

using a boron trifluoride-phosphoric acid mixture.<sup>5</sup> We prefer not to comment on this paper since the reaction appears to be heterogeneous in nature.

The results of diazotization cannot be interpreted on the basis of the relative electronic or chemical properties of the aromatic hydrocarbons. Our tentative interpretation is that a cage effect is in operation. The isopropylamine-nitrous acid intermediates, including the original isopropylamine-acetic acid salt, are surrounded by the more polar components, particularly the free acetic acid molecules. The benzene, toluene, and *p*-xylene are distributed sparsely in the cage according to their sizes or shapes rather than in relation to their bonding abilities. According to bulk, the population of benzene molecules in the cage is very small but greater than that of toluene or of *p*-xylene. Thus, the isopropyl intermediate has the opportunity to attack in the sequence: acetic acid  $\gg$  benzene  $>$  toluene  $>$  *p*-xylene. The only other interpretation possible is that the intermediate carbonium

(5) R. N. Volkov and S. V. Zavgorodnii, *Dokl. Akad. Nauk, SSSR*, **133**, 843 (1960).

ion is so reactive that it attacks the aromatic hydrocarbons in a statistical manner. This interpretation is not so attractive because the *meta/para* ratio in isopropylation of toluene is about 0.7, rather than close to the statistical factor of 2. The invariant yield gives weight to the cage theory also.

A great deal of work remains to be done, but it is important at this time to point out (1) that aromatic alkylation by diazotization has been accomplished, and (2) that unusual activity sequences in competition reactions carried out in nonpolar solvents were encountered. It is well for chemists to be alerted to the possibility that activity sequences having nothing to do with electronic effects may be encountered in other reactions involving nonpolar solvents.

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## BOOK REVIEWS

**Progress in Reaction Kinetics.** Volume II. By G. PORTER, F.R.S., Editor, Professor of Physical Chemistry, University of Sheffield. The Macmillan Co., 60 Fifth Ave., New York 11, N. Y. 1964. vii + 391 pp. 16  $\times$  24 cm. Price, \$15.00.

With the publication of this second volume, this series may be described as having "arrived" in terms of the importance and seriousness of its contribution to the broad field of chemical kinetics. The present work offers a selection of eight articles, mainly by well-recognized authorities, the subject matter being about equally divided between gas phase and solution kinetics. Its catholicity of coverage is also indicated by the fact that fields such as photochemistry, biochemistry, polymer chemistry, as well as physical organic and inorganic chemistry, are involved. This diversity of subjects is perhaps but a reflection of the fact that the techniques of chemical kinetics are becoming as broadly used a tool in the sciences as thermodynamics. And this in turn has raised a difficult problem of jurisdiction which must surely be plaguing the editors of this and other "Advances in . . ." or "Progress in . . ." series.

Drs. G. C. Fettis and J. H. Knox have contributed a timely and well-done article on halogen atom reactions. They have gone beyond the usual bounds of reviewers in trying to systematize and rationalize the data, both internally from an empirical point of view and externally with regard to transition-state theory. Of particular interest is their criticism of the classical Bodenstein work on  $\text{Br} + \text{H}_2$  and their proposed revision of the rate constant for this reaction *vis-à-vis*  $\text{Cl} + \text{H}_2$  and  $\text{I} + \text{H}_2$ . They list some very interesting tables of *A* factors calculated by transition-state theory which show the present state of the art fairly well, *i.e.*, agreement with observed values to about  $\pm 40\%$  on the average and disparity factors seldom beyond  $1/3$  or 3 in the extreme.

Another very timely and thorough article is on Hg photosensitized reactions by Dr. R. J. Cvetanović, one of the outstanding practitioners of this difficult art. There has been a good deal of controversy about the nature of the primary and secondary steps in  $\text{Hg}^*$  reactions, and this is very ably presented here if not settled. A very strong case is made that for olefins the major process is the formation of highly excited molecules or biradicals. Their multiplicity, singlet or triplet, is still being

actively investigated. Quite fascinating are the recent reports of cyclic products from butenes and pentenes. The recent history of isotopic enrichment studies of Hg mostly by Gunning, *et al.*, is also included.

Dr. H. M. Frey who is well known for his studies on the decompositions of small ring compounds contributes a very compact and readable survey of  $\text{CH}_2$  and simple carbene reactivity. The intensity of interest in this subject is indicated the fact that this will make the fourth such survey to appear this year.

Strongly related to each of the three preceding articles is the fourth chapter by R. B. Cundall on the kinetics of *cis-trans* isomerizations. This is again a very well-written survey of the early and recent history of the subject covering gas phase, catalyzed and uncatalyzed reactions, as well as solution phase reactions including photosensitization by Hg and triplet-state molecules. It is a pity that this otherwise well-done article appears to be marred by having an unusual number of errors in some of the tables.

As noted by the authors, Dr. M. Szwarc and Dr. J. Smid, anionic polymerization is a revitalized, rather than a new field. The present article on the kinetics of propagation of anionic polymerization and copolymerization is a most thorough and scholarly account of the field from earliest days by one of its most famous revivers, Dr. M. Szwarc. The stage of sophistication recently achieved in this art using modern physico-chemical techniques is well illustrated by the discussion of ion-pair and ion-pair dimers involved in some of the systems studied.

An equally new and "hot" field of fast reactions in solutions is presented by one of its discoverers, Dr. M. Eigen. Chapter VI, "The Rate Constants of Protolytic Reactions in Solution," by M. Eigen, W. Kruse, G. Maass, and L. DeMaeyer, discusses the theory and findings on diffusion-controlled reactions mostly in aqueous solutions. The methods employed are the relaxation techniques introduced by Dr. Eigen and co-workers, and useful tables list almost all of the extant data. The field appears ripe for a discussion of these data in terms of structure but this is not a major concern of this chapter.

The difficult but important biochemical subject, "Rates of Reaction of some Haem Compounds," is lucidly covered by Dr. Q. H. Gibson in a short section. These include reversible complex formation and some enzyme reactions.

The last article by Dr. R. M. Noyes, well known for his explorations of diffusion-controlled reactions, is an attempt to systematize the terminology and techniques for the mathematical treatment of the kinetic equations for consecutive reactions. This will not be an easy article to read for most kineticists, but the treatment and approach can be very useful. In particular Dr. Noyes presents some quantitative thermodynamic criteria in terms of free energies for the use of such familiar approximations as "rate-controlling step" and "uniform flux treatment." This is perhaps more of a new contribution rather than being a review of old work, but this has become a growing trend in such books.

Dr. Porter, the editor, is to be congratulated on putting together a most useful adjunct to the literature of chemical kinetics. It will be must reading for any researchers venturing into the fields covered, and a most useful starting point for graduate students beginning their studies in these areas. It is rather a pity that literature references seldom go beyond Feb. 1962, and this seems surely too long a time lag for this type of book. This is not the most useful way to distinguish this series from annual reviews. It also occurs to this reviewer that many potential readers would be interested in purchasing individual articles. What are the prospects for this happening?

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**Elastic Liquids. An Introductory Vector Treatment of Finite-Strain Polymer Rheology.** By A. S. LODGE, The Manchester College of Science and Technology, England. Academic Press Inc., Ltd., Berkeley Square House, Berkeley Square, London, W1, England. 1964. xii + 389 pp. 16 × 23.5 cm. Price, \$12.00.

This carefully prepared and well-documented book will be of interest to polymer chemists, chemical engineers, fluid dynamicists, and applied mathematicians. It will be particularly valuable to those who are doing research in rheology and to those charged with planning and directing laboratories concerned with viscometry and mechanical testing. In addition, it will serve well as a textbook for an introductory course in mechanics of continua.

The introductory chapter gives a brief exposition of those aspects of vector analysis and nonorthogonal coordinates needed for the subsequent chapters. The next two chapters summarize the description of strain and stress, but consider only very simple flow situations (*e.g.*, pure shear, steady shear flow, steady elongational flow), thereby keeping the discussion relatively elementary; no tensor analysis is used in this discussion, and emphasis is placed on straightforward geometrical pictures. In the chapters which follow, the concepts thus developed are used to describe the mechanical phenomena observed in rubberlike solids, Newtonian liquids, and rubberlike liquids; in connection with the latter, considerable space is devoted to elastic recoil phenomena. By this time, the reader is equipped to understand most of the observed rheological phenomena, including normal stresses, the Weissenberg effect, and various types of elastic recovery. These first seven chapters (about 150 pages) constitute a well-organized "short-course" in rheology, which uses only vector analysis, analytic geometry, and ordinary calculus. A reader thus equipped will find much of the rheological literature meaningful to him.

The remaining five chapters are of a more specialized nature and reflect the particular research interests of the author. These chapters will have considerable appeal to various specialized audiences. Chapter 8 deals with the general problem of constructing rheological equations of state. Chapter 9 is probably the best available summary of normal stress experiments and their interpretation. Chapter 10 is a survey of the various unusual properties of concentrated polymer solutions, which are of both scientific and industrial interest. Chapter 11 is a set of complete solutions to the problems at the end of Chapters 1-7. And Chapter 12 is a recapitulation of Chapters 1-7 in the more general language of tensor analysis; this chapter will appeal to those whose mathematical training has included a study of tensor analysis, equivalent to McConnell's book, for example. This final chapter gives formal justification for the elementary approach used previously.

This lucid book is unique in its field. It emphasizes the viewpoints developed by Weissenberg, Oldroyd, and, of course, the author himself. It has excellent balance between theory and experiment, and between mathematics and physics. The book will help bridge the gap between the experimentalist (who may not know what he should be measuring) and the theoretician (who may not be sufficiently concerned with the experimental verification of his theories). The author emphasizes the urgent need for various types of data, in particular viscosities of concentrated polymer solutions, elongational viscosity, finite amplitude oscillatory shear, and oscillatory normal stresses. The orderly presentation, careful literature citations, economy of notation, and frequent word-summaries of mathematical results give indication of the author's sympathetic attitude toward the reader as well as his pride in sound scholarship. Typographical errors seem to be few and far between.

This reviewer feels that a few additional items could well have been included to make the book even more useful: somewhat more quantitative information on non-Newtonian viscosity and linear viscoelasticity would give readers a better feeling for orders of magnitudes of some important effects; even the inclusion of some sample constants for empirical models would have been useful. It is unfortunate that no mention was made of the work of Eyring on the molecular theory of non-Newtonian viscosity in about 1935; also the Kuhn-Kramers-Kirkwood-Zimm line of development of molecular theories of linear viscoelasticity deserve mention. Some word of warning should have been given concerning viscous heating as a possible disturbing factor in viscometry. Also, it is unfortunate that the author did not include H. Markovitz's excellent summary of the faults of various rheological models in describing normal stress phenomena (*Trans. Soc. Rheol.*, Vol. 1); as it is, the reader is not left with much of a feeling as to the practical applicability of the various models presented in Chapters 4 through 8. Finally, this reviewer feels that many a beginner will be confused because Chapter 1 does not include an explanation of the idea of covariant and contravariant components; certainly some readers will wonder why the author writes  $p_{ij}$  but  $\pi^{ij}$ .

The author is to be congratulated for his judicious restriction of the scope of the book and his literary craftsmanship. "In der Beschränkung zeigt sich der Meister."

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**Selected Works in Organic Chemistry.** By A. N. NESMEYANOV, U.S.S.R. Academy of Sciences. The Macmillan Co., 60 Fifth Ave., New York 11, N. Y. 1964. xvi + 1172 pp. 18 × 25 cm. Price, \$30.00.

In 1959 there was published in Russian four volumes containing all the scientific papers of Professor A. N. Nesmeyanov. Of these, the first three volumes were devoted to Nesmeyanov's experimental findings together with generalizations and theoretical interpretations concerning them. The present volume brings together in English most of the work described in the original three volumes. As such it should prove a highly valuable and useful source of reference for much of his extensive and important studies.

The divisions of the book are headed as: Part I—Organometallic Chemistry (a) Diazo method of synthesis of organometallic compounds; (b) Synthesis of organometallic compounds; (c) Quasi-complex and unsaturated organometallic compounds. Tautomerism and  $\beta$ -conjugation; (d) Stereochemistry of substitution reactions; (e) Ferrocene and metal carbonyls. Part II—Chemistry of Element-Organic Compounds (a) Onium compounds; (b) Organic compounds of Si, Ti, F. Part III—Investigations in Organic Chemistry (a) Synthesis on the basis of  $\beta$ -chlorovinyl ketones; (b) Synthesis of polychlorohydrocarbons and related compounds, and their chemical conversions.

As the divisions indicate, the book is concerned very largely with his numerous and significant studies in the field of organometallic chemistry. All of the papers have appeared in Soviet periodicals, and some of them have also been published in journals such as *Berichte*, *Tetrahedron*, *Zeitschrift fuer anorganische allgemeine Chemie*, and *Quarterly Reviews*. It would have been more helpful to most readers to have replaced the *Quarterly Reviews* article by other original papers.