$$\mathbf{4} \xrightarrow{h\nu} {}^1\mathbf{4}^* \xrightarrow{k_{st}} {}^3\mathbf{4}^* \qquad (1)$$

$$^3\mathbf{4}^* \xrightarrow{k_r} \mathbf{7} \qquad (2)$$

$$^3\mathbf{4}^* + \mathrm{R'H} \xrightarrow{k_a} \mathbf{10} + \mathrm{R'}\cdot \qquad (3)$$

$$\mathbf{10} \longrightarrow p\text{-cresol} + \cdot\mathrm{CCl_3} \qquad (4)$$

$$^3\mathbf{4}^* + \mathrm{Q} \xrightarrow{k_q} \mathbf{4} + {}^3\mathrm{Q}^* \qquad (5)$$

$$\mathbf{7} \xrightarrow{k_1} \mathbf{8} \qquad (6)$$

$$\mathbf{7} \xrightarrow{k_2} \mathbf{4} \qquad (7)$$

$$\mathbf{7} + \mathrm{ROH} \xrightarrow{k_3} \mathbf{5} + \mathrm{Cl^-} + \mathrm{H^+} \qquad (8)$$

$$\mathbf{7} + \mathrm{Cl^-} \xrightarrow{k_4} \mathbf{9} + \mathrm{Cl^-} \qquad (9)$$

to ground-state dienone, although a symmetry-forbidden reaction, is included because of some evidence that this may be the pathway for the residual inefficiency (usually 15–25%) observed in these rearrangements.[12,13] From this scheme, the lifetime of zwitterion 7 in the absence of added chloride is

$$1/\tau_z = k_1 + k_2 + k_3[\mathrm{ROH}] \qquad (10)$$

and the following relationships for product yields as a function of chloride concentration can be derived, where Φ_z (the yield of zwitterion 7) = $k_r\tau_T$.

$$(\Phi_0/\Phi)_5 = (\Phi_0/\Phi)_8 = 1 + k_4\tau_z[\mathrm{Cl^-}] \qquad (11)$$

$$\frac{\Phi_9}{\Phi_z - \Phi_9} = k_4\tau_z[\mathrm{Cl^-}] \qquad (12)$$

The quantitative data for competitive formation of **8** and **9** in CF_3CH_2OH as a function of LiCl concentration, plotted according to the expressions on the left side of eq 11 and 12, respectively, give excellent straight lines of common slope, 7.8 ± 0.4 M^{-1}, as required by the kinetic scheme. The slope $k_4\tau_z$ cannot be broken down to give values of k_1, k_2, and k_3 because of the current lack of information about the magnitude of k_4. Similarly, the data for formation of ethers **5** (R = isopropyl) and **9** in 2-propanol as a function of [LiCl], plotted as above, also give straight lines of common slope = 2.03 ± 0.15 M^{-1}. In this solvent *p*-cresol is a major product, and addition of LiCl up to 1 *M* reduced its yield by at most 10%,[14] much less than the effect on the yield of **5**. This is consistent with the scheme and the earlier postulate[4,9] that *p*-cresol is derived directly from the dienone triplet by a hydrogen abstraction–radical fragmentation pathway,[9a] and that the zwitterion is a later intermediate along the reaction pathway. Quenching experiments show that all photoproducts of **4** are derived from a common triplet excited state intermediate.[15]

Addition of LiCl was found to have no effect on the efficiency of formation of lumiketone from 4,4-diphenylcyclohexadienone[1] (**11**) and α-santonin (**12**),[16] suggesting that the zwitterions from these two dienones have much shorter lifetimes τ_z than for **7**. This is reasonable if τ_z in nonnucleophilic solvents is determined mainly by the rate constant k_1 for [1,4] sigmatropic rearrangement to lumiketone. In the intermediate stage of this rearrangement, positive charge should be localized to some extent on C_6. Thus, the rearrangement rate should be decreased in the case of **7** → **8** because of the electron-withdrawing CCl_3 group, in contrast to the stabilization offered by phenyl and alkyl substituents, increasing k_1 in the cases of **11** and **12**.

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[12] K. Liu, unpublished results from these laboratories.

[13] H. E. Zimmerman and G. Jones, II, *J. Amer. Chem. Soc.*, **92**, 2753 (1970); D. I. Schuster and W. V. Curran, *J. Org. Chem.*, **35**, 4192 (1970).

[14] This is probably due to a salt effect on reaction 2, increasing Φ_z.

[15] S. Denver and K. Liu, unpublished results.

[16] D. I. Schuster and A. C. Fabian, *Tetrahedron Lett.*, 1301 (1968); M. H. Fisch and J. H. Richards, *J. Amer. Chem. Soc.*, **85**, 3029 (1963), and earlier references cited in these papers.

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*Book Reviews**

The Interpretation of Vibrational Spectra. By D. Steele (University of London). Barnes and Noble, Inc., New York, N. Y. 1971. 67 pp. $4.00.

This softbound volume is a workbook for teaching interpretation of infrared spectra of organic molecules. There is an 11-page introduction to vibrational spectroscopy, and the rest of the book consists of the spectra of 26 compounds, each of which is analyzed on the following page for the structural information that can be deduced from it. An unusual feature of the book is a "Flow Chart," reproduced on an inside fold-out of the front and back covers. It is a systematized key to infrared spectra, wherein to look up a given band frequency and find out, firstly, the possible origins of it, and, secondly, other bands to look for that will confirm, extend, or modify the interpretation. It is all very handy, but the book is such a wee thing!

Crystal Structures. Second Edition. Volume 6. Part 2. By R. W. G. Wyckoff (University of Arizona). Wiley-Interscience, New York, N. Y. 1971. viii + 615 pp. $37.50.

This latest volume in this standard work attests to the steadily mounting rate at which crystal structures of organic compounds are being determined. In order to keep the large amount of mate-

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* Unsigned book reviews are by the Book Reviews Editor.

rial in manageable form, the presentation is now more condensed than in the previous edition, and packing drawings have been almost completely eliminated.

In this part, compounds containing two or more benzene rings and condensed ring systems such as naphthalene and coronene, are listed. For each are given the crystal system, dimensions of the unit cell, space group, parameters of the atoms, a projection of the structure, and a schematic drawing giving angles and bond distances, plus a very brief descriptive paragraph. The references are presented in a peculiar fashion that requires the reader to consult two separate lists. The compounds are arranged in a systematic fashion, but there is also a name index and a formula index.

XXIInd International Congress of Pure and Applied Chemistry, Sydney, 1969. Plenary Lectures. Butterworth's Scientific Publications, London. 1971. 287 pp. £7.50.

This book contains the fourteen plenary lectures, all but one in English; four of them constitute the symposium on Fifty Years of Valence Theory (R. S. Mulliken, R. Daudel, J. H. VanVleck, C. A. Coulson). The papers have evidently been carefully written for publication and are not simple transcripts of the lectures. The bibliographies are quite long, and the texts have the character of summarizing reviews, such that these published lectures are a useful addition to the literature and will have substantial reference value.

Introduction to Marine Chemistry. By J. P. Riley and R. Chester (The University of Liverpool). Academic Press, London and New York. 1971. xiv + 465 pp. $17.50.

This book is intended as a text for "undergraduate and postgraduate students of oceanography, chemistry, marine biology, geology and geochemistry," but it serves quite well as a reference book also. It assumes a sound knowledge of inorganic and physical chemistry, as well as fundamental mathematics, geology, and biology, and makes no concessions to the ill prepared. There are no pedagogic accoutrements, such as problems, but there are excellent lists of references, which include more journal articles than books, and do not shy away from foreign languages. There are thirteen chapters, dealing with composition of sea water, dissolved gases, physical processes, organic substances and nutrients and their production, and the nature of sediments. There are lots of diagrams, graphs, and tables, but few pictures. An author index and a detailed index help to make this a valuable book.

Adsorption of Organic Compounds on Electrodes. By B. B. Damaskin, O. A. Petrii, and V. V. Batrakov (Moscow State University). Translated by E. B. Uvarov and edited by Roger Parsons. Plenum Press, New York, N. Y. 1971. xvi + 499 pp. $35.00.

This is a book written by three of the younger workers in the well-known institute for fundamental electrochemistry in Moscow.

The book starts by reviewing the methods of studying organic adsorption on mercury. The middle section is concerned with organic adsorption on solid electrodes, and the last part concerns the controversial application of electrocapillary thermodynamics to adsorption on solids.

The book is rich, not only in its tremendous material (2000 references) but because it is so leisured and detailed. The whole story is given. The book breaks the monotonous practice of so many books in which the work of the country of origin is overstressed: eight out of twelve of the first dozen quoted authors are non-Russians. Would that our own books could treat Russian work with the same acumen and knowledge with which this book treats the work of the rest of the world. The solidity, and stress upon facts and thermodynamics, which this book exhibits has, of course, another side: it somewhat underplays the modelistic side of such studies.

This book is certainly a "must" for fundamental electrochemists, and also those physical chemists who would like to read a book about physical chemistry which is written in a Rolls Royce manner. The book is an "Alpha" (Lorenz)—there won't be as good a one in the field for a long time.

J. O'M. Bockris, *University of Pennsylvania*

Organic Semiconductors and Biopolymers. By L. I. Boguslaskii and A. V. Vannikov (Academy of Sciences of the USSR, Moscow). Plenum Press, New York, N. Y. 1970. xii + 221 pp. $18.50.

This is an English translation of a volume published in Russian in 1968. The preface states that the intent of the translation is to acquaint Western specialists with Soviet work, which has concentrated mostly on polymeric materials. The rather dated references to the Russian literature—there are few citations later than 1966—may be helpful in this regard, but the text itself is disappointing. It appears hastily put together with no overall organizing theme.

The chapters "Biology and Organic Semiconductors" and "Prospects of the Practical Application of Organic Semiconductors" are probably the ones most readers would turn to first, and they are particularly disappointing. The former is a cursory review of several biological topics, such as oxidative phosphorylation, which have no obvious connection to the body of organic semiconductor research. Since this is the only place where biological topics are discussed, the title of the book is somewhat misleading. The chapter on practical applications is speculative. Indeed, after passing through a maximum nearly ten years ago, organic semiconductor research has withered precisely because no practical applications have been forthcoming.

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General Electric Company, Research and Development Center

Modern Aspects of Solid State Chemistry. Edited by C. N. R. Rao (Indian Institute of Technology). Plenum Publishing Corp., New York, N. Y. 1970. xiii + 626 pp. $27.50.

A Winter School in Solid State Chemistry was organized in November 1969 by C. N. R. Rao at the Indian Institute of Technology, Kanpur, India, to provide an up-to-date background in solid state chemistry for scientists and teachers in India. The lectures were given over a six-week period starting in November 1969 to about 100 participants, from various universities. In order to extend the benefit of these lectures to a wider audience, Rao has now published a condensation of these lectures in book form.

The book includes twenty-two chapters (from Lattice Dynamics by J. Mahanty to Phase Transformations in Solids by C. N. R. Rao) written by the lecturers summarizing the contents of more than 200 hours of lecture time. Many of the lecturers will be unknown in the West, but J. M. Honig of Purdue, J. S. Anderson of Oxford, and N. Menyuk of the MIT Lincoln Laboratory are well-known scientists in the Western World, and the chapters maintain the same quality throughout. Although my knowledge of some of the fields covered is scant, those that I am more familiar with seemed to be very well covered.

I had anticipated from the low level of solid state research in India that the book would be highly theoretical, and indeed many chapters start with a presentation of theory that probably would leave most graduate students behind. However, I was glad to find also in most sections discussions of experimental details and results on real compounds which were quite up to date. These were augmented with well-prepared tables, diagrams, and figures to give a well-rounded picture of each subject.

This book will make an excellent source book for libraries dealing with solid state physics and chemistry at the broadest levels because many of the subjects covered are not found in standard solid state physics texts, yet are part of the general subject of solids, and one might use it as one would an encyclopedia to get a first look into a field one had not previously considered important. I think that it should serve its stated purpose of helping a wider audience of teachers get a broad perspective in the field for teaching. It can also be recommended to a bright graduate student looking into some specialty for the first time.

Thomas B. Reed, *Massachusetts Institute of Technology*

Vinyl and Diene Monomers. Part 2. Edited by Edward C. Leonard (Kraftco Corporation). Wiley-Interscience, New York, N. Y. 1971. xi + 479–1202 pp. $37.50.

The purpose of this book, according to the preface, is to emphasize commercial manufacture, laboratory synthesis, purification, and physical and chemical properties of vinyl monomers. The contributors to this book are scientists whose achievements should have them eminently qualified for such an undertaking. This volume presents a rather comprehensive collection of information relating to the monomers concerned and covers their histories from discovery up to recent commercial positions. The contributions of individual authors vary somewhat in style and content and allow each to inject his personal feelings and interests into the reviews. The authors are easily understood.

Some of the monomer preparations given and some of the historical information given would have to be considered "trivia" and are of little worth except to record historical facts. The greatest value of this work probably lies in its detail of manufacturing processes, economics, and end uses. It does face the problems of such a review in that some processes, reported as current practice, are now already obsolete by at least five years.

This book will be of greatest value to the reader who is not well versed in the subject, but it will also be of real worth to the knowledgable scientist as a very detailed and highly referenced work. In spite of the few minor weaknesses, this book should be a very useful and worthwhile library addition.

K. M. Taylor, *Monsanto Company*

The Chemical Analysis of Electroplating Solutions. By TERENCE H. IRVINE (Lyon Chemicals, Inc.). Chemical Publishing Co., Inc. New York, N. Y. 1970. vii + 183 pp. $8.50.

The author's stated purpose is to provide the chemist with the knowledge necessary to understand the analytical method rather than just use it. The first chapter, "Analytical Techniques," and the Appendix, which contains several useful charts, serve this purpose well, but the theory behind analytical procedures is too complex to be explained to a person without prior training in the subject except in a much larger book.

Analytical work with plating solutions is done by two different types of personnel. The highly trained analytical chemist will have little use for this book. He already knows "why." The normal control analyses of an electroplating facility are usually performed by a technician. He uses rapid simplified analytical procedures provided by the supplier of the proprietary electroplating solutions employed. Presumably, it is for this technician that the book is intended. However, few technicians will have the background necessary to understand the significance of "buffer systems," "dissociation constants," "milliequivalents," "half reactions," etc., and the "Understanding the Process" explanation following each analytical procedure will be beyond his understanding.

The analytical procedures themselves are more sophisticated than those normally in use for electroplating control. Chromic acid is normally estimated by specific gravity measurement in a chromium plating solution rather than by a volumetric analysis of the chromium content. Zinc and cadmium are determined by EDTA rather than by ferrocyanide titration with uranyl acetate as an external indicator.

The author has proposed a difficult objective and will only be successful with a small percentage of analytical technicians (or chemists) concerned with electroplating solution analysis.

C. F. Waite, *Chrysler Corporation*

Topics in Organic Polarography. By P. ZUMAN (Clarkson College). Plenum Press, New York, N. Y. 1970. ix + 530 pp. $18.00.

This book is a collection of forty-three original papers by the author on (1) the preparative methods used in determining electrode processes involving organic compounds and (2) the polarography of carbonyl compounds, activated C–N, C–S, and C–O bonds, azomethines, benzonitriles, and nonbenzenoid aromatic compounds such as sydnones, azulenes, and tropylium ions in aqueous solution. Continuity of the subject matter is accomplished by grouping the publications into eight parts; each part is preceded by an introduction of the material involved. The introductory part relates all of this material to the general field of organic polarography.

The publication of such a compilation is defensible and useful since the topics covered are varied and illustrate most of the applications of polarography to problems in organic chemistry. The papers deal with the determination of equilibrium constants, rate constants, reaction mechanisms, and the optimal conditions for the electrolytic preparation of organic compounds. Comparison of reactivities of organic compounds and correlation of structure with polarographic data are also well illustrated.

The usefulness of this book would have been increased if an index had been provided of the compounds studied, the techniques employed, and the applications made.

Stanley Wawzonek, *University of Iowa*

Recent Topics in Mass Spectrometry. Edited by R. I. REED (University of Glasgow). Gordon and Breach Science Publishers, New York, N. Y. 1971. ix + 357 pp. $29.50.

The chapters in this book are based on lectures which were delivered at the NATO Advanced Study Institute in Mass Spectrometry held in Lisbon, in 1969. Although the Study Institute instructed the participants in basic aspects of the theory and practice of mass spectrometry, the discussions in the book cover only the more advanced material which was presented. Twelve topics are included, each written by a scientist actively working in the area under consideration. The Institute was held in 1969 and references are made to articles published during that year.

Half of the topics are related to ionization processes and techniques and to types of ions formed. For example, Wacks and Scott have written a chapter on multiply charged ions, and Beckey and Levson report results of a study of rearrangement reactions by field ionization mass spectrometry. However, ion cyclotron resonance spectroscopy, chemical ionization, and ion kinetic energy spectrometry are not included among the topics. Quayle has surveyed many of the industrial applications of mass spectrometry; applications in the petroleum industry are emphasized whereas applications in biochemistry and medicinal chemistry are not covered. Some of the topics are discussed in a general nature, such as metastable ions by Robert-Lopes and photoionization and photoelectron spectroscopy by Collin. However, other chapters are more narrow in scope. The only class of organic or organometallic compounds discussed is ferrocenes and related complexes by Junk and Svec. High resolution mass spectrometry is included as a topic, but only its applications to complex mixtures are presented by Sharkey. Author, compound, and subject indexes are included, along with a list of participants at the Institute.

There is no central theme connecting the chapters, and the emphasis and level of sophistication vary from chapter to chapter. Thus, each reader will have to scan the Table of Contents and read the introductions to the chapters in order to determine how useful the book will be to him.

Don C. DeJongh, *Professeur invité*
Université de Montréal

Organotin Compounds. Edited by ALBERT K. SAWYER (University of New Hampshire). Marcel Dekker, Inc., New York, N. Y. 1971. xiv + 252 pp. $30.00.

This book is the first of a three-volume treatment of organotin chemistry designed to provide a much needed comprehensive, current coverage of this highly active area of research. The treatment has been divided into chapters each dealing with a particular element or group of related elements bonded to organotin species, and written by one or more international authors recognized for their expertise in the field. After a short introductory chapter on the scope, history, and importance of the field, this volume deals with tin–hydrogen, tin–halogen, and tin–oxygen bonds.

The chapter on organotin hydrides by E. J. Kupchik does an excellent job of describing their preparations and reactions, particularly as applied to organic synthesis, and presents an exhaustive bibliography of work in these areas. The principal weakness of the chapter is the limited description of physical properties and molecular structure studies.

The chapter on organotin halides by G. P. Van der Kelen, E. V. Van den Berghe, and L. Verdonck provides an excellent summary of the synthesis, chemical and physical properties, and structure and bonding of these compounds and their coordination complexes where the tin coordination number is greater than four. A bibliography of 554 references is included.

The final chapter by A. J. Bloodworth and A. J. Davies deals with the Sn–O bond in hydroxides, oxides, peroxides, alkoxides, and alkyl peroxides. Other tin–oxygen compounds will be treated in the subsequent volume. Again an exhaustive bibliography is included, along with a descriptive summary of preparations, structures, and physical properties.

This volume is a most valuable, up-to-date review of the areas of organotin chemistry mentioned above and should prove invaluable to workers in the field and related fields. If the other volumes are of comparable quality, the series will represent a much needed comprehensive review of the current state of research in organotin chemistry.

E. O. Schlemper, *University of Missouri*