

Isotope Effects in Chemical Reactions. ACS Monograph No. 167. Edited by C. J. COLLINS and N. S. BOWMAN. Van Nostrand Reinhold, New York, N. Y. 1971. xii + 435 pp. \$22.50.

A monograph that one has now read and used for more than two years—like a wife or an automobile of similar vintage—is an uncomfortable subject for public appraisal. The bias of loyalty colors the lessons of experience. Still it remains that this particular collection of six very different chapters is the single definitive work for any specialist in this area. Two of its chapters—"Isotope Effects in Biological Systems" by Katz and Crespi and "Heavy Atom Isotope Effects in Organic Reaction Mechanism Studies" by Fry—are indeed sufficiently broad in scope as to recommend themselves much more widely.

The appeal of the Katz-Crespi contribution to the chemist is very much that of the unfamiliar and of the exotic. One learns that only the lower plants can fully adapt to a world in which the hydrogen atoms are deuterium. Save *Euglena* (the exception that emphasizes the rule), all animals seem to require some protium to survive, increasingly so as they ascend the evolutionary scale. Yet even a dog can be partially deuterated! More fascinating are the physiological and biochemical consequences. Yeasts become "nutritionally more fastidious." Algal photosynthesis is depressed in rate and sucrose is no longer manufactured. From the organism to the cell and then to the biopolymer and the enzyme, the narrative is linked by the authors' successful exploitation of fully deuterated algae as a source of fully deuterated food for bacteria and molds, of proteins and of nucleic acids, of physiologically active mold metabolites, and on down to very simplest fully deuterated natural products. Less happily, space limitations have precluded a more thorough treatment of isotope effects at the enzymic and molecular level. Those seeking a thorough review of the very beautiful applications of this technique that are due to Abeles, Arigoni, Battersby, Rose, and others will need look elsewhere.

Fry's chapter on heavy atom isotope effects fits most comfortably within the mainstream of mechanistic organic chemistry. Although hydrogen isotope effect data are introduced as appropriate, it is the extraordinary power of a very limited number of heavy atom isotope effect experiments that remains the central theme. These can now be said to have identified the rate-determining steps of the Chugaev reaction, the Dieckmann condensation, the Baeyer-Villiger rearrangement, the Wolff/Curtius/Hofmann/Schmidt/Lossen complex of rearrangements, and of many more. The more subtle analyses of isotope effects in the classical carbonyl, aliphatic nucleophilic displacement, and elimination processes are performed clearly, critically, and with dispatch. (The occasional use of the Goepfert-Mayer-Bigeleisen $G(u)$ formalism, an unnecessary if minor distraction here, has vanished from this author's more recent publications.)

The latter conform more closely to a point of view that is emphasized in three other chapters—those of V. J. Shiner, Jr. ("Deuterium Isotope Effects in Solvolytic Substitution at Saturated Carbon"), of D. E. Sunko and S. Borčić ("Secondary Deuterium Isotope Effects and Neighboring Group Participation"), and particularly in that of E. K. and E. R. Thornton ("Origin and Interpretation of Isotope Effects"). In brief, the magnitude of a kinetic isotope effect is now most simply understood to reflect the difference in force constants, experienced at an isotopically substituted atom, as that atom arrives in a transition state. The historical origins of this consensus can be traced, in part, to Westheimer's 1961 exposition of the triatomic model for hydrogen transfer. No less important have been Wolfsberg's model calculations which, by their nature, demand force constants as adjustable parameters.

All three chapters illustrate the simplified understanding of secondary isotope effects which the force constant language allows. That by the Thorntons more explicitly recognizes this development within its broader context. It is sad but true that both the hypotheses of chemical kinetics (*e.g.*, energy distribution) and its quantitative parameters (vibrational frequencies, moments of inertia, etc.) are properties of entire molecules. Those of the organic chemist (stereospecific bond cleavage and formation, substituent and isotope effects, etc.) pertain to a small part of the

molecule—often a very small part. Local force constants provide a satisfying, if hardly sufficient, way to bridge this gap. For the reader who is not dissuaded by sentences of Germanic dimensions, by qualifying clauses that modify other qualifications, and by occasional lapse into stridency and dogmatism, the Thorntons' chapter will reveal a rare and brave attempt to shine light on an important problem.

A second recurring theme is the increased reliability and precision of often difficultly achieved experimental data. These now quite adequately dilute the occasionally noted lapses and set the stage for the next, as yet unrealized, step of statistical sophistication—hypothesis testing. (The additivity hypotheses of Shiner and of Thornton would provide admirable substrates.) Until then, one must await details of the numerous reports that were unpublished in 1969 and remain so today: fully eight out of ten such citations in one chapter and one still unsubstantiated claim of experimental unreliability in yet another.

As is increasingly the custom this monograph begins with a theoretical benediction ("Kinetic Isotopic Effects: Introduction and Discussion of the Theory," by W. A. Van Hook) with a heavy historical orientation. This reviewer's opinion is that fewer theoretical topics, each one more critically selected and more thoroughly developed, might have held more appeal for the critical novice. Van Hook's more traditional approach is not entirely without its advantages. And it is indeed in this same traditional vein that one notes the adequate quality of the paper, the rarity of typographical errors, and the convenience of a subject and author index that encompass all six chapters.

M. J. Goldstein, Cornell University

Macromolecular Physics. Volume I. Crystal Structure, Morphology, Defects. By B. WUNDERLICH (Rensselaer Polytechnic Institute). Academic Press, New York and London. 1973. xiv + 549 pp. \$35.00

This book initiates what is to be an extensive series of books devoted to the physics of macromolecules. It itself is the first half of a pair of books on the nature of crystallinity and the crystallization process in polymeric materials. This volume emphasizes the structure, morphology, and defects in such materials, while the second is to focus on the processes of nucleation, crystallization, annealing, and melting.

The first chapter, "The Structure of Macromolecules," is relatively brief and is primarily a discussion of the characterization of chain molecules in terms of their molecular weights, chemical and stereochemical structures, and conformations or spatial configurations. The second chapter is entitled "The Microscopic Structure of Crystals"; it contains, of course, the usual discussions of symmetry, lattices, point groups, space groups, etc., but also presents a great deal of information on calculations of chain conformational energies, rotational isomers, helical conformations, and the packing of intermolecular arrangements of macromolecules. Also presented is a very extensive survey of polymer crystal structures. Chapter Three, "The Crystal Morphology," contains discussions of lamellar crystals and chain folding, multilayer crystals, epitaxy, twinned crystals, dendrites, spherulites, fibrous crystals, and isometric crystals. The last chapter, "The Defect Crystal," is concerned with the methods used to study crystal defects, the various types of defects, and theories regarding their molecular origins. Most of the systems described in the book are "synthetic" polymers, but there is much information on the crystalline state in biopolymers as well.

As would be expected from the nature of this subject, there are numerous photographs and drawings (nearly 300). Many of the photographs obtained by electron microscopy are quite fascinating, and the illustrative drawings seem to have been very carefully prepared. In addition, there are over forty tables containing structural and related information, extensive compilations of pertinent references, and both author and subject indexes. The material is in general clearly written, the format is quite attractive, and there are very few typographical errors.

To this reviewer, the major shortcoming of the book is the rather one-sided picture presented in the discussion of such topics as the existence of ordered regions in amorphous polymers, the type of chain folding occurring in lamellar crystals, and the nature of the

* Unsigned book reviews are by the Book Review Editor.

"paracrystalline state." The failure to acknowledge the highly controversial nature of some of these interpretations and the existence of results supporting other points of view does a serious disservice to the reader.

Nonetheless, this book does represent a very significant contribution to the polymer physics literature and will unquestionably be extremely useful to anyone interested in the solid-state properties of crystalline polymers.

J. E. Mark, *The University of Michigan*

Modern Methods of Steroid Analysis. Edited by ERICH HEFTMANN (Western Regional Research Laboratory, U. S. Department of Agriculture). Academic Press, New York, N. Y. 1973. xx + 523 pp. \$37.50.

Erich Heftmann included a review of the analysis of steroids in his first book on "Biochemistry of Steroids" published in 1960. However, no such review was included in his 1970 publication "Steroid Biochemistry," and his editorship of the present work is intended to serve as a companion volume to the 1970 publication.

The book reviews steroids analysis in the following seven sections: chromatography, mass spectrometry, infrared and Raman spectroscopy, nuclear magnetic resonance, X-ray diffraction analysis, optical rotatory dispersion and circular dichroism, and radioisotope methods. For the most part references cover the literature from 1960 through 1971.

According to the editor, "The treatment of the subject matter approaches the level at which an investigator entering the steroid field or a steroid specialist contemplating the use of a new method will not only find an introduction to it but guidance to further study as well." These objectives are met by the inclusion of a brief introduction to a given technique followed by a review of specific examples of applications to steroid analysis. Two noticeable exceptions to this pattern are the section on Infrared and Raman Spectroscopy and the Nuclear Magnetic Resonance section.

The infrared discussion is limited to an example of the use of a time-shared computer program, InfraRed Information Search. It is certainly misleading to imply by default that this is the only significant development in the last decade in ir technology of interest to the steroid chemist. The nmr section has an introductory chapter on the techniques but without specific references to steroid analysis and is followed by a chapter on the application of lanthanide shift reagents. Again it is misleading to imply that nmr is so limited in its applications to steroid research. This is especially true in light of the potential applications of ^{13}C and proton Fourier transform nmr spectra in steroid biotransformation studies.

Since there is not much in modern organic analysis and separation techniques that has not been applied to steroid analysis, it is an ambitious and difficult task to review the field in a single volume. It is especially difficult when that review ranges in level from the practical aspects of chromatography and radioimmunoassay to a discussion of automated Faltmolekül X-ray analysis. In general the 37 contributors under Erich Heftmann's editorship have produced a text of interest to steroid analysts.

Joseph E. Sinsheimer, *The University of Michigan College of Pharmacy*

Chimie-Physique des Phenomenes de Surface. By J. FRIPIAT, J. CHAUSSIDON, and A. JELLI. Masson et Cie, Paris. 1971. vii + 387 pp. 150 F.

This book is designed for students and those initiating a research career to acquaint them with fundamentals and applications of surface chemistry and physics. Particular reference is given to adsorbed films on inorganic oxides and silicates. This reference would be expressly valuable to one beginning research in catalysis, ion exchange phenomena, and semiconductors, as well as those engaged in the characterization of an adsorbed film on a solid surface.

There are twelve chapters which include the following: Thermodynamics of Interfaces, Physical Adsorption, Application of Statistical Mechanics, to Adsorption Phenomena, Chemisorption, Spectroscopic Studies of Adsorption, Heterogeneous Catalysts, Electrical Charge on Surfaces, Ion Exchange, Nucleation, Hydrophobization of Mineral Surfaces, Colloid Formation, and, finally, Porosity of Porous Structures.

The authors reference both current texts and technical literature on a world-wide basis. Fundamental equations are well developed and clearly presented. In addition, the applications of this technology are sequentially presented following fundamentals

and are developed in a manner designed to stimulate further research.

Even though this book is in French, it would be a valuable reference addition to any researcher in the field of surface chemistry and physics.

J. Wade Van Valkenburg, *3M Company*

IR—The Theory and Practice of Infrared Spectroscopy. Second Edition. By N. L. ALPERT, W. E. KEISER, and H. A. SZYMANSKI. Plenum Publishing Corp., New York, N. Y. 1973. xiv + 380 pp. \$7.95

This is a paperback edition of the work that appeared in hardcover form in 1970. Although there is a chapter on theory, the main thrust of the book is to help interpret infrared spectra. Data abound in tables, some of them several pages long. Quantitative as well as qualitative analysis is treated. Although the book is said to be intended as a textbook as well as a reference book, it does not have exercises for students. It does, however, have a group of spectra reproduced in conveniently large form, tucked in a pocket in the back, which are interpreted in the body of the text. Each chapter has a good bibliography, and there is an appendix of point group tables. It is good that this successful book has now been made available at a price that should substantially widen its use.

Liquid Crystal Devices. Edited by THOMAS KALLARD. Opto-sonic Press, Box 883, Ansonia, New York, N. Y. 1973. xxiv + 365 pp. Price not stated.

This soft-bound volume is part of a "State of the Art Review" series and is a sequel to a similar work published in 1970. Four brief introductory papers review the principal applications and orient the reader. The most generally familiar application is for display of alphanumeric information, as seen in small electronic calculators, and makes use of the orienting effect of an electric field on layers of aligned liquid crystal molecules through which polarized light may be transmitted. Most of this book, however, consists of summaries and illustrations of patents, followed by a variety of indexes that greatly facilitate accessibility.

Modern Electrochemistry. By J. O'M. BOCKRIS and A. K. N. REDDY. Plenum/Rosetta Editions, New York, N. Y. 1973. Volume 1, lx + 622 pp. Volume 2, lvi + 809 pp. \$8.95 per volume.

This book, which has been reviewed earlier, was very well received when it appeared in hard-bound form in 1970. Its appearance now in a paperback edition more suitable to students' budgets is most welcome.

MTP International Review of Science. Organic Chemistry, Series One. Consultant editor: D. H. HEY. **Volume 3: Aromatic Compounds.** Edited by H. ZOLLINGER. **Volume 4: Heterocyclic Compounds.** Edited by K. SCHOFIELD. **Volume 7: Carbohydrates.** Edited by G. O. ASPINALL. **Volume 8: Steroids.** Edited by W. F. JOHNS. **Volume 10: Free-Radical Reactions.** Edited by W. A. WATERS. Butterworths, London, and University Park Press, Baltimore, Md. 1973. Volume 3, 336 pp. Volume 4, 350 pp. Volume 7, 344 pp. Volume 8, 286 pp. Volume 10, 319 pp. \$24.50 per volume.

This series, some volumes of which have been reviewed earlier, is the first stage of an attempt to meet the chemist's need for recent awareness in the face of an increasingly overwhelming mass of newly published material. In the ten volumes of Organic Chemistry, Series One, the published achievements of 1970 and 1971 are organized under appropriate headings and are summarized succinctly yet in much detail; results and conclusions are reported, but in general are not considered critically. Each contributed chapter is thoroughly documented with, typically, several hundred references.

The contributors are quite international in origin, although the British Commonwealth is the largest source. The concept of these reviews as a whole is vast, and the effort to obtain the services of the large number of contributors and to keep them working to schedule must have been most taxing. It indicates impressive determination that this undertaking is planned to be repeated at two-year intervals.

Reviewing the literature over a short span of time has become a widespread phenomenon rather suddenly during the last decade, and is a natural result of the accelerating production of new research results. Such rapid growth has naturally led to duplication of effort to varying extents. The most obvious comparison in the present case is with the Chemical Society's "Specialist Periodical Reports."

The organization of the two series is somewhat different, although not drastically so, and the spans of time covered are in some instances longer or shorter, and the emphasis of choice by the various contributors is bound to show some differences. Quality appears to be similar, although a detailed comparison might possibly bring to light some significant differences. Cost does not seem to differ greatly, but cannot be assessed precisely at this stage. There is, of course, convenience in having a review series appear all at once as a complete whole, and at uniform intervals. Neither series has volume indexes, and each relies on a detailed table of contents; the MTP series, however, is planned to include a comprehensive index volume. Technical libraries with limited budgets will have to consider carefully which series best meets their clients' needs, for it would be a considerable luxury to buy both. Either series would be a useful asset.

Practical Liquid Chromatography. By S. G. PERRY, R. AMOS, and P. I. BREWER. Plenum/Rosetta Editions, New York, N. Y. 1973. xiii + 230 pp. \$7.95.

This book originally appeared in hard-bound form in 1972, and it is now made available to a wider market in paperback. It is intended for use by chemists in the laboratory, including students. After a chapter on background, it launches directly into practical matters, from band spreading to equipment, and concludes with a chapter on "Current Status of Liquid Chromatography: Place Among Family of Chromatographic Techniques." All varieties of liquid chromatography are included, from thin-layer to high-pressure. There is, indeed, much practical detail, and with the reservation that its value cannot properly be assessed until one actually makes use of it, it appears to be the sort of how-to-do-it detail that the title suggests. References and suggestions for further reading increase the value of the book.

Mechanism. An Introduction to the Study of Organic Reactions' By R. A. JACKSON (University of Sussex). Oxford University Press, Oxford. 1972. xiii + 136 pp. \$2.95.

The author of this small book attempts to make the reader take an intellectual and fundamental look at the subject of organic reaction mechanisms; he does not attempt to survey and summarize even the common reaction mechanisms. To this end, the meaning of, the purpose of, and the methods of establishing reaction mechanisms are considered and probed. I believe that this book will make valuable supplementary reading in an advanced undergraduate course, since it will give the student a solid, rational basis for criticizing the mechanisms he is studying in class.

There are mechanistic problems at the end of each chapter that give the reader an opportunity to put into practice what has been learned. Answers are given to all problems, and there are also hints to the solution of selected problems.

Victor L. Heasley, *Point Loma College*

Applied Photographic Theory. By P. KOWALISKI (Kodak-Pathé, Vincennes, France). John Wiley & Sons, New York, N. Y. 1972. x + 533 pp. \$32.50.

The aim of this book is to apply theory as a working guide to the use of photography in scientific, industrial, and professional applications, and to provide a better understanding by the user of the capabilities and limitations of the photographic medium. Accordingly, the author begins with a discussion of the characteristics of the finished photographic record. Approximately the first two-thirds of the book is devoted to tone and color reproduction, detail reproduction, and information recording and transfer. The latter is an important and rapidly growing application of photography, and the chapter devoted to it is a particularly valuable part of the book.

The remainder of the book, under the heading "The Mechanisms of the Classical Photographic Process," deals with the structure and chemical composition of silver halide photographic materials, the action of light in producing the latent image, and the chemistry of development and after-processing. No detailed discussion of mechanisms is attempted; instead the author states that for his purpose "all that is required are simple working hypotheses, descriptive of the essential and well demonstrated aspects of the intrinsic mechanisms," and limits the description of basic phenomena to "their most concrete aspects, the only ones required for the correct use of the photographic materials." Accordingly, the book does not contain a comprehensive or critical treatment of

theoretical aspects of the chemistry of the photographic process, although extensive literature references are given. The simplified treatment, satisfactory in most respects for the intended purpose, sometimes results in generalizations that should have been qualified and presentations that are too brief to be clear (*e.g.*, on ways to compensate for reciprocity failure, p 403).

The user of photography in scientific and industrial applications should find this book a valuable and welcome addition to the Wiley series on "Photographic Science and Technology and the Graphic Arts."

T. H. James, *Eastman Kodak Company*

Organic Photochemistry. Volume 3. Edited by O. L. CHAPMAN (Iowa State University). Marcel Dekker, New York, N. Y. 1973. viii + 311 pp. \$18.75.

This is the third volume of a series published biennially since 1969. There appears to be a trend in the series toward fewer, more comprehensive chapters. The present volume has three chapters dealing with olefin isomerization, the photochemistry of three-membered heterocycles, and the photochemistry of cyclic ketones. The first and third chapters were presented at a symposium held thirty months prior to publication. This delay is unfortunate in such a rapidly moving field. Large portions of the material in the second and third chapters have appeared in the review literature since the chapters were written.

The chapter on olefin *cis-trans* isomerization by J. Saltiel and coworkers reflects the authors' interest in stilbene isomerization, a topic which occupies over half of the chapter. A detailed account of the controversy over singlet *vs.* triplet mechanisms for isomerization is given; however, it is clear that the final words have not been written on this subject. The chapter on heterocycles by N. R. Bertoniere and G. W. Griffin deals mainly with the cleavage reactions of oxiranes and aziridines. The chapter on cyclic ketones by O. L. Chapman and D. S. Weiss contains extensive tabulations of spectroscopic properties as well as photochemical data on saturated and α,β - and β,γ -unsaturated cyclic ketones.

The chapters are in general clearly written. Readers with only a passing knowledge of photochemistry as well as a specialist will benefit from this volume.

Frederick D. Lewis, *Northwestern University*

The Chemistry of Platinum and Palladium. By F. R. HARTLEY (University of Southampton). John Wiley & Sons, Inc., New York, N. Y. 1973. 544 pp. \$45.00.

Chemists seeking a convenient first reference on the chemical complexes of platinum and palladium will be pleased with this book. Because it represents an attempt to assimilate within one volume a review of all facets of the chemistry of palladium and platinum, it cannot be considered a final source for any topic. It is a collection of vignettes each on a different chemical aspect. But it is the most comprehensive source available on these elements, and therefore it would make an excellent reference volume for chemical libraries.

Some of the topics covered in the text include oxidation states and stereochemistry, hydride complexes, π -allyl complexes, substitution reactions, and olefin and acetylene compounds. The chapter on the hydride complexes of the divalent metals seems typical of the treatments of the other topics. Other hydride reviews are referred to where appropriate. General features of platinum and palladium hydride chemistry are discussed with examples. No effort is made to incorporate generalities to complexes of other transition metal hydrides into the discussion. There is ample cross-referencing among the various chapters by page which makes the book coherent and more suitable as a reference source. Thus, the chapter on divalent hydrides contains references to the sections on zerovalent hydrides, complexes with group IVb elements, substitution reactions, and organometallic complexes involving metal-carbon σ bonds. This reduces the duplications which must exist when each chapter has its own reference list and the book contains about 2600 references.

The usefulness of this book is increased by the inclusion of two appendices. The first appendix contains preparations and physical properties of the most common complexes of palladium and platinum. The second appendix has bond angles and bond lengths for 212 compounds of these elements, including references.

Roger B. Saillant, *Ford Motor Company*