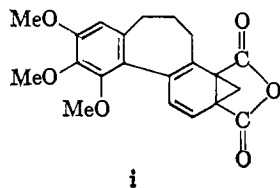


stantial downfield shift of one resonance are in accord with structure VIIIa where the methylene is doubly allylic. From models¹⁹ it is apparent that the methylene proton resonating at 63.8 c.p.s. is shielded by the 2,3-double bond in VIIIa where ring A cannot be planar.



That the enol derivatives are represented structurally by VIIIa-c, and are not resonance hybrids of which structures VII and VIII represent contributing forms, is further evidenced by the consistency of *J* values (10 c.p.s.) for the geminal cyclopropyl protons in VIIIc, irrespective of the solvent polarity.

The action of the fluoramine on other tetracyclic and bicyclic alcohols will be the subject of future communications.

RESEARCH LABORATORIES
SYNTEX, S. A.
APARTADO 2679
MEXICO, D. F.

LAWRENCE H. KNOX
ESPERANZA VELARDE
ALEXANDER D. CROSS

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BOOK REVIEWS

Traité de Biochimie Générale. Tome II. Les Agents des Synthèses et des Dégradations Biochimiques. Premier Fascicule. Vitamines, Oligoéléments, Hormones. By M. JAVILLIER, M. POLONOVSKI, M. FLORKIN, P. BOULANGER, M. LEMOIGNE, J. ROCHE, and R. WURMSER. Masson et Cie, 120, Boulevard Saint-Germain, Paris VI, France. 1962. 700 pp. 17.5 × 25.5 cm. Price, broché, 140 NF.; cartonné toile, 155 NF.

This is the third volume of a series of six, comprising this "Traité de Biochimie Générale." The first two volumes dealt with the chemical composition of organisms and appeared in 1959. The present third volume is the first of two parts covering the agents of biochemical syntheses and degradations and is limited to vitamins, trace-elements, and hormones, while the second part, which will appear shortly, will cover enzymes. Volumes 5 and 6 will discuss the biochemical processes and their coordinations, and are expected some time in 1963.

Part I deals with Vitamins. The first chapter covers vitamins A₁ and A₂ and represents a very good summary of the state of our knowledge in this field. Chapter II presents vitamins D in the same comprehensive way. Chapter III describes vitamins R (tocopherols) while Chapter IV covers the vitamins K.

The first 130 pages are therefore devoted only to the fat-soluble vitamins. Pages 131-372 discuss the water-soluble vitamins. Here again, a chapter is reserved for each kind, including vitamin B₁ (thiamine), vitamin B₂ (riboflavin), vitamin PP (niacinamide), vitamin B₆ (pyridoxine, biotine, pantothenic acid, inositol, thioctic and lipoic acid, folic acid), vitamin B₁₂, vitamin C or ascorbic acid, and vitamin P.

There is even an appendix on "Pteridines" in which the subject is treated in much the same way as a regular chapter on the more clearly defined vitamins. While no attempt is made to exhaust any of these subjects in depth, a great amount of effort is made throughout the book to cover at least adequately every subject which could be considered as coming under the official heading, "Vitamins."

Part II of the book, which in fact covers only 55 pages, describes the trace elements. The treatment here is quite different. Most of this part concerns the experimental determination of these trace elements in green plants, in animals, and in various organisms, while only a few pages are devoted to general and more specific roles played by these elements in the life processes.

The third part, pages 439-637, describes hormones in four chapters and the first one deals with phyto hormones like the gibberellins. Chapter II, in two parts, discusses the hormones of the vertebrates, the first part covering the peptide hormones and the second part the hormones which are derived from amino acids, such as serotonin, adrenalin, thyroxine, etc. Chapter III discusses the sterol hormones while Chapter IV, the last and shortest of the book, describes the hormones of the arthropods.

After spending so much time to cover so adequately the vitamins, one has the feeling that no attempt was made to cover as adequately the fields on trace elements and on hormones. This is especially true of the hormones where the amount of knowledge available today is very large indeed, but the coverage is sparse, resulting in a feeling of improper balance between the three parts of the book. One would like to see a much more thorough treatment of the peptide hormones. It is true, however, that the volume to come covering enzymes will deal with subjects which are closely related to peptide hormones. However, in the steroid hormone field, one would expect to see at least a brief mention of some of the highly potent corticoid and progestational

hormones used in therapy today, even if these are mostly synthetic steroids. The very fact that they are generally more potent than the naturally occurring steroids and have become so important to the modern treatment of many metabolic diseases would seem to justify their coverage in this book.

However, as is often the case in French textbooks, this one is highly readable, clear, and the presentation is very clear and systematic. The tables of contents make it relatively easy to find what is to be found in the book, although, especially in the hormone field, many valuable data could have been added. Fortunately, there is a good author index and a good subject index which make this book all the more valuable as a source of general reference in the covered fields.

Summarizing, this edition of the "Traité de Biochimie Générale" is still in the very high tradition of the French scientific publishers and certainly has its place between the long comprehensive treatment of the more limited fields and the short but broad coverage of text books.

AYERST, MCKENNA AND HARRISON, LTD.
P. O. Box 6115
MONTREAL, CAN.

ROGER GAUDRY

Adsorption and Collective Paramagnetism. By PIERCE W. SELWOOD, University of California, Santa Barbara, Calif. Academic Press, Inc., 111 Fifth Avenue, New York 3, N. Y. 1962. ix + 189 pp. 15.5 × 23.5 cm. Price, \$7.50.

In the study of heterogeneous catalysis, a variety of experimental techniques has produced a variety of interesting results. In particular, the study of the adsorption of gases has proceeded to such a great extent that it has become a self-sufficient field by itself. In fact, the most successful studies of adsorption often have only a secondary application to catalysis itself; for example, the estimation of surface area by nitrogen adsorption (the BET method) is important to catalysis, but has many applications to systems that are not catalysis, such as carbon blacks.

The problem is that the simple measurement of adsorption gives little information as to the state or chemical nature of the adsorbed species; for that reason collateral studies, such as infrared spectra, electric conductivity, and electron emission potentials have been applied to catalysts in the presence of adsorbed gases.

One of the most successful and promising of these techniques is described at length in this monograph. Relatively small particles, typical of supported catalysts, that would be ferromagnetic in the bulk phase, often exhibit a species of paramagnetism. If a particle contains *n* atoms of individual moment μ these can produce a total moment $n\mu$ that interacts with similar particles. This particle-particle interaction is not ferromagnetic, as it would be in the bulk phase, because the relatively large distance between particles reduces the interaction energy between them.

Because of complications, notably the heterogeneity in size of the particles, the treatment of systems of this type is not as simple as, say, the paramagnetism of a gas, but the author is able to present a successful treatment of the problem. When this treatment is then applied to the same catalyst, after the chemisorption of a gas such as hydrogen, a powerful tool for the study of catalyst-substrate interaction is provided.

This book is particularly useful in that the complete details of the procedure are elaborated; it gives both the theoretical back-

ground and the exact experimental set-up required to make the measurements. For example, the change in saturation magnetization of the adsorbent caused by one atom of adsorbed hydrogen is evaluated for the hydrogen-nickel system, and this is compared with the adsorption isotherm. It would appear that, except for the unfortunate presence of heterogeneity in both the size and surface of the particles, a straightforward analysis would be possible.

This difficulty brings up the main drawback to the method; because of the more or less poorly characterized nature of supported catalysts reduced by hydrogen, it is not possible to compare directly this work with the more "fundamental" studies on super-clean, single crystal surfaces. It would appear then that this elegant method, which has been largely developed and exploited by the author and his associates, does not answer many of the old questions about the mechanism of catalysis by metal surfaces. However, no worker in the field can afford to neglect this important book.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE 5, WASHINGTON

G. D. HALSEY, JR.

Methods of Organic Elemental Microanalysis. By G. INGRAM A.R.I.C., Research Laboratory, Courtaulds Limited, Maidenhead. Reinhold Publishing Corporation, 430 Park Avenue, New York 22, N. Y. 1962. xvi + 511 pp. 15.5 × 23.5 cm. Price, \$15.00.

This useful volume covers the quantitative determination of the elements in organic compounds and devotes 500 pages to this subject. As the title suggests the scope of the work has been deliberately limited to this area and does not include the determination of physical constants such as melting point or molecular weight, nor does it cover functional group analysis. Indeed, if these subjects were to be included with the same exhaustive treatment the volume would have become unwieldy and would have required subdivision.

Part 1 deals with the determination of carbon, hydrogen, oxygen, nitrogen, the halogens, and sulfur. The treatment is thorough, describing alternate methods and giving enough detail to permit the practicing analyst to duplicate the equipment and to operate the methods. In most cases the author has been careful to evaluate the alternate methods and to make clear the applicability of each. Adequate references to the original literature are given.

Some of the newer developments in microanalysis have not been given the attention they deserve. Better methods for the colorimetric determination of fluorine are now available and the coulometric determination of the halides will become important. The flask method of combustion for sulfur and the halogens is described but is not given the emphasis that it deserves.

Part 2 deals with the determination of the less common elements and here the treatment, of necessity, is less complete. Forty-three elements are considered in 90 pages of text. Procedures (mostly gravimetric) are described and working details are given. This text will serve adequately as a point of departure, but many analysts will prefer to choose more modern methods. The very useful EDTA titrations, for example, are not included.

Part 3 is a timely discussion of microgram analysis. The recent development of rugged and sensitive microgram balances permits the use of samples in the 1-100-microgram range. Such methods provide adequate accuracy and can now be considered not only for the occasional situation imposed upon the analyst by limitation of sample size but also for the more routine uses. Ingram gives a good general discussion of technique and specific procedures for carbon, hydrogen, nitrogen, the halogens, sulfur, and phosphorus.

The book is well organized and the subject matter is presented with great skill and clarity. This reviewer noted almost no ambiguities or errors. It will prove a valued addition to the library of the practicing microanalytical chemist.

RESEARCH LABORATORIES
EASTMAN KODAK COMPANY
KODAK PARK
ROCHESTER 4, NEW YORK

CARL W. ZUEHLKE

Ion Association. By C. W. DAVIES, D.Sc., F.R.I.C., Associate Director of Research, Battersea College of Technology, and Emeritus Professor at the University of Wales. Butterworth Inc., Medical and Scientific Publishers, 7235 Wisconsin Avenue, Washington 14, D. C. 1962. 14.5 × 22 cm. 198 pp. Price, \$7.50.

Professor Davies, as might be expected from his long research experience in the field, presents an excellent review of a fundamental part of electrochemistry. The development of the subject is in the sequence: methods, results, and consequences. In the introduction, Davies makes it clear that he is considering ion

association in the sense of the Bjerrum definition although it is "a mathematical fiction" with "an arbitrary element is its definition"; it is, however, a convenient fiction that has proved useful for many years. The contact model for the pair [*J. Am. Chem. Soc.*, **80**, 5059 (1958)] is, however, equally useful and avoids the arbitrary cut-off of the Bjerrum model and seems more realistic physically. This model is treated in a seven-line addendum to the detailed treatment of the Bjerrum model in Chapter 15. Fortunately most of the material presented in the monograph does not depend on the theoretical interpretation of association constants.

In Chapters 2-6, the various methods of determining association constants are presented, beginning with conductance, which receives the emphasis it should. Most of the examples cited are salts of higher valence type in water, a natural consequence of the author's special interest in these systems. In the discussion of activity coefficients, a previously unpublished empirical equation

$$-\log f_{\pm} = 0.5z_1z_2[I^{1/2}/(1 + I^{1/2}) - 0.30I]$$

is shown to reproduce data on a wide variety of valence types in aqueous solution up to about 0.1 *M*. The careful distinction between ionic and stoichiometric activity coefficients and the attendant discussion on pp. 34-36 merits attention. Other methods of calculating association from observations are summarized in three short chapters which contain a bibliography of 56 references. Then, in Chapters 7-9, results are reviewed, again with emphasis on aqueous systems and on mixtures of water with other solvents. In the reviewer's opinion, the one adverse criticism to be made against the monograph is the cursory treatment of nonaqueous systems. When the voluminous literature on the latter is considered, six pages (two of which are tables) does indeed seem skimpy. The monograph disregards all association higher than pairwise, and it is precisely in nonaqueous solvents, especially those of dielectric constant below ten, that clusters of three and more ions become significant. In the light of this comment, "Ion Pairs" rather than "Ion Association" would have been a more apt title.

The first two parts of the monograph are essentially descriptive; the next 63 pages (Chapters 10-15) treat the consequences of the hypothesis of ionic association. An original treatment of the dissociation minimum theoretically possible for higher valence types is presented first; it is shown how it can bring about the sudden flattening of conductance curves observed for these electrolytes. As the author admits, however, this effect cannot lead to minima in the conductance of 1-1 salts in solvents of low dielectric constant, which are explainable in terms of three-ion clusters. The thermodynamics of ion pairs and reactions involving ion pairs are competently reviewed. The chapter on solvation is written from a realistic point of view. The opening sentences merit quoting: "The idea that ions are hydrated in aqueous solution has been a familiar one for fifty years or more, and much effort has been devoted to finding a quantitative measure of the effect. Almost the only common factor, however, in the variety of approaches that have been used is the undoubted fact that solvent and ion interact, with resultant effects on most of the properties of both." The monograph closes with a useful table of *pK*'s of ion pairs in aqueous solutions. The book is recommended to physical chemists in general and especially to electrochemists; a lot of information is compactly and efficiently presented.

DEPARTMENT OF CHEMISTRY
YALE UNIVERSITY
NEW HAVEN, CONNECTICUT

RAYMOND M. FUOSS

Topics in Organic Chemistry. By LOUIS F. FIESER, Sheldon Emery Professor of Organic Chemistry, Harvard University, and MARY FIESER, Research Fellow in Chemistry, Harvard University. Reinhold Publishing Corporation, 430 Park Avenue, New York 22, N. Y. 1963. 16.5 × 24.5 cm. 668 pp. Price, \$10.00.

This book has two main parts. The first part consists in excellent surveys of the following special topics: polynuclear hydrocarbons; aromatic heterocyclic compounds; alkaloids; terpenoids; vitamins; chemotherapy; synthetic polymers; and dyes. In these surveys the main points of interest are pointed out so that a reader unfamiliar with the fields can easily grasp some of the fascination offered by these areas. There are many well drawn structural formulas to help the reader interpret the problems and biographical data (now typical of a Fieser book) of important contributors which add to the interest.

The second part consists of a collection of the modern art of chemistry covering the period from July, 1961, through December 13, 1962. The collection is too extensive to review here, but a trip to this gallery is highly recommended, especially when the gallery can (and should) be in one's home.

THE DEPARTMENT OF CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS 10, OHIO

MELVIN S. NEWMAN