

in the case of CH<sub>3</sub>I. A full report of our kinetic and mechanistic studies will be presented in a subsequent paper.

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## References and Notes

- (1) K. R. Mann, J. G. Gordon II, and H. B. Gray, *J. Am. Chem. Soc.* **97**, 3553 (1975).
- (2) This complex was prepared by a standard method: J. Chatt and L. M. Venanzi, *J. Chem. Soc.*, 4735 (1957).
- (3) Anal. Calcd for [Rh<sub>2</sub>(bridge)<sub>4</sub>](BPh<sub>4</sub>)<sub>2</sub>·2CH<sub>3</sub>CN: C, 66.37; H, 5.41; N, 10.75. Found: C, 65.59; H, 5.49; N, 10.24.
- (4) According to simple Hückel theory, the tetramer, hexamer, and octamer transition energies are given by:  $E_{D_2} = E_D + \beta$ ;  $E_{D_3} = E_D + 2^{1/2}\beta$ ;  $E_{D_4} = E_D + [(5^{1/2} + 1)/2]\beta$ ;  $E_D = E(1a_{2u} \rightarrow 2a_{1g})$  and  $\beta = \beta_{1a_{2u}} + \beta_{2a_{1g}}$ . Theory and experiment accord closely for  $\beta = -5500 \text{ cm}^{-1}$ :  $E_{D_2}(\text{calcd}) = 12\,500$ ,  $E_{D_2}(\text{obsd}) = 12\,820$ ;  $E_{D_3}(\text{calcd}) = 10\,220$ ,  $E_{D_3}(\text{obsd}) = 10\,080$ ,  $E_{D_4}(\text{calcd}) = 9\,100$ ,  $E_{D_4}(\text{obsd}) = 8\,770 \text{ cm}^{-1}$ . The broad absorption system centered at about 1735 nm (5760  $\text{cm}^{-1}$ ) probably represents overlapping bands owing to oligomers with  $n > 4$ . For  $n = \infty$ , the calculated limit is  $E_D + 2\beta$ , or 7000  $\text{cm}^{-1}$ .
- (5) When the I<sub>2</sub> oxidation was performed at high concentrations of [Rh<sub>2</sub>(bridge)<sub>4</sub>]<sup>2+</sup>, a green intermediate species was observed. The concentration of this intermediate was maximal for the stoichiometric ratio 2[Rh<sub>2</sub>(bridge)<sub>4</sub>]<sup>2+</sup>:I<sub>2</sub>. Furthermore, the concentration of the intermediate was found to be proportional to [[Rh<sub>2</sub>(bridge)<sub>4</sub>]<sup>2+</sup>]<sup>2</sup>. The green species is formulated as [I-D-D-I]<sup>4+</sup>.
- (6) Anal. Calcd for [Rh<sub>2</sub>(bridge)<sub>4</sub>]<sub>2</sub>(I<sub>3</sub>)<sub>2</sub>: C, 15.0; H, 1.50; N, 7.05; I, 63.5. Found: C, 15.8; H, 1.65; N, 7.09; I, 62.2.
- (7) Anal. Calcd for [Rh<sub>2</sub>(bridge)<sub>4</sub>Br<sub>2</sub>](Br<sub>3</sub>)<sub>2</sub>: C, 19.67; H, 1.98; N, 9.17. Found: C, 19.97; H, 1.93; N, 9.06.
- (8) Anal. Calcd for [Rh<sub>2</sub>(bridge)<sub>4</sub>(CH<sub>3</sub>)(I)](BPh<sub>4</sub>)<sub>2</sub>·2CH<sub>3</sub>CN: C, 60.66; H, 5.09; N, 9.69. Found: C, 58.74; H, 5.08; N, 9.29.
- (9) R. A. Levenson and H. B. Gray, *J. Am. Chem. Soc.*, **97**, 6042 (1975).
- (10) Complexes of the type [Rh<sub>2</sub>(CNR)<sub>6</sub>X<sub>2</sub>]<sup>2+</sup> obtained by mixing solutions of [Rh(CNR)<sub>4</sub>]<sup>+</sup> and *trans*-[Rh(CNR)<sub>4</sub>X<sub>2</sub>]<sup>+</sup> (R = alkyl; X = halide) have been reported [A. L. Balch and M. M. Olmstead, *J. Am. Chem. Soc.*, **98**, 2354 (1976)]. These adducts exhibit electronic spectral properties that are very similar to those of analogous [Rh<sub>2</sub>(bridge)<sub>4</sub>X<sub>2</sub>]<sup>2+</sup> complexes. Of the two structures for [Rh<sub>2</sub>(CNR)<sub>6</sub>X<sub>2</sub>]<sup>2+</sup> species suggested by Balch and Olmstead, our results favor the one containing a direct Rh(II)-Rh(II) bond in preference to the Rh-X-Rh-X alignment. Balch and Olmstead also argued that their spectral data were more consistent with a Rh(II)-Rh(II) bonded species.

Nathan S. Lewis, Kent R. Mann  
J. G. Gordon II, Harry B. Gray\*

Contribution No. 5374  
Arthur Amos Noyes Laboratory of Chemical Physics  
California Institute of Technology  
Pasadena, California 91125

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## Book Reviews\*

**Aldehydes—Photometric Analysis. Volume 3.** By EUGENE SAWICKI and CAROLE R. SAWICKI. Academic Press, New York and London, 1976. xiv + 341 pp. \$26.75.

Volumes 1 and 2 of this work, which is a part of the series "The Analysis of Organic Materials" edited by Belcher and Anderson, appeared last year and have been reviewed; four more volumes are promised. This work is really of more general applicability than its title suggests, for its concern is with analysis of other types of substances, which can be converted to aldehydes in one way or another. The authors anticipated future development of the subject by including discussions of other reactions that give rise to aldehydes, even when no analytical application has yet been published.

More than 30 aldehydes, including acetaldehyde, aldoses, aldosterone, and various amino aldehydes, are covered in this volume, but the actual emphasis is on the substances from which they can be formed. Under acetaldehyde, for example, are considered acetals, 2-alkenes, ethylene oxide, several glycols, phenothiazines, pyruvic acid, etc. The aldehydes are taken up in alphabetical order, so one should have the full set, but this volume like the earlier ones, is separately indexed. It looks very useful.

**Concise Etymological Dictionary of Chemistry.** By S. C. BEVAN, S. J. GREGG, and A. ROSSEINSKY. Applied Science Publishers, Barking, Essex, 1976. ix + 140 pp. £7.00.

This is a rather small book, especially in terms of the number of words defined. Nevertheless, it is adequate and promises to be very useful. Its purpose is, of course, not so much to define words as to give their origin and the roots, mostly Greek and Latin, from which they are derived. Many of these etymologies are obvious, such as "citric acid" from citrus, but such words as "eutrophication" (from Greek roots for "well" and "to nourish"), and "griseofulvin" (from Latin roots for gray and yellow) become more comprehensible when their origins are explained. An understanding of these matters can be helpful when the necessity arises to coin new terms.

It is not difficult to spot gaps in a work of this kind (hosts of natural products are omitted, on practical grounds), but they are not serious. A more important fact is that the definitions given consistently show a high level of scientific as well as etymological scholarship. There are

also occasional euphemisms of charming delicacy, as in the etymology of "viscous", which comes from the Latin for "full of bird lime". This term might be put to new use by authors wishing to dispute a referee's unkind comments, by alleging that the referee is truly viscous.

**Immunology. Readings from Scientific American.** Edited by F. M. BURNETT. W. H. Freeman & Co., San Francisco, Calif. 1976. vi + 275 pp. \$14.00 (hard cover); \$7.00 (soft cover).

The chapters in this book are reproductions of the authoritatively written and sumptuously illustrated articles that originally appeared in "Scientific American". Those selected date from 1955, stated by the editor to mark the beginning of modern immunology. In that year, the Salk vaccine came into general use; the advances since then "have been specially concerned with bringing immunology into step with the rest of biology . . .". The understanding of protein biosynthesis and of the role of DNA in coding information brought consideration of immunology to the molecular level during the past twenty years. There is much to interest organic and biological chemists in this book, which is especially helpful in providing broad orientation to those who are not specialists in the area.

**Carbanions: Mechanistic and Isotopic Aspects.** By E. BUNCEL (Queen's University). Elsevier Scientific Publishing Co., Amsterdam, The Netherlands, 1975. x + 270 pp. \$30.80.

This book is a clear and highly readable account of some of the mechanistic and structural aspects of carbanion chemistry. The presentation is at an introductory level and would be suited to undergraduate as well as graduate students. Chapter One is a very good introduction to structural considerations for carbanions and the kinetic and equilibrium acidity of carbon acids. The remaining six chapters discuss the topics of stereochemistry of carbanion reactions, tautomerism, nonclassical carbanions, enolate and homoenolate rearrangements, orbital symmetry control in carbanion rearrangements, and carbanions in reactions of organometallic compounds. Discussion of the last topic is primarily restricted to electrophilic substitution reactions of mercury, silicon, and tin. No discussion of the role of carbanions in synthesis is attempted. The book has over 700 references, up to 1973, and has an author and reasonably complete subject index.

Michael W. Rathke, Michigan State University

\* Unsigned book reviews are by the Book Review Editor.

**The Primary Battery. Volume 2.** Edited by N. C. CAHOON and G. W. HEISE (Union Carbide Corp.). John Wiley & Sons, Inc., New York, N.Y. 1976. xvi + 528 pp. \$37.50.

This second volume continues on from the first with information on additional commercial or military primary battery systems and testing. Despite the title, there is a well-written chapter on reversibility of battery systems which covers rechargeable batteries and system-design criteria.

The editors have assembled an extremely well-qualified group of authors. Mr. Cahoon's chapter on Leclanché and zinc chloride cells gives one an excellent technical background without too many details of art. Similarly very good chapters on magnesium, aluminum, and low-temperature cells are provided. Thermal and water-activated batteries are well described. There is a valuable chapter on organic cathodes for cells. Two chapters provide insights, techniques, and nomenclature for the testing and evaluation of batteries. A final chapter on sources of energy and energy conversion methods rounds out the volume very well.

The text supplies an excellent concise background in battery technologies for the interested student, scientist, or engineer and is a fine indexed reference. It is surprisingly complementary to similar recently published efforts.

Although the price is rather impressive for an individual to pay, these volumes of the Electrochemical Society Series deserve a place in most technical libraries.

Brooke Schumm, Jr., *Union Carbide Corporation*

**Advances in Polymer Science (Fortschritte der Hochpolymeren Forschung). Volume 15.** Edited by H. J. CANTOW ET AL. Springer-Verlag, Berlin—Heidelberg—New York. 1974. iii + 155 pp. \$27.80.

The 15th volume of this popular series offers four reviews in areas of polymer science which are of current interest to researchers in both industry and academia. The problem of oligomerization of ethylene by soluble Ti-Al and Zr based Ziegler-Natta type catalysts is reviewed by G. Henrici Olivé and Salvador Olivé. The authors also deal with the kinetics and mechanism of the various systems. A. Zambelli and C. Tossi follow with an excellent discussion on the stereochemistry of propylene polymerization. Emphasis is on the mechanism of the polymerization, especially the stereochemical aspects. The authors show, by carefully evaluating the evidence, that propagation proceeds by monomer insertion into carbon-transition metal bonds via an activated four-center complex. Steric control results in isotactic or syndiotactic placements depending on whether the insertion is into a metal-primary or metal-secondary carbon bond. A chapter by Chien Da S. Lee and W. H. Daly focuses on polymers which contain the biologically important thiol function. Various synthetic approaches leading to these polymers are reviewed, such as the use of vinylmercaptan precursors (e.g., vinyl thioesters, vinyl mercaptals and vinyl thiocarbonates), ring-opening polymerization of cyclic monomers, and the formation of mercaptan-containing condensation polymers. Also discussed is the incorporation of the mercaptan function into several types of preformed polymers and proteins. The closing chapter is a thorough study by Yu V. Kissin on the structures of copolymers of high olefins. After evaluating the various experimental approaches to the study of copolymer structures, the author discusses the experimental results of studies pertaining to ethylene, propylene, butene, styrene, and other olefin copolymers with a variety of olefins, including higher and branched olefins. The review also contains a discussion of compositional inhomogeneity of olefin copolymers and the activities of various olefins in homo- and copolymerization. A useful table of reactivity ratios is included. The various authors have succeeded in clearly presenting their material, and the result is a volume that undoubtedly will contribute to the popularity of this polymer science series.

Johannes Smid, *State University of New York  
College of Environmental Science and Forestry*

**The Organic Chemistry of Electrolyte Solution.** By JOHN E. GORDON. John Wiley & Sons, Inc., New York, N.Y. 1975. 554 pp. \$27.50.

As late as 50 years ago, ionic reactions were still believed to be the domain of inorganic chemistry, whereas organic reactions were thought to proceed by nonionic mechanisms. This belief has been shattered by the continuously increasing volume of experimental ev-

idence amassed during the last few decades. The participation of ionic intermediates in numerous organic reactions is undeniable now, and hence organic chemists have to be acquainted with the various aspects of electrolyte solutions, especially with those taking place in the nonaqueous systems.

"The Organic Chemistry of Electrolyte Solution" by John E. Gordon is therefore timely published. The author surveyed the whole field of ions' interaction with solvents and their effect on organic solutes as well as on the course of their reactions. The book is divided into three large chapters, each treating the discussed problems from the thermodynamic and kinetic points of view.

The first chapter deals with the effects exerted by salts on the solubility and behavior of organic compounds in a variety of solvents. The presence of salts affects the activity coefficients of other solutes, and a rigorous thermodynamic treatment of this phenomenon is outlined. An effort is made to explain the discussed phenomenological relations in terms of the various forces operating in these systems. In addition, numerous semiempirical relations are reviewed and pertinent references are provided to the original papers.

Salts affect the acid-base equilibria of organic substrates, their electronic spectra, and often their conformation. These phenomena are reviewed and their origins briefly explained.

Finally, salt effects on rates of organic reactions are extensively reviewed in the last part of this chapter.

The second chapter treats the problems of ions' solvation in aqueous and nonaqueous solvents. The structure of solvation shells is examined, the various models proposed in the literature are reviewed, dynamics of formation of the solvation shell are discussed, etc. The importance of the newest solvating agents is stressed and illustrated. Again, an effort is made to understand the factors governing the ion solvation in terms of interactions between the pertinent molecules.

In the last chapter, the ion-association phenomena are discussed. The treatment includes the thermodynamics and kinetics of formation of low aggregates, such as ion pairs, triple ions, etc., and is extended to micelles and polyions. Physical as well as chemical consequences of ions' aggregation are considered, the latter being particularly important to organic chemists interested in reactivities of carbonium ions and carbanions.

This is not a textbook, but the interested reader will find numerous references to texts and original papers dealing with the various aspects of organic ionic reactions and with the effects exerted by ions on organic substrates. This monograph is most useful as a reference book, especially for a newcomer. The literature survey is very extensive; approximately 1500 references are amassed covering the literature up to 1973.

The author should be congratulated for collecting and elucidating in one volume the immense amount of material pertaining to this large subject.

Michael Szwarc, *SUNY, Syracuse*

**Progress in Inorganic Chemistry. Volume 19.** Edited by STEPHEN J. LIPPARD (Columbia University). John Wiley & Sons, Inc., New York, N.Y., 1975. 367 pp. \$22.50.

This volume contains reviews of the literature of the following: (a) the oxidation-reduction reactions of metal-metal bonds; (b) transition metal complexes containing tridentate amino acids; (c) cryogenic inorganic chemistry (involves the use of matrix-isolation infrared and Raman spectroscopic techniques); (d) the structural and magnetic properties of some of the bridged complexes of the first row transition metals; and (e) the coordination chemistry of indium. Each review has an extensive bibliography with 1972-73 publications being the latest entries. Many tables of data are included along with numerous graphs and diagrams. Each review has well-defined scope and is well written. A cumulative index for Volumes 1-19 is included.

Several groups of people should find the volume valuable to their work. Investigators working in fields related to the review topics should find direct application of the data presented and the techniques described. Others will be able to keep abreast in their knowledge of these topics. Teachers and students should use the material to enrich their studies.

The goals set forth by the editor of this series of volumes will be well served by this latest volume; it provides a "forum" for evaluation of data and presentation of advanced knowledge and will also lead to "cross-fertilization" in diversified fields of study.

Lewis A. Walker, *Goucher College*