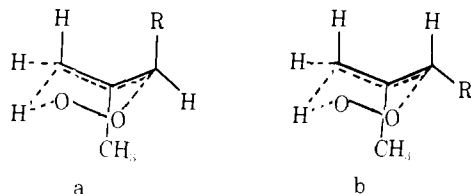
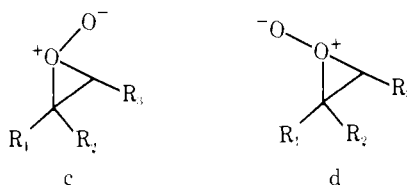


groups in the reaction of $RCH=C(CH_3)_2$ derivatives (3-5, for example).



Likewise it is not clear why a peroxide intermediate should favor orientations which would lead to the observed products. Fukui¹¹ has argued that formulation c is favored over d where polar substituents (i.e., $R_3 = OCH_3$) are concerned, but this argument does not easily extend to the alkyl cases presented here. Similarly, Goddard's⁷ explanation of Conia's results (8



and 9) based on conformational preferences in a diradical relies on the presence of the $-OCH_3$ grouping and again will not easily extend to the other examples presented here, but is probably important in the systems analyzed.

These results clearly demonstrate that the overall reactivity of a given C-H bond is greater on the more crowded side of the trisubstituted olefin. These results do not obviously support any of the current proposals for the singlet oxygen ene reaction. The observation is sufficiently general, however, that it must be

incorporated into any ultimately successful rationalization of this reaction.

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References and Notes

- (1) (a) D. R. Kearns, *Chem. Rev.*, **71**, 395 (1971); (b) A. M. Trozzolo, Ed., *Ann. N.Y. Acad. Sci.*, **171**, 50 (1970).
- (2) K. R. Kopecky and H. J. Reich, *Can. J. Chem.*, **43**, 2265 (1965).
- (3) C. S. Foote, *Acc. Chem. Res.*, **1**, 104 (1968).
- (4) (a) K. R. Kopecky and J. H. van de Sande, *Can. J. Chem.*, **50**, 4034 (1972); (b) A. Nickon et al., *J. Am. Chem. Soc.*, **94**, 5517 (1972); (c) L. M. Stephenson, D. E. McClure, and P. K. Sysak, *ibid.*, **95**, 7888 (1973).
- (5) (a) A. Nickon and J. F. Bagli, *J. Am. Chem. Soc.*, **83**, 1498 (1961); (b) A. Nickon, N. Schwartz, J. B. Di Giorgio, and D. A. Widdowson, *J. Org. Chem.*, **30**, 1711 (1965); (c) A. Nickon and W. L. Mendelson, *Can. J. Chem.*, **43**, 1419 (1965); (d) C. S. Foote, *Pure Appl. Chem.*, **27**, 635 (1971).
- (6) (a) D. B. Shart, Abstracts, 139th National Meeting of the American Chemical Society, New York, Sept 1960, p 79P; (b) W. Fenical, D. R. Kearns, and P. Radlick, *J. Am. Chem. Soc.*, **91**, 7771 (1969); (c) F. McCapra and I. Beheshti, *J. Chem. Soc., Chem. Commun.*, 517 (1977); (d) M. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, **97**, 3978 (1975).
- (7) L. B. Harding and W. A. Goddard, *Tetrahedron Lett.*, **No. 8**, 747 (1978).
- (8) A. Nickon and J. F. Bagli, *J. Am. Chem. Soc.*, **81**, 6330 (1959).
- (9) One might argue that 3-5 are simply consistent with a large isotope effect. An effect on the order of $K_H/K_D = 5-7$ would be required, however, substantially larger than any previously observed. Demonstrations which show the isotope effect to be small in compound 3 come from the recognition that the ratio of tertiary to secondary hydroperoxide from trimethylethylene, 50:50, is almost exactly the same as in our trideuteriomethyl derivative, 53:(40 + 7) = 53:47.
- (10) G. Rousseau, G. LePerche, and P. M. Conia, *Tetrahedron Lett.*, **No. 29**, 2517 (1977).
- (11) S. Inagaki, H. Fujimoto, and K. Fukui, *Chem. Lett.*, 749 (1976).

Michael Orfanopoulos, Sr. M. Bellarmine Grdina
L. M. Stephenson*

Department of Chemistry, Case Western University
Cleveland, Ohio 44106

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Book Reviews

Structure Determination by X-Ray Crystallography. By M. F. C. LADD (University of Surrey) and R. A. PALMER (University of London). Plenum Press, New York, 1977. xvi + 393 pp. \$29.50.

This book is a welcome addition to the field of single crystal X-ray diffraction. It provides basic introductory material in an area which has few texts for the novice. Main topics discussed include crystal geometry, space groups, diffraction theory, Fourier theory, film techniques, and approaches to the phase problem. Many examples and drawings are included to clarify the more difficult material. The inclusion of many crystallographic problems and solutions using real chemical compounds has helped greatly to bridge the gap between theory and practice for the nonprofessional crystallographer.

William M. Butler, *University of Michigan*

Minicomputers and Large Scale Computations. Edited by PETER LYKOS (Illinois Institute of Technology). American Chemical Society, Washington, D.C. 1977. xi + 239 pp. \$21.50.

This collection of papers presented at the June 1, 1977 Symposium in Montreal describes a number of scientific problems which have been approached using minicomputers. Several papers deal with complex mathematical problems including: simultaneous partial differential equations, algebraic eigenproblems, and general numbercrunching with a minicomputer. Other topics include large scale simulation, theoretical chemistry calculation, molecular dynamics, APL and analysis, vector processors, fluid mechanics, process design, and molecular orbital calculation. Computer-aided data acquisition and analysis for both X-ray structure and cloud chamber studies are included.

William M. Butler, *University of Michigan*

Carbonogenic Activity of Zeolites. By PETER A. JACOBS (Katholieke Universiteit Leuven, Belgium). Elsevier, Amsterdam and New York, 1977. xvi + 253 pp. \$29.50.

Zeolites are crystalline aluminosilicates with a three-dimensional framework. They are among the most important industrial catalysts. Because of their unique porous crystalline properties, they also have considerable scientific interest. This volume covers a great deal of ground, ranging from crystal structure to the use of zeolites in industrial processes. The principal aim is to review developments between 1970 and 1975. (The earlier literature is well covered by other books and reviews, and there is no need for repetition.) Nevertheless, this book is well balanced, giving a complete picture even to a reader unacquainted with earlier literature. The volume should prove to be an excellent reference for students and researchers interested in catalysis over zeolites. The author is well known for his work in the field of zeolites.

The first of five chapters briefly describes the crystal chemistry of zeolites of catalytic importance. This chapter is more superficial than the others; however, an adequate bibliography is attached so the reader can find more details, if needed.

The second chapter presents an overview of industrial catalytic processes using zeolites. Catalytic cracking, hydroisomerization, hydrocracking, selective forming, (sic!, instead of "Selectoforming"), and low temperature isomerization and disproportionation of aromatics are discussed briefly, perhaps too briefly.

The third chapter, characterization of the acid sites in zeolites, contains an excellent table summarizing the various hydroxyl groups present in zeolites. Acid activity is associated with the 3650-cm^{-1} OH infrared band.

The longest, most comprehensive, and most extensively referenced chapter discusses acid-catalyzed reactions over zeolites. Many organic reactions are systematized and discussed according to new concepts. The possible nature of the active sites is described after each reaction type. The author skillfully waded through the voluminous, and often contradictory, literature. The "General Conclusions" is the best part of this chapter and the whole book.

The last chapter describes zeolites as part of bifunctional catalysts. Since many industrial catalysts use metal-loaded zeolite catalysts, this chapter covers important ground. Many questions remain, however, on reaction mechanisms and on the nature of active sites in these catalysts.

An appendix lists the locations of cations in dehydrated faujasites. A diagram showing these locations would have been very helpful.

There are a few omissions, errors, and shortcomings. The new ZSM-type zeolite catalysts and silicalite are not mentioned in the book. The cage- or window-effect in erionite-type zeolites would have merited more discussion. Hydrogenolysis is not among the most important reactions occurring in hydrocracking (p 27), and paraffins are not inert to alkylation on nonzeolitic catalysts, such as fuming H_2SO_4 and HF (p 118). (The author probably meant *normal* paraffins here!) Some of the equations (e.g., 28b on p 122) have some atoms missing from formulas, and some are not balanced properly. This reviewer doubts that hydrocracking of *n*-decane proceeds through cyclodecane and cycloheptane intermediates (p 219). Alkyl- and dialkylcyclopentanes and -cyclohexanes are more likely intermediates. The Subject Index is too brief, but this is compensated by a rather detailed list of contents.

In summary, this is a good book. The author should be complimented for collecting, organizing, and systematizing a tremendous amount of work and for correlating structure and catalytic activity in this well-described, easily understandable work.

Sigmund M. Csicsery, *Chevron Research Company*

Chemistry of Natural Protein Fibers. Edited by R. S. ASQUITH (The Queens University of Belfast). Plenum, New York. 1977. xx + 417 pp. \$35.00.

This book was compiled in an effort to provide a source of information for undergraduate and postgraduate students on protein fibers by combining chemistry of proteins and technology of fibers. The first chapter is an introductory one on protein chemistry, the second discusses the chemistry of silk, and the last chapter (nine) covers all other animal fibers in a general manner. The order of the intermediate chapters could be improved. Chapters Three, Five, and Six discuss keratins and Chapters Four, Seven, and Eight dwell on wool. Chapter Eight on wool finishing should, perhaps, precede Chapter Seven on wool dyeing. Although two of the chapters on wool processing contain somewhat less than 100 references, all of the other chapters are extremely well documented, commonly with 200 to more than 300 references and with as many as 357 references. Each chapter is uniformly presented, beginning with an excellent introduction to the topic. Another helpful organizational approach is in the numbering of sub-headings using the decimal system.

The book is comprehensive with excellent reproductions of electron micrographs, structures, drawings, etc. It, however, may suffer the same fate as all compositions which are assembled by numerous authors, that is, the lack of a smooth continuity throughout the text. There does seem to be some overlap in the writing, although this is certainly a minor weakness.

In order to take full advantage of such a book a student would certainly need to have completed organic and preferably biochemistry, in other words, an advanced undergraduate. However, the author has accomplished his goals nicely with a pleasant and extremely helpful blend of chemistry and technology.

Patrick E. Cassidy, *Southwest Texas State University*

Elementary Molecular Orbital Theory. By G. H. WAGNIÈRE (The University of Zurich). Springer-Verlag, New York. 1976. 109 pp. \$6.10.

This volume in the "Lecture Notes in Chemistry" series provides a brief introduction to molecular orbital theory and selected semi-empirical methods. The topics presented in the first five chapters are arranged under the headings of the hierarchy of approximations, simple Huckel theory of π electrons, many-electron theory of π electrons, self-consistent-field methods, and all-valence MO procedures. The topics presented in these chapters are treated in greater detail in

many standard texts on quantum chemistry. The level of treatment of topics varies, and the order of presentation of some of these is somewhat unusual. This leads to some confusion concerning the definitions of terms, approximations, and methods in specific cases. The discussions early in the text of configuration interaction for ground-state wave functions, and of spin operators, appear premature. The sixth and final chapter, which comprises 25% of the book, includes the special topics of optical activity, selection rules for electrocyclic reactions and cycloaddition reactions, and molecular orbital theory with periodic boundary conditions.

Janet E. Del Bene, *Youngstown State University*

Mass Spectrometry. Volume 4. Senior Reporter: R. A. W. JOHNSTONE. The Chemical Society, London. 1977. xii + 357 pp. £22.50 (\$45.00).

This is the fourth in The Chemical Society's useful and respected biennial series of surveys of mass spectrometry. While it is by title a review of the literature, many of the 13 reporters (authoring 12 chapters) have taken a sufficiently broad view of their task to provide some critical evaluation and personal outlook. Given England's preeminent role in the history of mass spectrometry, it would be ungrateful to argue with the almost exclusive limitation of the Reporters to Commonwealth laboratories, and in any case the obviously high level of expertise and diligence displayed in these chapters disarms any doubts. Altogether this is an attractive book of high quality and interest, although unfortunately expensive for individual purchasers.

This is definitely not an introduction to the field; the writing invariably presumes a solid and often rather specialized background. On the other hand, the coverage includes perhaps all of the active areas of mass spectrometric activity and would provide an excellent introduction to the techniques, concerns, and capabilities for someone with a good, but not necessarily up-to-date, knowledge of the basics. This volume will, of course, be valuable to workers in any area of mass spectrometry as a reference to current work, and a literature checklist.

The first chapter ("Theory and Energetics") gives a concise account of computational and experimental methods being used to find ion structures and energies. It makes the valuable point that while large computations on small ions are now getting to be very good, the widely used programs with minimal basis sets are "not of predictive value" for ions. This chapter is sketchy on ion energetics, partly because its time of writing misses by a year or two the truly revolutionary impact of ion-equilibrium results. One hopes that this field will be accorded major coverage in Volume 5.

Chapter 2 on "Structure and Mechanism" is appropriately brief for this well-reviewed area, while the details of specific-compound fragmentations are well covered in four chapters on organic, natural product, drug, and inorganic compounds (the last an impressive and timely review with over 800 citations).

The six chapters on aspects of instrumentation and techniques are up to date and useful, happily making some effort to sort out the more significant work from the large number of trivial or ineffective ideas. These chapters cover "Computerized Data Acquisition and Interpretation"; "Trends in Instrumentation"; "Alternative Methods of Ionization and Analysis"; "Field Ionization and Field Desorption"; "GC-MS"; and "Negative Chemical Ionization". Inevitably some overlap and duplication between chapters can be found, but the coverage is in general well distributed and excellent.

Robert C. Dunbar, *Case Western Reserve University*

Growth of Crystals. Volume 10. Edited by N. N. SHEFTAL. Consultants Bureau, New York. 1976. x + 290 pp. \$37.50.

The majority of the well-known "Growth of Crystals" series are reports of All-Union or other Soviet Conferences on crystal growth. Volume 10 is, therefore, unusual in that it did not originate in a conference. There are 25 papers, with emphasis on theoretical and fundamental rather than technical aspects. The editor, N. N. Sheftal, is the major contributor as author or coauthor of six papers, and he exerts a strong influence over the whole volume. In spite of the absence of contributions from many noted theoreticians, like Alexandrov, Chernov, and Temkin, there are a number of stimulating articles which often have the characteristics that they appeal to fundamentals, adopt an historical approach, but tend to make assumptions which are unorthodox. As an example, consider two of the five principles adopted for simulation purposes by Sheftal and A. N. Buzynin: (3)