The relative positions of these absorptions is almost certainly due to the effects of p-π bonding between oxygen and boron. A similar result was observed for the alpha hydrogens of the alkoxy groups in the corresponding ethoxy compounds. The diethoxy quartet is centered at 3.41 p.p.m. above benzene and the monoethoxy quartet at 3.35 p.p.m. above benzene.

In 33% benzene solution the ethoxy quartets do not overlap the methoxy singlets and these singlets may thus be used for quantitative analyses of equilibrium mixtures. The analytical procedure was checked with samples of known composition.

Equilibrium mixtures resulting from the reaction of diisobutylmethoxyborane (A) with isobutyldiethoxyborane (B) to produce diisobutylethoxyborane (C), isobutylmethoxyethoxyborane (D), and isobutyldimethoxyborane (E) were obtained by mixing the reactants in molar ratios ranging from 2A:1B to 2B:1A. Four different ratios of A and B for the forward reaction and a 2C:3E ratio for the reverse reaction were analyzed by p.m.r. As soon after mixing as possible, the solutions were analyzed[6] and found to have reached a statistical distribution of alkoxy groups between monoalkyl- and dialkylalkoxyboranes.

The most dilute solution which was analyzed satisfactorily had initial concentrations, $a = b = 0.1\ M$. Within an analytical uncertainty of 5%, this solution was found to reach equilibrium in 30 seconds or less.

On the basis of the reactions

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C + D$$

$$A + D \underset{k_4}{\overset{k_3}{\rightleftharpoons}} C + E$$

$$E + B \underset{k_6}{\overset{k_5}{\rightleftharpoons}} 2D$$

(6) In the analysis isobutylmethoxyethoxyborane could not be distinguished from a mixture of isobutyldimethoxyborane and isobutylethoxyborane because the chemical shift of the alpha hydrogen is determined by the number of oxygens attached to boron and not on the nature of the alkoxy group. This analytical difficulty does not, however, interfere with calculations of the rate constants.

and taking $k_1 = 2k_2 = 2k_3 = k_4 = {}^1/_2k_5 = 2k_6$ from statistical considerations, the rate equation, $\frac{-dA}{dt} = k_1[(A)(2b + a) - a^2]/2$, was obtained for the approach of the system to equilibrium. On the assumption that the reaction products reached at least 95% of their equilibrium values in 30 seconds or less, a minimum reaction rate constant, k_1, of 0.66 M^{-1} sec.$^{-1}$ was calculated.

In an equilibrated mixture formed by adding 2 moles of A to 1 mole of B, the populations of methoxy groups on A is equal to the sum of the populations of methoxy groups on D and E. Using the minimum rate constant, the maximum mean lifetime of methoxy groups on the two sites was calculated to be 1.8 seconds. This 2:1 mixture was examined in the absence of benzene and found to give separate, essentially non-broadened, singlets for the monomethoxy and dimethoxy hydrogens with a separation of 10 c.p.s., compared to a separation of 5 c.p.s. in 33% benzene. Since, in the 2:1 mixture of A and B, the populations on the two alternate sites are equal, and in view of the noncoalescence of the two methoxy peaks, the equation[7] $\tau\pi(V'_A - V'_B) = 10$ was used to calculate a minimum mean lifetime of 0.32 second for the methoxy groups on the two sites. From this minimum mean lifetime and the rate equation, a maximum reaction rate constant of 3.8 M^{-1} sec.$^{-1}$ was calculated. Thus from the 95% approach to equilibrium in less than 30 seconds, and from the noncoalescence of absorption peaks, the reaction rate constant, k_1, is given an upper limit of 3.8 and a lower limit of 0.66.

Measurements at higher temperatures are planned to determine whether the exchange can be accelerated sufficiently to produce coalescence of the absorption peaks.

Similar results were obtained when mixtures of diisobutylethoxyborane and trimethoxyborane were examined. Further details on this and related work will be reported at a later date.

(7) Pople, Schneider and Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 223.

DEPARTMENT OF CHEMISTRY
RADIATION LABORATORY
UNIVERSITY OF NOTRE DAME
NOTRE DAME, INDIANA

PATRICK A. MCCUSKER
PHILLIP L. PENNARTZ
RICHARD C. PILGER, JR.

RECEIVED SEPTEMBER 10, 1962

BOOK REVIEWS

Basic Principles of the Tracer Method. Introduction to Mathematical Tracer Kinetics. By C. W. SHEPPARD, Professor of Physiology, University of Tennessee Medical Units, Memphis, Tennessee. John Wiley and Sons, Inc., 440 Park Avenue South, New York 16, N. Y. 1962. xviii + 282 pp. 15.5 × 23.5 cm. Price, $8.00.

Tracer techniques are being used in many areas of chemistry and biology, particularly in applications of radioisotopes to problems in biological research. In the latter area, multi-compartmented, polyphasic systems of cells, organs and intact animals are the rule. The intrinsic complexity of such systems has discouraged rigorous mathematical analysis of the dynamics of exchange between the various compartments. The great majority of published tracer studies in biology involve a variety of assumptions which in retrospect are gratuitous, if not indefensible.

Although from time to time writers have dealt with the simplest possible problems of precursor–product relationships in intermediary metabolism, and with problems in the dynamics of distribution and exchange in living organisms, in most instances the validity of their conclusions was severely restricted by the limiting nature of the basic assumptions. In brief, there has existed a real need for a rigorous mathematical approach toward a definition of the principles and solutions of the problems associated with the tracer method, particularly as it applies to living systems. This need is met by Dr. Sheppard's book, which presents concisely and, for the most part, rigorously, mathematical analyses of the basic principles of the tracer method. As the author himself indicates, the book does not purport to tell how to do a tracer experiment, but it does present a thoughtful treatment of the complicated problems inherently posed in attempting to follow quantitatively the migrations of tracers, not only in their original form but also in the form of possible metabolic conversion products.

Throughout the book, the illustrations are well executed and add much clarity to the arguments. The detailed, well organized table of contents allows the reader to find a particular subject of interest without tedious searching through the index. The latter appears to be satisfactorily complete. While a complete table of special symbols is given, happily the author does not thereby fall into the grievous sin of constantly introducing undefined symbols into the text.

The first two chapters are straightforward enough to fulfill the author's promise that those without a very high level of mathematical sophistication will be able to follow the analysis. Chapter 1 may be slightly marred by a brief and not altogether clear exposition on tracers and information. In general, this section is peripheral and might have been omitted without serious loss. Furthermore, the final section of chapter 2 dealing with incomplete mixing leaves something to be desired. The author's optimistic conclusion that "in a mammilary system there is a tendency for inhomogeneity to average out to some extent" is true for the particular example cited. However, this may be a comforting but inaccurate assumption if extrapolated to other systems.

In chapter 3 the author begins the development of more sophisticated mathematical methods. Unfortunately, the foundations laid for these developments are probably inadequate for the reader unaccustomed to thinking in mathematical terms. This need not detract from their value, for the persistent reader who works straight through sometimes imposing mathematics, skipping where necessary, will usually arrive at clear and understandable summary statements. However, from chapter 4 on, the reader may well miss the substance of many of the arguments unless he takes the time to develop some feeling for the use of the Laplace transform. The development of this elegant method is quite brief, and the non-mathematician will likely find collateral reading necessary.

Chapter 6 presents a valuable and interesting discussion of analog simulation of compartmental tracer experiments. The author has obviously used and enjoyed analog computational techniques, and this chapter is written with refreshing vigor and admirable restraint in the use of professional jargon. While some may decry as trivial the inclusion of specific wiring diagrams of particular operational amplifiers, these nicely fulfill their stated function of helping to remove any air of mystery which may surround analog computational methods.

Probably because of our own bias on this point, the author's discussion in chapter 7 on the use of digital computor methods is less impressive. Apparently, it is not possible to go far in a discussion of digital computors without becoming enmeshed in professional computor terminology. The most useful information obtainable from this chapter may be the parting advice that the novice should have access to the services of an experienced programmer.

Chapters 8 through 10 on continuous systems are difficult but exciting. The level of mathematical sophistication used in dealing with such systems is impressive, with many of the problems treated with precision, rigor and elegance. It is particularly in these chapters that the admirably complete bibliography will prove of considerable value to the serious researcher.

In the final chapter, the first few sections on matrix methods seem to inject a not altogether necessary level of sophistication. For one skilled in matrix methods it may well be that the grace and compactness of matrix equations will allow him better to see through to the underlying physics of a given system and will suggest appropriate experimental measurements and procedures. However, one agrees with the author that "it would seem debatable whether it is necessary for those untrained in matrix calculus to master the necessary elements required for tracer kinetics."

In contrast, the final sections of this chapter dealing with statistics and curve-fitting are most useful. Somewhat heavier stress might have been laid on the point that best results in an experiment will be achieved if an experienced statistician is consulted before an experiment is performed. Certainly the author's treatment of the problem should convince the reader that the handling of experimental data is not a trivial matter to be assigned to an untrained technician.

It is important not to underestimate the difficulty and the significance of the task which has been undertaken here: the establishing of communication between specialties. On the whole, Dr. Sheppard has succeeded in this task; and if there be any fault with this book it is that the communication is rather one-way, from the mathematician to the tracer chemist. At present, this is probably the logical direction for the flow of information, and the time is not yet here for a companion volume addressed to the mathematician demanding that he learn the language and the problems of tracer techniques. This book will be a distinct asset to those engaged in applications of the tracer method and could well serve as a basic text in an advanced course in tracer chemistry.

DEPARTMENT OF RADIATION BIOLOGY
SCHOOL OF MEDICINE AND DENTISTRY
UNIVERSITY OF ROCHESTER

THOMAS P. DAVIS
LEON L. MILLER

Carbohydrates of Living Tissues. By M. STACEY, F. R. S., Mason Professor and Head of the Department of Chemistry, University of Birmingham, and S. A. BARKER, D.Sc., Lecturer in Organic Chemistry, University of Birmingham. D. Van Nostrand Company, Inc., 120 Alexander Street, Princeton, New Jersey. 1962. xvii + 215 pp. 15.5 × 23.5 cm. Price, $7.50.

The resurgence of interest in the chemistry of carbohydrates, which has taken place during the past decade, has so greatly enriched our knowledge of this domain that it has been inevitable a rash of books would follow, some good, some indifferent. The volume reviewed here is the second by these well-known authors to make its appearance within two years. Their first dealt with the polysaccharides of microörganisms. This second book concerns itself with those carbohydrates which are to be found in living mammalian tissue.

The first four chapters of this new volume, comprising nearly half the book, are much the best; indeed, they are good fare. They are lucid, up-to-date accounts of the chemistry of glycogen, heparin, hyaluronic acid and the chondroitin sulfates. One will be rewarded for their reading. The remainder of the book is by no means as good, nor does it fulfill the promises found on the dust jacket and written, one may suppose, by the publisher. The staccato accounts of the blood group polysaccharides, the lipocarbohydrates and, in particular, of the mucoproteins in health and disease are little more than a compilation of the literature of the past few years. Yet the authors are to be commended for assembling in array the advances in these fields and for executing their task so thoroughly. These chapters might have been the richer, however, had they been more generously larded with critical evaluations and scholarly reflections upon the accomplishments which they list. Perhaps, in our fast-paced scientific era, this is asking too much. The task of compiling a volume in a field so vast and so rapidly developing as that of the polysaccharides is formidable and seems to leave but little time for intellectual exercises. Yet despite these animadversions, the book is not without merit, if only because it brings together the developments of the past few years in a field which is growing so rapidly in importance. Libraries might do well to place it upon their shelves.

THE ROCKEFELLER INSTITUTE
NEW YORK 21, N.Y.

WALTHER F. GOEBEL