ferric complex **1** (μ = 5.8 BM)[8] reduces the magnetic moment to 4.5 BM (25°)[8] in **2**. This change may tentatively be interpreted as a reduction of **1** by NO to give a high-spin and formally octahedral ferrous complex (although the μ of **2** is somewhat lower than the calculated spin-only value, 4.9 BM; alternatively, the magnetic result may reflect the presence of a spin equilibrium). The relatively high ν_{NO} is consistent with the presence of formal NO^+ in **2**. These observations and their interpretation have interesting analogies pertaining to related systems in molecular biology and surface chemistry: (a) it has been shown that the reaction of nitric oxide with methemoglobin is accompanied by the reduction of the latter,[6b] and (b) the reversible chemisorption of NO on ferric oxide gel results in ir absorption bands ranging from 1738 to 1927 cm^{-1}, the principal ν_{NO} occurring at 1806 cm^{-1}.[9]

If our NO adduct **2** is viewed as a high-spin Fe(II) complex, one is then tempted to speculate that the apparently low Fe–NO bond energy results from the inability of the ferrous atom to move into the porphinato plane, and is thus responsible for the implied relatively long Fe–NO linkage. The iron atom in **1** is known to be located out of the planar N_4 porphinato core by *ca.* 0.4 Å,[1] and there is much current evidence for and discussion of the importance of the relationship between the out-of-plane high-spin (large) and in-plane low-spin (small) Fe(II) in biological heme[10] and model heme-like[11] systems (*cf.* also ref 5b).

The preliminary interpretation considered here involves pairing of two electrons whose energy may amount to several tens of kilocalories[12] and which would hence rationalize the low heat of NO adduct formation and "elevate" the Fe–NO bond energy to a "weak single bond" category even when other energy terms (associated with changes in crystal structure and NO bond order) are neglected.[13] According to a suggested scheme,[14] the formally octahedral **2** is a 22-electron system and should exhibit a linear Fe–N–O bonding. It should be noted that no detectable reactions of [FeCl(TPP)] (in the solid state or solution) take place with CO, SO_2, or O_2 under normal conditions. Complex **1** does, however, take up N_2O_4 and the reaction appears to include nitration of the porphinato ligand.[15]

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[8] Corrected for the diamagnetism of the complex.

[9] A. N. Terenin and L. M. Roev, as quoted by L. H. Little, "Infrared Spectra of Adsorbed Species," Academic Press, New York, N. Y., 1966, pp 86, 87.

[10] R. E. Dickerson, *Annu. Rev. Biochem.*, **41**, 815 (1972).

[11] D. M. Collins, R. Countryman, and J. L. Hoard, *J. Amer. Chem. Soc.*, **94**, 2066 (1972), and references quoted; J. P. Collman and C. A. Reed, *J. Amer. Chem. Soc.*, **95**, 2048 (1973).

[12] F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 3rd ed, Interscience-Wiley, New York, N. Y., 1972, p 565.

[13] See ref 4c for discussion of a related problem.

[14] C. G. Pierpont and R. Eisenberg, *J. Amer. Chem. Soc.*, **93**, 4905 (1971).

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Book Reviews

Carbon-13 Spectroscopy. By J. B. Stothers (University of Western Ontario). Academic Press, New York and London. 1972. xi + 599 pp. $24.00.

Carbon-13 Nuclear Magnetic Resonance for Organic Chemists. By George C. Levy and Gordon L. Nelson (General Electric Corporate Research and Development). Wiley-Interscience, New York and London. 1972. xii + 222 pp. $9.95.

Stothers' book, which is Volume 24 of "Organic Chemistry. A Series of Monographs," will be very useful to any type of scientist who is considering the application of ^{13}C nmr. The author has presented us with a well-written, superbly organized, and highly documented account of developments in ^{13}C spectroscopy through mid-1970 at a time when instrumental developments have made the acquisition of ^{13}C nmr spectra practical on a routine basis. The book is divided into four parts. Part I is a survey of the experimental methods which have been and are being used (including pulse-Fourier transform techniques) for the detection of ^{13}C resonances. This section is particularly useful, for it discusses the errors which were inherent in the early measurements. Carbon-13 shieldings are exhaustively dealt with in Part II. The chemical shifts of hydrocarbons, their functional derivatives, organometallic compounds, carbonium ions, heterocyclic systems, and metal carbonyls are tabulated and discussed. Empirical additivity relationships and data trends are presented and analyzed. A separate chapter deals with the theory of hydrocarbon shielding The author should be applauded for presenting all the chemical shift data relative to a single standard (tetramethylsilane). In Part III the author surveys the area of carbon-13 coupling constants. The discussion includes experimental techniques, theory, and a concise tour of the ^{13}C–^{1}H, ^{13}C–^{19}F, ^{13}C–^{13}C, and ^{13}C–X coupling constant literature. It was not the author's intention to present an exhaustive treatment in this section since there are several other good reviews in existence. In Part IV, the author illustrates the application of ^{13}C nmr to structure elucidation, stereochemical assignments, conformational analysis, natural products, polymers, tracer techniques, and solute–solvent interaction. An especially useful feature of this book is that in addition to a subject index and an author index it possesses a compound index. The clarity of writing, the depth of organization and presentation, the frequent and lucid use of tables and structures, and the extensive cross referencing all make this a very useful and enjoyable book.

Levy and Nelson have used principally the ^{13}C nmr literature of 1970–1971 as a data base to construct a concise discussion of the application of ^{13}C nmr to organochemical problems. It is the authors' goal to bring the reader to a state of knowledge which will enable him to use ^{13}C in his research, and it appears that this is the case as long as the book is used carefully and the references are consulted frequently. The book emphasizes the use of ^{13}C nmr in structure assignment and includes problems with answers. The authors have not attempted to present theory in anything but a very qualitative manner and have also not attempted to cover the literature prior to 1970. The differences between ^{1}H and ^{13}C nmr are continually pointed out, and the book begins by discussing pulse-Fourier transform nmr techniques and the general characteristics of ^{13}C spectra. Data trends in the chemical shifts of hydrocarbons and their functional derivatives are discussed in the next several chapters. The data are clearly tabulated, and the various methods of spectral assignment are presented with emphasis on the more recent literature. Additivity relationships, steric and electronic effects, and solvent effects are appropriately mentioned where they are important but are not amplified or critically analyzed. Succeeding chapters deal with ions, organometallic species, polymers, and biomolecules. One of the strong points of this book is the discussions of relaxation studies and their applicability to structure assignment and other organochemical problems. In their effort to make the book as current as possible, the authors have cited the later appearing work of 1970–1971 in a list of supplementary references at the end of each chapter. Since these supplementary references are not cited in the text or the index, they are unfortunately easily overlooked. This book contains a single index which refers more to classes of compounds than to specific entries. The book is well written in a pedagogical style and is well suited for graduate student use.

This reviewer has found both books quite useful in the practice of ^{13}C nmr. They are complementary in their coverage of the literature. The Stothers book presents the material in depth and analyzes it, while Levy and Nelson just acquaints the reader with the trends and concepts. The Stothers book presents more on experimental methods and theory but is not highly mathematical. The Levy–Nelson book presents material on relaxation-time studies which are not found in Stothers book, while the latter deals with coupling constants in contrast to the former. Both books are well documented, but the Stothers book is far superior in indexing.

Richard N. Loeppky, *University of Missouri—Columbia*

Peptide Transport in Bacteria and Mammalian Gut. A Ciba Foundation Symposium. Edited by K. ELLIOTT and M. O'CONNER. American Elsevier Publishing Co., New York, N. Y. 1972. viii + 161 pp. $7.25.

This volume contains papers presented at a symposium held at the Ciba Foundation, London, in November 1971. The symposium was an attempt to bring together scientists working with bacteria and gastroenterologists interested in the gut.

As summarized in this volume, bacteria possess a transport system for dipeptides and a system for oligopeptides which are distinct from the various amino acid transport systems. Bacteria can utilize these systems to obtain amino acids from the external medium. There is evidence that the mammalian intestine contains dipeptide transport systems, but the existence of an oligopeptide transport system is less well documented. The nutritional significance of these findings for bacteria and mammals is discussed. Questions are raised as to whether the peptide enters the cell as such or is hydrolyzed in the process. In bacteria, peptidase mutants will accumulate dipeptides, suggesting that uptake of the peptide occurs followed by its hydrolysis.

Certain genetic errors of amino acid transport in mammals, including man, have provided models for the study of the importance of peptide transport. Such studies have proved that peptide uptake in mammals is a separate process from that for amino acids and that it is quantitatively important, being sufficient to maintain normal nutrition in diseases of impaired intestinal amino acid transport.

The subcellular localization of the hydrolysis of the peptides forms the basis of a long discussion. A model of protein digestion involving the membrane surface of the gut is discussed.

Many of the features of peptide transport in bacteria appear to be common for the mammalian gut. The information currently available from the gut is less complete.

Inclusion of the long discussion following each of the papers and the addition of a subject index provides valuable information and adds to the utility of the volume.

Dale L. Oxender, *University of Michigan*

Lead in the Environment. Edited by P. HEPPLE (Institute of Petroleum). Applied Sciences Publishers, Ltd., Barking, Essex, England. 1972. ix + 82 pp. £3.00.

This book is a series of six papers, the proceedings of a conference, held at the Zoological Society of London, early in 1972. The conference dealt with sources of lead in the environment, airborne lead uptake by inhalation, lead uptake by plants and its significance for animals, trace lead in food, and possible health effects of lead in adults and children.

All of the papers are good summaries of the data in these respective areas. The paper "Airborne Lead and Its Uptake by Inhalation" by P. J. Lawther, P. B. Cummins, J. McK. Ellison, and P. Biles is of special interest. Prior estimates of the absorption of lead from the air in the lung have ranged from 10 to over 50%. This research group, part of the Medical Research Council in London, presents new data which convince them that the absorption of lead from the atmosphere is only 10 to 15%. Additionally, they show electron micrographs indicating that the shapes of the lead-containing particles in the atmosphere and from automobile exhaust are far from the well-defined, spherical particles which have been used in earlier studies on this question. They differ in every relevant aspect from those for which the concept of aerodynamic diameter was devised. This study showed need for further research in this area.

The book makes it very clear that there are strong differences of opinion with regard to the hazard to human health from lead in the environment. The discussions on this point which are included in the book are enlightening and help one to understand the problems which scientists have in evaluating the effects of small amounts of lead in the air.

While the book deals with a very narrow aspect of environmental problems, nevertheless, it should be of interest to many people in environmental work. This book gives a good summary of the impact on the environment of lead from various sources and points out the controversy that exists on the public health aspects.

Gary Ter Haar, *Petroleum Chemicals Research, Ethyl Corporation*

The Early Transition Metals. By D. L. KEPERT (University of Western Australia). Academic Press, New York, N. Y. 1972. x + 499 pp. $25.00.

This book reflects the growing interest in the chemistry of the early transition metals and is a useful addition to the reference texts which are now available to the inorganic chemist in this area. Chapter 1, entitled "General Properties of the Early Transition Metals," deals with three topics (high coordination numbers, metal–metal bonding, and isopoly- and heteropolyanions) which are favorites of the author. Unfortunately, although this chapter is well written, the opportunity is not taken to discuss other important features, such as the general stability and reactivity patterns of compounds of the early transition metals and the importance of the commonly encountered nd^1, nd^2 and nd^3 metal ion electronic configurations. Consequently, the restricted content of this chapter is disappointing. Chapters 2, 3, and 4 survey in turn several aspects of the chemistry of groups IV (titanium, zirconium, and hafnium), V (vanadium, niobium, and tantalum), and VI (chromium, molybdenum, and tungsten). Systems which are covered include oxides, polyanions, oxyhalides, halides, oxysalts such as nitrates and sulfates, amides, alkoxides, coordination complexes, and organometallics. The author is at his best when discussing the oxide, polyanion, and halide phases of these elements. On the other hand, the treatment of the organometallic compounds is generally rather sketchy, and there is no coverage of the boride, carbide, nitride, phosphide, sulfide, selenide, etc., phases of these elements, which might therefore restrict the appeal of this text. For those systems which are considered in some detail, emphasis is generally placed upon their synthesis, structure, and reactivity. However, although the structural features of the oxides and isopoly- and heteropolyanions of these metals are nicely presented, few preparative details are given, and this might detract from the overall usefulness of this particular survey.

The organization of Chapters 2, 3, and 4 is generally good and the material is clearly presented, but the subject index is barely adequate. Rather surprisingly, although this book was published in 1972, it only covers the literature prior to 1970. In spite of this limitation, the author has done an excellent job in covering the available literature (there are almost 2500 references).

In summary, I feel this text will be particularly useful to those chemists who are actively interested in the chemistry of compounds of the early transition series which contain metal–oxygen and metal–halogen bonds. The reader who is also interested in a broad general coverage of the chemistry of these elements will also find this an acceptable text.

Richard A. Walton, *Purdue University*

Organic Molecules in Action. By MURRAY GOODMAN and FRANK MOREHOUSE (University of California, San Diego). Gordon and Breach Science Publishers, New York, N. Y. 1972. xii + 492 pp. (paperback).

In my opinion, the authors have written a book which will perform a necessary function—to show the student who has completed a course in organic chemistry the significance and relationship of organic chemistry to the world around him. Too often, a student does not fully appreciate the importance of chemistry in his everyday life.

The book is well written. It is presented in a clear, lucid, well-organized manner, and at a level which can be understood as an introductory chemistry text. The authors' selection of topics is quite appropriate and representative of several areas of current interest, such as hallucinatory drugs. I particularly enjoyed the historical development of the topics discussed. The correlation between organic and biochemistry was presented on a clear, fundamental level when called for. The authors made good use and explanations of the organic reactions that they used throughout the text. The abbreviated appendix was a good idea to serve as a refresher for the reader if he was not familiar with certain terms used in the text. I also felt that the authors made excellent use of their structure proofs in elucidating certain complex structures and showing how they could be broken down into fragments which were derivatives of rather simple molecules. Overall, I was impressed favorably with the text. Now, I would like to mention some specific comments about some of the sections in the text, which I hope will help the authors improve upon the material cited.

Chapter VII (p 198). In discussing the biosynthesis of cholesterol, it should be mentioned that although the isoprene unit structure is of paramount importance, it is never found free, as such in nature. The discussion of prostaglandins is most significant today. I was glad to see it briefly presented here.

Chapter VIII. The LSD story is much more complicated than presented here. Some discussion of the relationship of halucinatory drugs to serotonin, adrenaline, tranquilizers, other brain chemicals, etc., should be mentioned. Although adrenochrome was mentioned, another abnormal metabolic product of adrenaline, adrenolutin, was not discussed. Nor was the significance of monamine oxidase. Some mention of the current chemical theories of schizophrenia should be mentioned. Other inborn metabolic defects leading to mental retardation such as phenylketonuria would enhance the material also.

On page 265 the authors discuss the preparation of 2-amino-6-nitrotoluene from 2,6-dinitrotoluene. They use Zn + NH_4Cl for the reduction. I believe they would probably get the hydroxylamine rather than the amine from this reaction. One nitro group can better be reduced selectively to an amino group by using NH_4HS.

In discussing cyclization reactions, the stability of five- and six-membered rings should be mentioned.

The discussion on page 273 about bufotenine in the urine is a very poor correlation with schizophrenia. The error in the assumption made here is that over 95% of the serotonin (which forms bufotenine) is found in the gastrointestinal tract. Only about 5% of the serotonin is found in the brain and this is being turned over very rapidly. Thus, most of the bufotenine in the urine can be attributed to the serotonin in the gastrointestinal tract. Hence, there is no evidence for any correlation with schizophrenia from these data.

In Chapter IX it should be mentioned that experimental evidence has shown that an excess of vitamins A and D are harmful in that they destroy cell membranes. The current interest in vitamin E merits some mention of its use in treatment of heart disease, arteriosclerosis, respiratory diseases, preventing scarring in burns, its antioxidant properties, etc.

These are merely some suggestions. I thought the ideas and presentation of the material was fine.

Reuben L. Baumgarten, *Herbert H. Lehman College*

Chemical Kinetics. Volume 9 of MTP International Review of Science. Physical Chemistry. Series One. Edited by J. C. POLANYI. Butterworths, London, and University Park Press, Baltimore, Md. 1972. 322 pp. $24.50.

This volume has ten chapters, each of which is a review of some particular research area in chemical kinetics. The authors of each topical review are active in the field discussed and therefore are in a position to not only assemble the recent work but to make critical and unifying comments on it. That they have all done so is one of the book's greatest virtues. The emphasis throughout is on recent work, with references through 1971.

Of the ten chapters, only the last two discuss in detail kinetic phenomena in condensed phases; one of these is on solvated electron reactions and the other on relaxation techniques in solution kinetics (Sir Frederick Dainton and J. E. Brooks, respectively). The first chapter (D. W. Setser) discusses unimolecular reactions with particular emphasis on the decomposition of activated molecules and ions under nonequilibrium conditions, and the relationship of the results to current theoretical concepts. The second chapter (I. M. Campbell and D. L. Baulch) treats bimolecular reactions of atoms and diatomic radicals; the third chapter (E. Whittle) treats reactions of free radicals with three or more atoms. Chapters 4, 6, and 7 treat hot atom reactions (F. S. Rowland), molecular beam reactions involving neutral species (J. L. Kinsey), and ion–molecule reactions (J. Dubrin and M. J. Henchman). These studies all involve reactions which occur under "non-Boltzmann" conditions and aim at obtaining details of the actual interaction dynamics and cross sections for reactive scattering. The molecular beam chapter contains a useful table listing all reactions studied in beams subsequent to a similar list cited in the chapter. The chapter on ion–molecule reactions discusses the relationship of such reactions to those involving neutral species. In addition, a discussion of the implications of gas-phase studies with regard to ionic solution phenomena is presented. Chemiluminescence in gas-phase reactions is treated in Chapter 5 (T. Carrington and J. C. Polanyi). Roughly half the chapter concerns vibrational–rotational excitation and includes a table of reactions for which infrared chemiluminescence data have been obtained. This section also discusses the sort of insight to be gained from computer trajectory calculations which simulate actual reactive systems. The remainder of the chapter treats reactions which lead to electronically excited products. Finally, Chapter 8 (J. I. Steinfeld) discusses collisional energy transfer processes. The emphasis is on the capabilities of various experimental techniques, although a brief discussion of vibrational and rotational energy transfer theory is included.

The eight chapters on gas-phase phenomena complement each other nicely, and anyone concerned with current developments in gas-phase kinetics should consider adding this volume to his personal library. The two chapters on solution phenomena stand apart; given the price of the book, institutional library purchase is probably more appropriate for workers in these areas.

J. D. Kelley, *McDonnell Douglas Corporation*

The Search for Organic Reaction Pathways. By PETER SYKES (Christ's College, Cambridge). Wiley-Halsted, New York, N. Y. 1972. xii + 247 pp. $6.25 (paper).

The stated purpose of this book is to show how different types o information about a reaction may be used to construct a reaction mechanism. It is not a book about the mechanisms of various organic reactions. It deals with kinetics, the use of isotopes, reactive intermediates, stereochemistry, and structure–reactivity relationships in individual chapters and closes with a detailed discussion of several well-chosen mechanisms. The level of the book makes it well suited for a student who has completed a "Morrison and Boyd" type of organic chemistry course. It requires, and uses, very little physical chemistry.

This book's greatest assets are the good choice of examples to illustrate the author's points and the detail with which they are discussed. In a book of this size some hard choices must be made and much relevant, important material must be omitted. Dr. Sykes has chosen very well indeed. The individual sections are of somewhat uneven quality. The section on isotopes is particularly good and the sections on intermediates and stereochemistry are quite good. In the chapter on kinetics, the emphasis (properly) is on moving from a rate law to a mechanism, not on determining a rate law. The steady-state approximation is summarily dealt with; its utility in the investigation of complex reactions is not apparent. The discussion of structure–reactivity relationships is quite good, although limited to the Hammett and Taft equations. Solvent effects receive a cursory treatment with only the Grunwald–Winstein equation receiving detailed discussion.

For American students the book has one serious drawback. The author has a tendency to produce long, extraordinarily complex sentences which occasionally cloud the otherwise clear presentation. For example, the first sentence in the book is "An erroneous belief—singularly difficult to convince oneself out of—is that the stoichiometry of a reaction, however lovingly determined, can tell us anything at all about the rate at which starting materials are, under given conditions, converted into products, or about the actual pathway by which this conversion takes place."

Subject to this one drawback, this book is an excellent introduction to the elucidation of organic reaction mechanisms. The examples are well chosen and presented in gratifying detail. This book is unique in its level and approach and should find a wide audience.

John W. Larsen, *The University of Tennessee*