The ^{18}O isotope effect at the phenolic oxygen for the alkaline hydrolysis of compound II, which possesses a leaving group with a higher pK_a (8.56), is 2.75% normal. Again, this is consistent with a transition state where there is significant cleavage of the bond to the leaving group and is considerably larger than that observed for paraoxon hydrolysis. This difference is rationalized on the basis of the resonance capabilities of *p*-nitrophenol where *p*-nitrophenol exists in a quinoid resonance form under the conditions of the experiment. As such, there is considerable double-bond character to the phenolic oxygen, thus compensating, qualitatively, for the bond breaking between the phosphorus and the phenolic oxygen. A similar comparison of the calculated and observed equilibrium ^{18}O isotope effect for the deprotonation of *p*-nitrophenol has been reported.[14] The secondary ^{18}O isotope effect for this compound is 1.025 and indicates a change in bond order to the phosphoryl oxygen leading to the transition state. The transition state is later relative to the effect observed with paraoxon and corresponds to a bond order of about 1.38. This is anticipated since 4-hydroxybenzamide is a somewhat poorer leaving group compared to *p*-nitrophenol.

The primary and secondary ^{18}O isotope effects measured for the enzymatic hydrolysis of paraoxon (I) are 1.0020 and 1.0021, respectively. These isotope effects are much smaller than those observed for nonenzymatic hydrolysis and are consistent with previous data which indicate that the chemical step is not totally rate limiting.[5] However, with the nonsticky substrate II, the primary and secondary ^{18}O isotope effects are 1.036 and 1.018, respectively. These values are similar to those for alkaline hydrolysis and therefore support the chemical step as totally rate limiting in the enzymatic hydrolysis of this substrate. At present, a complete interpretation of the measured isotope effects for the enzymatic mechanism is limited since the potential participation of active-site residues and a required zinc atom is unknown. Experiments are underway that will better define the role of the zinc atom in catalysis.

Acknowledgment. This work was supported by the Army Research Office (DAALO3-90-G-0045), Robert A. Welch Foundation (A-840), and the National Institutes of Health (GM18938).

(14) Rosenberg, S. Ph.D Dissertation, Department of Chemistry, University of California, Berkeley, CA.
(15) Hermes, J. D.; Morrical, S. W.; O'Leary, M. H.; Cleland, W. W. *Biochemistry* **1984**, *23*, 5479.

*Book Reviews**

The Chemistry of Functional Groups. Supplement A; The Chemistry of Double-Bonded Functional Groups. Parts 1 and 2. Edited by Saul Patai (The Hebrew University, Jerusalem). John Wiley & Sons: New York and Chichester. Part 1: xiv + 797 pp. $360.00. ISBN 0-471-91719-2. Part 2: xiv + 893 pp. $430.00 ISBN 0-471-92493-8.

These two volumes are paginated continuously, and the index, covering both, is only in Part 2, although the volumes can apparently be bought separately. Their content consists of one group of chapters devoted to subjects not treated before in this series and another group of "integrative" chapters, in which a "unified and comparative treatment of several double-bonded functional groups together" is presented. The nine chapters in the latter category make up most of Part 1. They cover views on homopolar bond structure, mass spectrometry, NMR, photoelectron spectroscopy, directing and activating effects, biochemical perspectives on double bondes, intramolecular 1,3-dipolar cycloadditions, the eve reaction, and radiation chemistry. The former category includes asymmetric induction in additions to C,O and C,N double bonds, electrophilic additions to C,C double bonds, mechanisms of base-catalyzed 1,2-eliminations, carbonylation of main-group organometalic compounds, rearrangements involving allenes, 1,1-diarylalkenes, fulvenes, the thiocarbonyl group, and cycloadditions of enones.

The literature coverage is "up to about the end of 1987 and in some cases even to the middle of 1988", and the bibliographies are extensive. As is characteristic of the series, there are good tables of data and an abundance of carefully drawn structure formulas.

The writing is essentially critical, insofar as the subject matter allows, and the contributors have successfully avoided presenting a mere recitation of facts. The valuable content is made accessible by a 22-page index of professional quality, augmented by a true author index of impressive magnitude.

This is an important work of basic reference, which should be acquired by all libraries serving organic chemists.

Biotechnology. A Textbook of Industrial Microbiology. Second Edition. By Wulf Crueger and Anneliese Crueger (Bayer AG). Sinauer: Sunderland. 1990. 357 pp. $44.95. ISBN 0-87893-131-7.

This book is an English translation of a German textbook by W. Crueger and A. Crueger. Professor T. D. Brock again did a commendable job in the translation. When one goes over the English version, there is no hint or evidence whatsoever that this is a translated version. When this reviewer took Industrial Microbiology under Professor A. L. Demain at MIT, he saved most of the lecture notes and articles given by Dr. Demain. This book literally replaces all these old notes and more. The book is divided into two parts. Chapters 1–6 discuss the traditional practices by the industrial microbiologists and bioengineers. The materials are condensed but they are usually a good start for students and scientists with minimal exposure to this area. The amount of information on fermentation (Chapter 5) and product recovery (Chapter 6) may be useful as background materials for many biologists and chemists. Bioengineers on the other hand, may find them too little and too sterile of any practical use. Again, it is a good start for non-engineering scientists and students unfamiliar with these subject matters. There are sufficient references at the back of each chapter for them to explore further any interesting topics.

Chapters 7–20 are divided based on product classifications. It is striking that there is no separate chapter on recent cell culture derived or recombinant DNA technology derived bioproducts such as TPA, HGH, r-insulin, etc. Only traditional fermentation derived products are emphasized with minimal discussion on the impact of recombinant technology on those products. Waste treatment is treated in Chapter 17 with little discussion on toxic waste remediation.

Overall, the book is well-written and well-organized. The new edition did include some information of recombinant DNA techniques on strain selection and new product development. But, these additions did not seem to distinguish the new edition from the first one. It is well-suited as a reference book for undergraduate level exposure to the field of industrial microbiology. Given the broad areas that the authors try to cover, some sacrifice on substances is inevitable. It is indeed a good book for many lay researchers to start and want to join in with the biotechnology revolution.

Henry Y. Wang, *The University of Michigan*

Spectroscopic Analysis of Coal Liquids; Coal Science and Technology, Volume 12. Edited by John R. Kershaw (CSIRO Division of Materials Science and Technology). Elsevier: Amsterdam and New York. 1989. xiv + 395 pp. $152.75. ISBN 0-444-87307-4.

This volume of the *Coal Science and Technology* series provides a strong overview of many of the different spectroscopic techniques that have been applied to the analysis of coal liquids. The broad range of techniques discussed in this volume include gas chromatography (K. D. Bartle), pyrolysis and hydropyrolysis (W. Steedman), mass spectrometry (B. D. Batts and J. E. Batts), infrared spectroscopy (P. M. Fredricks), ultraviolet and luminescence spectroscopy (J. R. Kershaw), nuclear magnetic resonance (M. I. Attalla, A. M. Vassallo, and M. A. Wilson), and continuous wave and pulsed electron spin resonance spectroscopy (S. Schlick and L. Kevan). Each of the contributors provides an overview of the technique as well as an in-depth discussion of its use in the analysis

*Unsigned book reviews are by the Book Review Editor.

of coal liquids. For the reader who wants more information each section has a detailed list of references to which the reader can turn.

What makes this book particularly valuable is the individual contributions of the editor, J. R. Kershaw, who tries to put the results from these differing spectroscopic studies into an overall perspective, with regard to the analysis of coal liquids. This description is provided in two separate chapters, the first dealing with average molecular structure which is associated with the NMR chapter and the second a long chapter entitled "overview of the composition of coal liquids". In this latter chapter many of the coal liquefaction processes are described along with a detailed look at the analyses that have been obtained.

The average molecular structure chapter attempts to both describe the methodology and assumptions used for obtaining average molecular structures and also ascertain the validity of the results obtained. The overview chapter is broken down into the different technologies for obtaining coal liquids. These include hydrogenation with solvent but no catalyst (e.g. the SRC-I, SRC-II, and Exxon donor solvent processes), catalytic hydrogenation with a solvent (e.g. Synthoil and H-Coal processes), hydrogenation without a solvent, flash pyrolysis, and supercritical gas extraction. In each section a description of the analyses that have been carried out and results obtained are described.

The quality of these two chapters in providing a general overview of the state of coal liquids analyses in combination with a more specific and detailed description of the different spectroscopic techniques gives this book an important role in defining the status of coal liquids analysis.

Karl V. Wood, *Purdue University*

Advanced EPR; Applications in Biology and Biochemistry. Edited by A. J. Hoff (State University of Leiden). Elsevier Science Publishers: Amsterdam and New York. 1989. xxiii + 918 pp. $248.75. ISBN 0-444-88050-X.

Many modern applications of Electron Paramagnetic Resonance (EPR) now involve much more than a simple application of the technique to some problem in physics, chemistry, biology, or geology. The pulse techniques, now so common in NMR, are now available in EPR. In addition there are several systems in which EPR is combined with another spectroscopy. The end result is an alphabet soup of techniques. This edited volume provides a broad survey of these advanced EPR techniques with particular emphasis on applications in biology and biochemistry. Many chapters are devoted, in whole or part, to the exposition of the theory of a particular technique, so that this book will prove an excellent reference for anyone interested in the basis of a given technique.

The 25 chapters are divided into four broad areas. Chapters 1–6 give the theory and many applications of pulsed EPR, including Electron Spin Echo (ESE), Electron Spin Echo Envelop Modulation (ESEEM), fourier transform ESE, and some novel two-dimensional techniques applied to ESE and Electron–Electron Double Resonance (ELDOR).

Chapters 7–12 introduce a variety of novel experimental methods and their applications; these include loop gap resonators, EPR at 1 mm wavelengths (250 GHz), EPR detection by temperature modulation, time-resolved EPR used to analyze polarization effects such as Chemically Induced Dynamic Electron Spin Polarization (CIDEP) or the kinetics of radical formation and decay, transient mutation EPR applied to photoinduced spin states in rigid matrices, and a theoretical analysis of polarized EPR spectra.

Chapters 13–19 survey various combination techniques, including Electron Nuclear Double Resonance (ENDOR), TRIPLE resonance, Optically Detected Magnetic Resonance (ODMR), and Reaction Yield-Detected Magnetic Resonance (RYDMR) with applications to metalloproteins, spin labels in biological systems, and paramagnetic states in photosynthesis.

Finally Chapters 20–25 review a number of new advances in the application of EPR to various biological and biochemical problems. These include methods for the simulation and analysis of spin-label spectra of nitroxides incorporated in lipid membranes under various time ranges of motion, the use of spin labels (including the possibility of the extension to EPR imaging) to monitor the concentration of oxygen in cells and tissue, a technique involving g-strain broadening of the EPR of metalloproteins, an extensive review of the EPR of iron–sulfur proteins, a treatment of the EPR of Mn–proteins including an extensive analysis of the Mn–protein in the oxygen-evolving complex of photosynthesis, and a review of the EPR and ENDOR of copper proteins.

The chapters are carefully written by acknowledged experts in each technique and the book is well-edited. In spite of the fact that the book is not typeset, the quality of the camera-ready copy is generally very good. This book is highly recommended as a reference book to advanced EPR techniques. It is unfortunate that the price is so high that it is likely that this book will only be found in the libraries of the few universities left with a reasonable library budget.

James R. Bolton, *The University of Western Ontario*

Energy Density Functional Theory of Many-Electron Systems. By Eugene S. Kryachko (Institute for Theoretical Physics, Kiev) and Eduardo V. Ludeña (Venezuelan Institute for Scientific Research). Kluwer Academic Publishers: Dordrecht. 1990. 864 pp. $235.00. ISBN 0-7293-0641-4.

Although well-grounded on the Hohenberg–Kohn theorem and its extensions, density functional theory has suffered from two main deffects: on the one hand, the elusiveness of the "universal" energy functionals which, if found, could considerably reduce the computational effort in atomic, molecular, and condensed matter calculations and, on the other hand, the absence of a clearly defined correspondence between variational treatments for approximate energy density functionals and those of rigorous quantum mechanics. Both problems are addressed in this book by Kryachko and Ludeña. The authors show that through the use of local-scaling transformations a variational density functional theory can be produced. In addition they show how to construct approximate N-representable functionals that can be refined successfully so as to yield accurate upper bounds to the exact energy. Perhaps more important, a unified vision of the field is given through the presentation of an N-representable version of density functional theory based on local-scaling transformations.

The book begins with an historical and bibliographic sketch designed to guide the reader into the vast literature on the subject. Chapter 2 introduces the reader to density matrices. Chapter 3 is devoted to the one-electron density and its relationship to molecular structure with particular emphasis to Bader's topological conditions. An easy access to density functional theory is provided in Chapter 4 by discussing some of its developments from the viewpoint of the independent particle model and its corrections. Thus, the authors are able to survey important concepts such as Coulomb and Fermi correlation and models advanced for their semiquantitative description, borrowing ideas from the more familiar Hartree–Fock theory. Chapter 5 deals with the Thomas–Fermi theory and its generalizations; it contains a discussion of the leading quantum corrections and of the post-Thomas–Fermi–Dirac–von Weizsacker developments in density functional theory.

The book does not limit itself to being a mere catalogue of different trends and achievements in density functional theory. Critical appraisals are provided, such as in the analysis given in Chapter 6 of the Hohenberg–Kohn theorems and their related N- and v-representability problems also in this chapter. The Levy–Lieb formalism for non-v-representable one-electron densities as well as several methods for the determination of universal functionals are critically discussed. Chapter 7 presents a formulation of the variational principle of the local-scaling transformation version of density functional theory. In this context a reformulation of the Hohenberg–Kohn theorems is presented and extensions of the local-scaling formalism to spin-dependent systems, excited states, and non-Born–Oppenheimer systems are discussed. In Chapter 8 the self-consistent-field concept in density functional theory is presented. Local and nonlocal energy density functional approximations and computational methods for their implementation are reviewed. A self-consistent-field theory based on local-scaling transformations is advanced and the Kohn–Sham formalism is analyzed from this perspective. The volume closes by reviewing several developments and applications of density functional theory to relativistic, time-dependent, temperature-dependent, multicomponent systems as well as its interfaces with nuclear theory and statistical mechanics.

The compendious bibliography comprising over three thousand references will certainly be of great utility to workers in quantum chemistry and condensed matter physics. Finally, one should emphasize the pedagogical slant of this book: a reader with little or no background in density functional theory may be easily guided into its recent developments. In addition, an ample collection of problems makes it a unique choice for a graduate course on the subject. In conclusion this volume will be of invaluable help to critical researchers in the field, especially to those more interested at understanding phenomena than computing. It is unfortunate that the printing was done on a somewhat translucid paper thus the reading offers a physical challenge.

Enrico Clementi, *IBM Corporation*

Heterogeneous Catalytic Science. By R. D. Srivastava (University of Delaware). CRC Press: Boca Raton, FL. 1988. vi + 174 pp. $110.00 ISBN 0-8493-6430-2.

This broad and rich topic is of interest to surface scientists, chemical engineers, and physical chemists in both industry and academia. A comprehensive review would be highly ambitious and the likely result unwieldy. Happily, that is not attempted here. Instead, the focus is on four catalytic processes, which are of industrial importance and have been well-studied. They are selective oxidation of hydrocarbons, epoxidation of ethene, hydrogenation of carbon monoxide, and catalytic reforming. Each of these is treated historically in separate chapters, providing the

reader with an opportunity to observe how the current understanding of the topic was developed in the literature.

The author begins with a brief introductory chapter, where the basic concepts of catalysis, kinetics, and reaction modeling are given. The following chapter is an excellent overview of the experimental techniques commonly employed in the characterization of metallic surfaces and the species adsorbed on them. XPS, AES, IR and Raman spectroscopy, EXAFS, PIXE, ISS, SIMS, LEED, HREELS, and TDS are introduced in general terms and tabulated with references to recent review articles. Rutherford backscattering spectrometry and Mössbauer spectroscopy are covered in more detail, but not exhaustively. Advantages and disadvantages of each technique are discussed as a guide to those unfamiliar with this territory. These two chapters serve as the background for the rest of the book, where corroborative and conflicting date are presented in the analysis of those four previously mentioned catalytic processes.

In chapter three, industrial selective oxidation processes are outlined, with particular emphasis on vanadium pentoxide based and bismuth molybdate based catalysts. Reaction mechanisms are investigated through the study of kinetics and catalytic structures. The following chapter covers the conversion of ethene to its epoxide, an important chemical intermediate. Included here is an examination of the controversy over the chemical states of oxygen adsorbed on various planes of silver and their role in the reaction. This process also serves as an example of how promoters may be used to influence the kinetic control of a reaction with multiple pathways. The production of methane and methanol, via the hydrogenation of carbon monoxide, is reviewed separately in the next chapter. Although methanation may occur over a variety of metals, the author concentrates on the widely used supported and unsupported nickel catalysts. The geometric and electronic effects of poisoning by sulfur on these catalysts proves to be particularly interesting. In the section on methanol synthesis, the bifunctional zinc–copper catalysts are studied. The final chapter is on the reforming of naphthas into high-octane gasolines. This complex topic has been successfully boiled down into a managable presentation. The industrial feedstocks, reforming reactions, and reactor designs are described, yielding the motivation for choosing the catalysts employed in this process. The nature of the platinum–alumina catalysts, including their bifunctional behavior, is given first. From there, the behaviors of three dispersed bimetallic systems are compared: platinum–rhenium, platinum–iridium, and platinum–tin.

This book works well as an overview, in that the author carefully selects representative topics on which to concentrate. Although there are a few grammatical errors, the text is well-organized, the diagrams are presented clearly, and each chapter includes an extensive reference list.

J. S. Hölder, *University of Michigan*

New Directions in Solid-State Chemistry. By C. N. R. Rao and J. Gopalakrishnan (Indian Institute of Science, Bangalore, India). Cambridge University Press: Cambridge and New York. 1989. 532 pp. $39.50 (paper). ISBN 0-521-37935-0.

This book provides an accessible overview of solid-state chemistry. As the title indicates, recent advances are covered in the greatest depth. Most of the chapters provide first a general review of more traditional aspects followed by an often absorbing account of that which is new and exciting. The first chapter is devoted to structure. The chapter starts with a description to the types of bonding, the Madelung constant, and the NaCl and CsCl structure, but then it progresses on to more complicated structures (e.g. zeolites) and the idea of chemical twinning and rationalizations of structures based on band calculation. The second chapter on structural characterization begins with X-ray diffraction but devotes much more space to the newer techniques of electron microscopy, EXAFS, XANES, and magic angle spinning NMR. Chapter 3 is devoted to preparative methods. Chapter 4 on phase transitions starts with a description of the thermodynamics of phase transitions. It goes on to survey a host of fascinating phase types such as charge density waves, cooperative Jahn–Teller systems, and liquid crystals. Chapter 5 is entitled New light on an old problem: defects and nonstoichiometry. It begins with an explanation of Schottky and Frenkel defects and their equilibria. Later sections cover, among other things, dislocation, ordered superstructures, intergrowths, and structures with crystallographic shear. Chapter 6 provides a fine overview of the physical properties of compounds. The various forms of magnetism and electrical properties are discussed through an approach close to the work of John Goodenough. Oxide, sulfides, and fluorides are covered on a case by case basis. Chapter 7 discusses how materials can be designed for specific functional purposes. Chapter 8 discusses solid-state reactions. Especial detail is devoted to intercalation chemistry, organic systems, and heterogeneous catalysis. The last chapter discusses the high T_c superconductors.

This is an excellent book for both students and solid-state researchers. The goal throughout appears to be to show how the field is evolving. Numerous references to the recent literature are given. It is remarkable that one highly readable volume is able so succinctly to introduce the reader to this diverse field. The new paperback is both attractive and reasonably affordable.

Stephen Lee, *University of Michigan*

Early Developments in Radiation Chemistry. Edited by J. Kroh (Institute of Radiation Chemistry, Technical University, Lodz, Poland). Royal Society of Chemistry: Cambridge, United Kingdom. 1989. xix + 513 pp. $171.00. ISBN 0-85186-284-5.

One of chemistry's younger branches is the science of radiation chemistry, which is concerned with the chemical consequences of the absorption of energy from ionizing radiation by matter. This volume attempts to put into historical perspective the early developments of this field, which commenced with the discovery of radioactivity. Since many of the contributors to this collective effort have been in the field since its infancy and all have witnessed its "glory days", the book is rich with detail which would be lost to future generations if not recounted by some of the founders and pioneers. What is impressive about this work is the large number and rich variety of researchers who, with remarkable candor, reveal significant parts of their scientific life's story. Despite this diversity of backgrounds and national origins, many common themes emerge, and for this reason, the book succeeds in its mission.

This volume illustrates very well how science works in the human dimension, how personalities play such an important role, how key discoveries are arrived at, and how such findings affect the scientists involved. We are told of the difficulties of working with the early, crude equipment, of explosions, of smuggled radioactive sources, of the elation which comes with a new discovery, of pulling radioactive sources down the street in a child's coaster wagon, of the wartime secrecy of the Manhattan Project, of smoking thermos bottles carried onto airplanes, of impromptu seminars demanded of subordinates to get at the truth without obfuscation, and of many more personal recollections which reflect the human character of the field.

The contributors to this volume are well-chosen representatives from many different countries on both sides of the recently dissolved "ionic" (Fe^{3+}) curtain. The tone of all of the chapters is generally positive even when it could have been bitter, e.g. the description by a Japanese scientist of the U.S. military's sudden decision to destroy several Japanese cyclotrons being used for radiation chemistry and biology. There is only one significant controversy raised by a number of authors in the book: Who really should get the credit for "discovering" the hydrated electron? This is an appropriate debate, since the case is made by a number of authors that in the history of radiation chemistry, this discovery was the single most exciting and perhaps was radiation chemistry's most fundamental contribution to the general field of chemistry.

Far from being just reminiscences of aging scientists about the "good old days", contributions contain a considerable amount of science, including important revelations of the reasons for choosing certain research projects and mistakes of judgement and interpretation made along the way. Younger scientists in any field would do well to read these accounts, especially those where the authors make it clear that in some cases it was both courageous and wise to go against the current thinking in the field and to ignore the advice of others with greater stature. It is also useful for the young scientist to read of the blind alleys and the scientific scoops which ultimately steered the author into a much more successful research area. There is a remarkable amount of excellent science in these accounts. For example, there are numerous times when the authors reveal interesting research problems which have never been followed up or areas which have been neglected. The faults of the volume are those which might be expected from such an undertaking and do not detract significantly. For the reader who is not an "old-timer", the occasionally long lists of collaborators will be dull and the newcomer will want to focus on the science. For all, the extensive bibliographies will be very useful.

This book is a "must" for the reading lists of those who are entering the field of radiation chemistry or related areas as well as for those who have spent a significant portion of his or her scientific life in this field. The breadth of topics covered and the freshness of different perspectives and styles give this volume a unique character. The opportunity to review this book was a rare privelege. For this reviewer, reading these accounts was "like déjà vu all over again".

Conrad N. Trumbore, *University of Delaware*