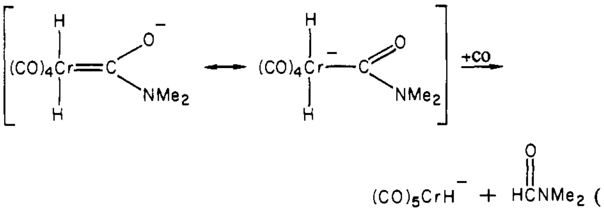

(11)

monoxide dissociation (reaction 9) is proposed in accord with Casey's observations.[7] The carbene complex is redrawn as an anionic carbamoyl complex in reaction 11 to show more clearly the postulated reductive elimination step. Several other binary transition-metal carbonyl complexes were investigated under analogous conditions; the results are presented in Table I. Though the activating nucleophile (NMe_2^-) is incorporated in the product (DMF) of the above reactions, precluding catalytic operation, the results nevertheless suggest that nucleophilic attack at transition-metal-bound carbon monoxide can indeed provide the activation required for reduction by molecular hydrogen under exceptionally mild conditions.

Several of the stoichiometric systems using HMPA as solvent were observed[14] to generate trimethylamine (Me_3N) in addition to DMF (see Table I). Though the yields of Me_3N were quite low (2–8%), several significant observations with regards to its formation in the $Cr(CO)_6/LiNMe_2$ reaction were made. If the reaction was run under deuterium (D_2) instead of hydrogen, the Me_3N product displayed a mass spectrum consistent with Me_3N-d_3, while if carbon-13 enriched $Cr(CO)_6$ was used, the Me_3N was similarly enriched. Hydrogenation at 70 °C instead of 130 °C gave no Me_3N, though DMF was still formed. Finally, hydrogenation in the presence of *N*,*N*-dimethylacetamide gave rise to both Me_3N and dimethylethylamine. Apparently, then, Me_3N arises from further reduction of the primary product DMF. Given the mechanistic scheme suggested in reactions 8–11, it seems likely that the active hydrogenation agent is the $(CO)_5CrH^-$ anion.[15] Indeed, we have found that $\{[(C_6H_5)_3P]_2N\}^+$-$[(CO)_5CrH]^-$ quantitatively reduces several amides (DMF, *N*,*N*-dimethylacetamide, and *N*,*N*-diethylacetamide) to the corresponding tertiary amines (Me_3N, dimethylethylamine, and triethylamine, respectively) when stirred with an excess of the amide in HMPA solvent at 130 °C under 35 psi of hydrogen (the same conditions used for the carbene hydrogenations). These are exceptionally mild conditions for a transition-metal mediated reduction of an amide, and studies to elucidate the mechanism of this reduction are currently in progress. The fact that $(CO)_5CrH^-$ can indeed reduce DMF to Me_3N gives credence to the proposed mechanism for DMF (and Me_3N) formation,[16] though the reasons for the low yields of Me_3N obtained are unknown. The NMe_2^- unaccounted for as DMF and Me_3N appears to be present as a metal complex (with either lithium or chromium; dimethylamine is produced upon hydrolysis), and perhaps this in some way interferes with the hydrogenation step.[17]

Homogeneous systems have been found, then, which are able to convert transition-metal-bound carbon monoxide to a formyl group (in DMF) and a methyl group (in Me_3N) once it is activated by nucleophilic attack. Though the activating nucleophile is incorporated in the products observed, the results suggest the validity of this approach to carbon monoxide activation and reduction. Obvious extensions of these reactions to other metals and nucleophiles are being vigorously pursued.

Acknowledgment. This work was supported by the Department of Energy. K.M.D. thanks the Fannie and John Hertz Foundation for fellowship support.

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[14] Furthermore, the group 6 metals [$Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$] appeared to produce small amounts of lower hydrocarbons [CH_4, C_2H_4, C_2H_6, C_3H_6, C_3H_8, 1-C_4H_8, and *n*-C_4H_{10}]. Yields were extremely low, however (typically 0.1–1.0%, based on carbonyl), precluding the labeling studies essential to a critical evaluation of these observations.

[15] The synthesis and characterization of this hydride anion has just appeared in print: Darensbourg, M. Y.; Deaton, J. C. *Inorg. Chem.* **1981**, *20*, 1644–1646. We prepared the bis(triphenylphosphine)iminium salt of this anion in an analogous fashion and are grateful to M. Darensbourg and J. Deaton for supplying us with a preprint of this publication.

[16] The active hydrogenation agent is not necessarily $(CO)_5CrH^-$; in HMPA at 130 °C, this complex may be converted to other species [e.g., $Cr_2(CO)_{10}H^-$] as well as exchange HMPA for CO ligands. As the model studies using preformed $[(CO)_5CrH]^-PPN^+$ show, however, either it or whatever species to which it may be converted is quite active as a hydrogenation agent.

[17] A referee questioned whether reaction of $LiNMe_2$ with H_2, a potential hydride source,[18] could provide an alternate mechanism for CO or DMF reduction in the hydrogenation systems. Control experiments preclude this possibility: (1) a mixture of $LiNMe_2$ and DMF in HMPA under the usual hydrogenation conditions produces no Me_3N; (2) addition of 1 equiv of LiH to the $Cr(CO)_6/LiNMe_2$ system in HMPA does not enhance DMF or Me_3N formation.

[18] Dirian, G.; Botter, F.; Ravoire, J.; Grandcollot, P. *J. Chim. Phys.* **1963**, *60*, 139–147.

Book Reviews

Quantitative Analysis. Fourth Edition. By R. A. Day, Jr., and A. L. Underwood (Emory University). Prentice Hall, Inc., Engelwood Cliffs, N. J. 1980. xi + 660 pp. $12.50.

This particular text has been widely used and survived three editions and field trials with both major and nonmajor chemistry courses. Basically, this text can be used readily by students who have had a course in general chemistry and elementary algebra. The 4th edition has been improved with regard to presentation of classical material such as titrimetric methods, concepts of stoichiometry, and gravimetric methods and separations. The authors also present a more than adequate presentation on errors and the treatment of analytical data. Topics such as propagation of error and test of significance of the result are included and are of value to any scientific field based on measurements.

The organization of chapters appears to be logical and follows a logical sequence of laboratory and classroom presentations, with the exception that the principles of mass measurement and associated problems with the ultimate accuracy of this fundamental measurement are relegated to the experimental part. Yet, historically, the measurement of mass is practically the backbone of analytical chemistry and should be presented following the analysis of error. The practical weighing procedure, the different types of balances, and care of the balances could be left in chapters dealing with laboratory techniques in the back of the book, as is.

This text presents quite an extended treatment on separations. In fact, three chapters are dedicated to liquid–liquid extraction, gas–liquid chromatography, and liquid chromatography. It is noteworthy that in these chapters the authors develop a suitable theoretical base which can be easily assimilated by the average student. Concepts such as multiple extraction, Craig-pseudocountercurrent extraction, and binomial distribution are clearly presented and are not overburdened by advanced material. In addition, concepts dealing with the height equivalent of theoretical plates, HETP, in gas chromatography and the importance of the van Deemter equation are presented clearly. Furthermore, the discussion of the separation factors affecting separation efficiency and detectors is treated adequately at the beginners's level.

In Chapter 5 and 6 the authors state that the pH = $-\log [H_3O^+]$ and they use the example that the pH for a solution having $[H_3O^+] = 0.1$ is equal to 1. This would be in agreement with the original concept proposed by Sørensen stating that pH = $-\log C_{H^+}$. However, the presently accepted definition for pH as modified by Sørensen and Lindstrøm-Lang is based on the activity of hydrogen or hydronium ions rather than on concentrations. It is true that the differences are negligible in dilute solutions, but should not be used indiscriminately for concentrated solutions. Furthermore, it would be desirable to stipulate under what conditions the autoprotolysis constant for water, K_w, can be used as such and what are the fundamental limitations for its usage. This may appear as a superficial criticism; however, if not considered, many practical problems may be ignored.

Oxidation–reduction equilibria have been treated logically and adequately. Practical calculations of potentials during the titration as well as the variety of analytically important reactions are well illustrated. Furthermore, various electrochemical methods used are arranged in a logical sequence.

Introductory chapters dealing with UV–visible, atomic absorption, and emission methods—fluorescence or flame—are adequate for this level.

The problems presented at the end of the chapters appear to be pertinent to the discussion. However, the authors occasionally tend to reach somewhat ahead; for example, in Chapter 3, problem 46 deals with coulometric concepts; this is yet to be discussed in the chapter dealing with electrometric methods. One of the errors dealing with the $Q_{0.90}$ for $n = 3$ does not agree with the tabular values in Dean and Dixon.

The amount of information presented by the authors is clearly sufficient for a two-semester course.

Bruno Jaselskis, *Loyola University of Chicago*

A Guidebook to Biochemistry. Fourth Edition. By Michael Yudkin (Oxford University) and Robin Offord (University of Geneva). Cambridge University Press, New York and Cambridge, U.K. 1980. xi + 261 pp. $44.50 (hardcover), $15.95 (paperback).

The present book is a revised and somewhat expanded edition of "A Guidebook to Biochemistry" originally written by Kenneth Harrison in 1965 and subsequently revised by Yudkin and Offord in 1971. The purpose of this book is to "introduce the reader to the important features of the subject by exemplifying and discussing crucial biochemical concepts." The "Guidebook" is a relatively concise and selective introduction to biochemistry, and is not meant to serve as a comprehensive introductory textbook. It does not contain, for example, any discussion of experimental methods or of certain topics normally found in introductory biochemistry textbooks, such as enzyme kinetics. It contains 23 chapters organized into four sections, entitled Structure and Function of Macromolecules, Metabolism, Molecular Genetics and Protein Synthesis, and Compartmentation and Regulation. In general, I found this book to be interesting, well-written, and quite readable. The explanations of biochemical principles are generally lucid and should be understandable to the undergraduate student or even the general reader. Although the information provided is generally accurate and current, I did detect a few errors of fact. For instance, in discussing biological membranes, the authors state on p 86 that, "The presence of cholesterol (which has a shape that does not fit tightly with aliphatic chains) has a similar effect on mobility as does *cis* unsaturation." In fact, cholesterol condenses and orders lipid bilayers in the biologically relevant liquid–crystalline state, thus reducing mobility, an effect opposite to that produced by cis unsaturation. Similarly, on p 221 the authors state that, "The movement, and the dependence of rate of transport on molecular size, can be completely explained by assuming the membrane to be permeated by pores approximately 0.8 nm in diameter." Much recent work on the passive permeability properties of lipid bilayer and biological membranes can in fact not be completely rationalized by postulating the existence of permanent pores of fixed diameter. Moreover, the major evidence for this postulate, the apparently larger osmotic flux as compared to the exchange diffusion water permeability coefficient, has been shown in most cases to be an experimental artifact resulting from unstirred water layers. Nevertheless, serious errors of fact are relatively few in the book as a whole.

I can recommend this book as a suitable text for a one-term course in biochemistry at the undergraduate university or college level, as auxiliary reading for a course in cell biology or a related area, or for someone seeking a concise and readable overview of the field. It would not be a suitable text for a full-year introductory course in biochemistry. The student with a rigorous chemical and physical grounding might derive greater benefit from reading a more rigorous and detailed treatment of this material than is provided by the "Guidebook". Nevertheless, this book represents a useful addition to the biochemical literature for that audience for which it is intended.

Ronald N. McElhaney, *University of Alberta*

Biochemistry of Nonheme Iron. By Anatoly Bezkorovainy (Rush-Presbyterian-St. Luke's Medical Center, Chicago). Plenum Press, New York. 1980. xviii + 435 pp. $45.00.

This book is Volume 1 in a series concerning the "Biochemistry of the Elements" (Earl Frieden, Series Editor). The author has limited the scope of this volume "... to provide a concise overview of the field of nonheme iron biochemistry." Physical techniques, especially spectroscopy, are not included; rather they are to be provided in Volume 2 which will deal with heme iron biochemistry. Thus readers of Volume 1 will, in all likelihood, also require Volume 2 in order to obtain complete coverage of iron biochemistry.

This volume consists of nine chapters, most of which deal with nonheme iron metabolism. The first chapter is introductory and includes iron distribution data primarily in human tissues. Hematological, physiological, nutritional, and in part clinical aspects are examined in the chapters concerning ferrokinetics, nonheme iron absorption, the interaction of nonheme iron with immature red cells, microbial iron uptake and transferrin antimicrobial properties, and iron storage. These chapters represent well-written, concise, up-to-date reviews of these topics in iron metabolism.

Biochemical aspects are detailed only in the chapters concerning transferrins, ferritins, iron–sulfur proteins, and to a lesser extent miscellaneous nonheme iron proteins (e.g., oxygenases). The most valuable information for biochemists and biophysicists is that presented in the chapters on transferrins and ferritins. The material is thorough and up to date. However, the absence of explanatory information concerning the physical techniques employed to obtain the data presented in these chapters does limit its educational value at the undergraduate level and in part at the graduate level. The iron–sulfur protein chapter represents a reasonable introduction to this class of nonheme iron proteins but has the same problem outlined above for the transferrin and ferritin chapters. It appears to this reviewer that these three chapters, and the one concerning miscellaneous nonheme iron proteins, should have been included in the forthcoming volume so that the biochemistry could have been more extensively developed.

David H. O'Keeffe, *The University of Akron*

Basics of Electroorganic Synthesis. By Demetrios K. Kyriacou (Dow Chemical Co., Pittsburg). Wiley-Interscience, New York. 1981. xiii + 153 pp. $27.50.

Electrochemical techniques have found widespread applications in analytical and inorganic chemistry, but their use by orgainic chemists has not been as extensive. The apparent intention of this book is to introduce the organic chemist to the use of electrolytic methods, especially in synthesis. It assumes no background, covers fundamental concepts in a nonrigorous manner, and then concentrates on applications. This latter part draws heavily on the author's background in electroorganic synthesis by including actual examples from his industrial laboratory. Some of the limitations and problems encountered in electrochemistry that traditionally may have kept organic chemists away are presented in a way that convinces the reader that these problems are no worse than the shortcomings of any synthetic technique. About one-third of the book is a brief survey of electroorganic reactions which draws highlights from the literature rather than reviewing it exhaustively.

The book is written clearly and concisely, and all the practical information will be extremely useful to anyone beginning the use of these techniques. Perhaps the author could have been more exhaustive in his coverage of literature reactions, techniques, and equipments, but as a source of information for the novice organic electrochemist who wants to use the techniques and not only read about them, the book is highly recommended.

Norbert J. Pienta, *University of Arkansas*

Vibrational Spectra and Structure. Volume 9. Edited by J. R. Durig (University of South Carolina). Elsevier Scientific Publishing Co., Amsterdam, The Netherlands. 1981. xvi + 519 pp. $139.00/Dfl. 285.00

The present volume, the ninth in this series, consists of six carefully written reviews which focus on subjects at the forefront of continuing developments in the discipline of vibrational spectroscopy and in the scientific art of deducing details of molecular structure from basic vibrational spectra. The contributed articles each provide thorough coverage of the conceptual and theoretical bases of their subjects and possess a critical air of examination and evaluation. As a result of this emphasis, together with clearly defined goals, these reviews each possess a cohesiveness which can be lacking when broad segments of the literature are merely surveyed for direct content.

In the first chapter, I. Nakagawa and Y. Morioka review the infrared and Raman spectra of optical phonons in ionic crystals having either cubic or uniaxial symmetry. A broad range of spectra is then interpreted with a rigid ion model and a description of the lattice dynamics in the harmonic approximation, using an extension of the Wilson GF-matrix method for free molecules. The authors then demonstrate that values of interionic potentials and latice spacings can be obtained by this approach.

The next two contributions deal with two specialized areas of Raman spectroscopy. In the first, J. A. Konigstein reviews the principles of selection rules in vibrational spectroscopy and then shows how these rules are generalized in Raman spectroscopy under the influence of vibronic coupling. Detailed attention is then given to Raman transitions involving degenerate electronic ground states including Jahn–Teller degenerate vibrations and the effects of spin–orbit coupling. In the second, P. V. Huong reviews the applications of resonance Raman spectroscopy from the standpoint of the unique advantages which resonance enhancement offers. Much of the discussion centers around the key results of recent theoretical work in this area and the emphasis is toward identifying the conceptually distinct advantages such as new depolarization ratios, the observation of new vibrational modes, better understanding of excited state potential surfaces and information contained in the frequency dependence of excitation profiles.

In the fourth chapter, G. N. Zhizhin and Kh. E. Sterin first describe the basic conformations of disubstituted cyclohexanes. After pointing out the inadequacies of rules predicting the conformation of these molecules based on physical methods, the reader is led through extensive examples of dialkylcyclohexanes to the establishment of firm correlation rules based on spectral markers. These in turn permit studies of conformational equilibrium in these molecules and provide the basis for studying the conformation of structurally related molecules such as the dimethoxycyclohexanes.

The final two chapters, although distinct in topic, are both concerned with torsional motions in gas phase molecules. The subject of asymmetric potential functions for internal rotation is discussed from both the experimental and theoretical viewpoint by D. A. C. Compton. Calculations of potential functions for a wide variety of molecules are critically compared with experimental results. The complexity introduced by anharmonicity is carefully developed and the shortcomings of asymmetric potentials developed under less than favorable circumstances are discussed. A view of this field as having developed extensive sophistication toward the delineation of highly accurate structural detail is transmitted in this article. The book concludes with a review of recent work on internal rotation in molecules possessing two C_{3v} rotors by P. Groner, J. F. Sullivan, and J. R. Durig. The interpretation of the torsional spectra of these molecules is carried out with use of the concept of the isometric symmetry group which is described in the review. Analysis of over a dozen molecules classified on the basis of the symmetry of the molecular fragment which connects the two C_{3v} groups demonstrates the effectiveness of this approach for understanding the structure and vibrational motion of molecules of this type.

This volume brings the reader up to date on a number of interesting areas of vibrational spectroscopy and is recommended to those who want to be aware of current developments in this area as well as to those seeking a deeper appreciation of the methods of vibrational spectroscopy.

Laurence A. Nafie, *Syracuse University*

Polluted Rain. By T. Y. Toribara, M. W. Miller, and P. E. Morrow (University of Rochester Medical Center). Plenum Press, New York. 1980. xii + 502 pp. $49.50.

This book is composed of 23 papers which were presented during the Twelfth Rochester International Conference on Environmental Toxicity: Polluted Rain. The conference, which was held at the University of Rochester Medical Center in Rochester, N.Y., in May 1979, included participants from Canada, Norway, Sweden, and the Netherlands, who collectively contributed five of the papers, providing some international perspective to the problem of polluted rain. The overall problem was subdivided into five sessions which separately addressed (1) the chemistry of polluted rain, (2) the mercury problem, (3) effects on plants, (4) anticipated problems as yet not quantified, and (5) control problems (monitoring systems and legal aspects). While a great deal of emphasis was placed on *acid* rain, the concomitant problems associated with mobilization of toxic metals were also addressed.

Because of the broad scope of this book, it is difficult for an individual reviewer to assess it overall quality and technical merit. There is, however, a noticeable variability in the depth of coverage of subject material. Each of the first three sessions contains at least one paper in which minimal new information is presented. Otherwise, the papers in these three sessions are of a technical nature, with emphasis on data collection and interpretation. The fourth session necessarily consists of papers of a more speculative nature, some of which raised interesting questions which this reviewer had not heretofore considered. The fifth session is rather descriptive, with discussions of monitoring and regulation strategies as well as the legal basis for addressing environmental problems arising from the interstate and international transport of polluted rain.

A specialist in any one of the areas covered in this book should not expect to encounter much new material that is at the cutting edge of his/her own field. The broad scope of the book, however, offers the specialist the opportunity to become reasonably familiar with those aspects of this important and complex environmental problem which are peripheral to his/her own area of expertise. Like other scientists who are not actively involved in the study of polluted rain, this reviewer's knowledge of the nature and scope of the problem is quite fragmentary. The collection of papers in this book certainly provides the balance and depth of coverage of the subject needed to adequately inform the interested reader of the chemical, biological, and legal aspects of the overall problem of polluted rain.

This book is recommended to the specialist in polluted rain research and to the interested nonspecialist, both of whom should benefit from exposure to a broad range of topics which collectively address the important aspects of this environmental problem.

E. Michael Perdue, *Portland State University*

The Hydrophobic Effect: Formation of Micelles and Biological Membranes. Second Edition. By Charles Tanford (Duke University). John Wiley & Sons, New York. 1980. 1x + 233 pp. $18.50.

This is a second edition of a book well known to researchers in the fields of aqueous solution chemistry, and of micelle and membrane formation. The pace of research into the molecular explanations of hydrophobic effects has quickened dramatically in the last decade. This is largely due to the vigorous flood of molecular detail which derives from condensed phase computer simulation techniques applied to aqueous solutions. An enormous amount remains poorly understood, and direct computer simulation of organized biological structures in solution is not yet broadly practical. However, there is no doubt that our understanding of these effects has been considerably deepened and clarified. The necessary synthetic task of consolidating and bounding what has been learned presents a truly daunting challenge. The second edition of "The Hydrophobic Effect" cautiously resists this challenge and remains much the same book as its predecessor.

Readers who are familiar with the first edition will find few surprises in the second. Tanford's conjectures about how hydrophobic interactions should be inferred from thermodynamic solubility data, and about what the derived parameters mean for micelle and membrane stability, have not substantially changed. Neither the type of data nor the arguments used to support these conjectures have substantially changed. There has been an obvious effort to cite research completed after the appearance of the first edition. However, in the area of most interest to me (molecular theory of aqueous solutions) the coverage was extremely sketchy, and even the modern work that was cited was largely ignored after the citation. This is apparently in line with Tanford's cautious assertion (p 39): "It is debatable whether any of the theoretical investigations published so far do more than restate in somewhat different language what is already known on an empirical basis."

In the second half of the book the discussion is progressively focused on systems of more exclusively biological interest. The major difference between the biological lipid systems and those discussed in the first half of the book is the chemical complexity of the associating species. This chemical complexity becomes a dominating concern which can be addressed aside from subtleties of the solvent influence on these structures. Here the book is much better, and Tanford's empiricism is difficult to fault. In contrast to the first half of the book, the treatment in the second half is less sketchy and current research seems to be dealt with more seriously.

In summary, this book does not provide a comprehensive overview of the interesting physical chemistry of these solutions. For those purposes, probably the recent and useful reviews of Lindman and Wennerström should be consulted (H. Wennerström and B. Lindman, *Phys. Rep.* **52**, 1 (1979); B. Lindman and H. Wennerström, *Top. Curr. Chem.* **87**, 1 (1980)); these reviews are apparently too recent to have been cited in the present book. In addition, "The Hydrophobic Effect" gives an archaic view of molecular understanding of aqueous solutions. In spite of this, it will probably be useful for researchers in the biochemical sciences who can afford to take the fundamental molecular description of hydrophobic effects for granted, and perhaps with a grain of salt.

Lawrence R. Pratt, *University of California, Berkeley*