timely account by Astruc is divided into a pair of more or less equal parts that nicely blend the two historical developments. Thus Part I presents a survey of the concepts and theories of electron transfer (Chapter 1), the mechanistic utilization of transient electrochemical techniques (Chapter 2), the structural elucidation of transition-metal (transient 17e and 19e) radicals and paramagnetic complexes/clusters (Chapter 3), and the application of electron/charge-transfer transitions to the design of electronic devices such as molecular wires, switches, sensors, etc. (Chapter 4). The broad coverage of electron transfer in Chapter 1 is from the traditional inorganic perspective—the outer- and inner-sphere mechanistic distinction (especially in mixed valence complexes and with bridging ligands), the physicochemical nomenclature of adiabatic/nonadiabatic, electron-transfer reorganization energy, etc., all having pedagogical utility in this electron-transfer primer of use to organometallic chemists. In Chapter 2, the electrochemical measurement of electron transfer is presented largely in the context of a fast followup chemical step (EC mechanism). An extensive set of interesting examples follows (~70 pages), but the coverage is not systematic—being weighted to metallocenes and *bis*(arene) and sandwich compounds. Thus, other comprehensive reviews of organometallic electrochemistry (*e.g.*, Geiger, Connelly, etc.) will be desirable supplements if the book is to be used for class presentation. The electrochemical discussion in terms of the followup reactions gives the chapter a satisfying clarity, and the chemically sophisticated reader can pick up the requisite electrochemical methodology (*e.g.*, Bard and Faulkner). Chapter 3 on organometallic radicals is a fairly comprehensive coverage of primarily low-spin complexes with strong field ligands (*i.e.*, organometallic types), particularly as reactive intermediates. The chapter contains the most references and is thus a very useful reference source. Chapter 4 on molecular electronics is devoted to the potential use of transition-metal complexes in practical devices for energy and information storage, nonlinear optics, etc. (J. M. Lehn's works are extensively cited). Astruc sees a connection between electron transfer, transition-metal radicals, and molecular electronics, but the global picture is still at the rudimentary (exploratory) stage. Overall, Part I reveals how Astruc is enlarging his original ideas on "electron reservoirs" into a more composite picture of electron transfer/organometallic radicals/molecular devices. It is a large undertaking and, thus, understandable if the execution does suffer somewhat in that the concepts do not always carry over well from chapter to chapter. For example, how do inner/outer-sphere mechanisms in Chapter 1 relate to the electrochemical processes in Chapter 2? Furthermore, what is the relationship between optical electron transfer in Chapter 1 and nonlinear optics in Chapter 4?

Part II represents the "heart" of the book, it being devoted to the various chemical transformations that can follow electron transfer. Chapter 5 covers stoichiometric reactions of transition-metal radicals—the generation, interconversion, coupling, atom abstraction, oxidative addition, and migratory insertion of Cp/arene-metal, alkylmetal, hydridometal types, etc. A characteristic feature (and strength) of this book is that extensive data and key arguments of important literature

papers are summarized in more depth than is typical in monographs. Chapter 6 on chain reactions (both electron-transfer and atom-transfer) is valuable since the subject has not been previously reviewed. The final chapter on the chemical applications of redox catalysis (electrochemical, photochemical, and biochemical) includes organic oxidations, reductive coupling, and activation of carbon dioxide, dioxygen, carbon monoxide, dinitrogen, etc. The sheer volume of novel chemistry included in Part II is impressive, and the sensible organization of the materials make for interesting and informative reading.

Astruc's book brings together for the first time the tremendous amount of electron-transfer chemistry that has evolved from organometallic systems. This, coupled with timely connections to electron-transfer theories and electrochemistry, makes for a valuable compendium to enlarge the scope and thinking of practicing organometallic chemists—with both provocative reading and as a useful reference. [Indeed, the application of the same focus, (*i.e.*, recognition of the seminal importance of following processes) would considerably advance the discussion of organic electron-transfer mechanisms.] The book could also serve as a textbook for a special-topics course in an inorganic/organic curriculum since the writing style is straightforward, direct, and easy to follow. The literature coverage is extensive and generally well chosen, and most of the classic papers are appropriately covered. The coverage is very up to date.

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Advances in Biochemical Engineering/Biotechnology. Volume 53. Downstream Processing Biosurfactants/Carotenoids. Edited by A. Fiechter (Institut Biotechnolgie, Eidgenossche Technische Hochschule) Springer: New York. 1996. ix + 190 pp. $135.0.00. ISBN 3-540-59308-X.

This volume is the latest addition to the ongoing series of *Advances in Biochemical Engineering/Biotechnology* that has become essential reading for biochemical engineers since the publication of the first volume in 1971. The contents of this volume reflect the diversity of biochemical engineering and biotechnology. The editor has enticed articles of topics from the relatively mature study of liquid chromatography to the emerging field of gas phase biosensors contributed by area experts. The five articles are Gas Phase Biosensors by Bárzana; Chromatography in Downstream Processing of Biotechnological Products by Freitag and Horváth; Extractive Bioconversion of Lactic Acid by Roychoudhury, Srivastava, and Sahai; Production of Rhamnolipid Biosurfactants by Ochsner, Hembach, and Fiechter; and Microbial Carotenoids by Johnson and Schroeder. Each article provides sufficient background so that researchers who are not experts in each specific area can profit from it.

The article by Bárzana clearly presented the need to develop gas phase biosensors by their advantages over aqueous phase biosensors, especially for the on-site monitoring of environment pollutants. The research interest in biosensors has been focused on the development of biosensors for analytes in aqueous phase for the past two decades. Nevertheless, recent advances in enzymatic applications under anhydrous conditions have stimulated the development of gas phase biosensors. This review paper describes the principles underlining the operation and phenomena dominating the performance of gas phase biosensors. It definitely will contribute to the development of this emerging technology.

The cost for downstream processing of biotechnological products may account for up to more than 90% of the overall production costs. Development of effective separation/purification processes has therefore been one of the most important topics in the field of biochemical engineering. Among the many processes for the recovery and purification of biomolecules, chromatographic techniques have been proven to be most effective for obtaining bioproducts with high purity. The article by Freitag and Horváth addresses concisely the fundamentals, design, optimization, and scale-up of chromatographic separation processes. It is an attractive article to researchers from both biological science and biochemical engineering communities. The article can only be further improved with the incorporation of more recent references and examples, especially on the recovery and purification of non-proteinous bioproducts.

The large scale production of some microbial metabolites such as ethanol and lactic acid is sometimes hampered by the inhibitory nature of the products to the growth of the producing microorganisms. To solve this problem, it is necessary to remove the excess inhibitory products from the growth culture. The article by Roychoudhury et al. discusses various approaches for the continuous extraction of lactic acid from the fermentation broth during the course of microbial growth. Continuous extraction not only leads to higher product yield but also facilitates the recovery of lactic acid. Although most of the references cited are relatively out-of-date, the approaches presented in this article can be adopted for the production of other bioproducts that are inhibitory to the producing hosts and/or easily degraded in the fermentation culture.

Biosurfactants with high surface activity are promising substitutes for synthetic surfactants because of their diversity and biodegradability. Although at present the use of biosurfactants in chemical industries is not generally competitive because of their higher production costs, increasing concern over the environment is beginning to weigh the economic balance in favor of microbially produced compounds. The topic should therefore be of wide interest to the general biochemical engineering community. The overview by Ochsner et al. systematically outlines the physiology, biochemistry, and genetics of rhamnolipid synthesis and investigates process engineering aspect of biosurfactant production. This article not only provides valuable information about rhamnolipid production but also reveals the systematic approach which the development of biotechnology products, especially biosurfactants, should follow.

The demand for carotenoids is expected to increase due to their potential in preventing chronic diseases in humans. Although simple carotenoids are currently produced by advanced chemical synthesis processes, microorganisms may become major sources for more complex carotenoids. The article by Johnson and Schroeder successfully addresses every aspect of microbial carotenoid biotechnology, including carotenoid structures and phylogeny, functions and properties of carotenoids, and biosynthesis and genetics of carotenoids production by microorganisms. It is an excellent review paper with well-documented references, which is extremely helpful for researchers who are interested in carotenoids.

Collectively these articles, which incorporate not only a comprehensive introduction to the past and present efforts but also approaches that will inspire further development in this area, should be of interests to diverse groups of biotechnologists. Overall this volume meets the high standards of excellence of *Advances in Biochemical Engineering/Biotechnology* series and is a valuable addition to this distinguished series.

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