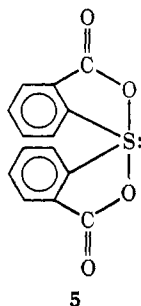


*tert*-butyl and to other proton,  $J_{AB} = 9.2$  Hz,  $J_{BC} = 2.0$  Hz), 7.745 (d, br s in absence of decoupling, total area for  $\delta$  7.750 and 7.745 = 4, proton ortho to *tert*-butyl and ortho to hexafluorocumyl group,  $J_{BC} = 2.0$  Hz), 1.39 (s, 18, *tert*-butyl protons). The  $^{19}\text{F}$  nmr shows two quartets at 74.6 and 75.2 ppm upfield from  $\text{CFCl}_3$  ( $J_{\text{FF}} \cong 8$  Hz).

In contrast to **1**, which shows great reactivity toward water or alcohols,<sup>2</sup> neither **2** nor **4** is readily hydrolyzed. Sulfurane **4** does not react with *tert*-butyl alcohol at room temperature and is stable to treatment with 9:1 tetrahydrofuran–water heated to reflux, and to hydrochloric acid or sodium hydroxide in the same solvent system when heated to reflux for 2 hr. The low hydrolytic reactivity of **4** is even more pronounced than that reported by Kapovits and Kálmán<sup>5</sup> for sulfurane **5**,



which was hydrolyzed to the sulfoxide upon heating for

(5) I. Kapovits and A. Kálmán, *Chem. Commun.*, 649 (1971).

30 min in 9:1 acetone–water. Attempts to hydrolyze **2** and **4** are currently underway in these laboratories along with further investigations of their chemistry.

An analogous oxidation employing ruthenium tetroxide was attempted on the much more sterically hindered compound **1** but no intermediate analogous to **2** could be detected.

The nonequivalence of geminal  $\text{CF}_3$  groups seen in the  $^{19}\text{F}$  nmr spectrum of **2** is consistent with a trigonal-bipyramidal geometry with apical alkoxy ligands and equatorial aryl and oxide ligands. The only other known<sup>6</sup> example of this sort of pentacoordinate sulfur compound,  $\text{SOF}_4$ , appears to have such a trigonal-bipyramidal geometry,<sup>7</sup> although there is some uncertainty as to the detailed structure.<sup>8,9</sup>

**Acknowledgment.** Support for this research was provided by Grant No. GP 30491X and by a departmental equipment grant for the purchase of nmr instrumentation from the National Science Foundation.

(6) F. B. Dudley, G. H. Cady, and D. F. Eggers, Jr., *J. Amer. Chem. Soc.*, **78**, 1553 (1956). Another possible example has been proposed by R. J. Gillespie and J. V. Oubridge, *Proc. Chem. Soc. London*, 308 (1960).

(7) K. Kimura and S. H. Bauer, *J. Chem. Phys.*, **39**, 3172 (1963).

(8) J. L. Hencher, D. W. J. Cruickshank, and S. H. Bauer, *ibid.*, **48**, 518 (1968).

(9) G. Gundersen and K. Hedberg, *ibid.*, **51**, 2500 (1969).

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## Book Reviews

**Organic Peroxides. Volume II.** Edited by DANIEL SWERN. Wiley-Interscience, New York, N. Y. 1971. ix + 963 pp. \$40.00.

This volume contains articles by eight authors and represents a very comprehensive review of peroxide chemistry covering the literature to 1969. Extensive coverage is given to alkyl hydroperoxides, metal-catalyzed reactions of peroxides, peroxy acids as oxidizing agents, and acyl peroxides. Considerable attention is paid in two articles to physical properties and detection of peroxides.

The text is well laid out with numerous structures, mechanisms, and exemplary tables. It is well documented with nearly 4000 references. The cost of this book, though in line with its size and scope, will dictate its use mainly as a specialized reference.

John T. Groves, *University of Michigan*

**Some Modern Methods of Organic Synthesis.** By W. CARRUTHERS (University of Exeter). Cambridge University Press, London. 1971. x + 399 pp. \$16.50 (hardcover); \$5.95 (paperback).

This recent addition to the Cambridge Chemistry Texts Series provides a survey of the more important new methods in synthetic organic chemistry. The treatment is necessarily brief and the emphasis is on synthetic utility rather than reaction mechanisms. The book is organized into seven chapters with the following headings: Formation of Carbon–Carbon Single Bonds, Formation of Carbon–Carbon Double Bonds, The Diels–Alder Reaction, Reactions at Unactivated C–H Bonds, Synthetic Applications of Organoboranes, Oxidation, Reduction. The nearly 400 references that are included represent a good combination of pertinent review articles and very recent work. In the opinion of this reviewer, the author has been eminently successful in his aim to prepare a text for advanced undergraduates and beginning graduate students. These

and other “students” of synthetic organic chemistry should find this book extremely useful.

Robert E. Gilman, *Rochester Institute of Technology*

**Physics of Electronic Ceramics.** Edited by L. L. HENCH and D. B. DOVE (University of Florida). Marcel Dekker, New York, N. Y. 1971–1972. Part A: xviii + 564 pp. \$29.50. Part B: xx + 552 pp. \$29.50.

The two parts of this volume cover the proceedings of the Electronics Phenomena in Ceramics Conference held at the University of Florida in 1969. The purpose of the conference and of these volumes is to provide a review of the electronic and structural properties of metal oxides and related material as well as to present some commercial applications of these materials. In this respect the editors and the conference organizers have done an admirable job. A perusal of both parts shows that the editors have gone to a considerable effort of bringing together experts in every conceivable aspect of ceramic theory and methodology.

Part A is divided into six parts: a brief introduction to the overall picture of quantum mechanical applications to ceramics; electronic and defect properties of *crystalline* ceramics; electronic processes in *amorphous* ceramics; thin-film structure and technology, surface structure, and dielectric properties. Part B continues with four more sections on static and dynamic properties of ferroelectrics, magnetic structure of ceramics, optical properties of ceramics, and related phenomena and concludes with device applications of crystalline and amorphous ceramics.

These volumes will thus serve as an extremely useful introduction to those physicists, chemists, and materials science engineers who wish to become acquainted with the theory and technology of metal oxides.

The preface suggests that the volumes could serve as a graduate course text in electronic ceramics. The wealth of topics covered in these books, however, prevents there being more than a summary of essential information in each area, information which will, however, be extremely valuable to graduate students doing research and teachers who need to beef up courses in solid-state chemistry and physics with applications from *real* systems. It is unfortunate that at \$59 per set this book may be out of reach of most students.

Jerome H. Perlstein, *The Johns Hopkins University*

**Inorganic Titrimetric Analysis: Contemporary Methods.** By WALTER WAGNER (University of Detroit) and C. J. HULL (Indiana State University at Terre Haute). Marcel Dekker, Inc., New York, N. Y. 1971. xii + 225 pp. \$13.50.

This book is intended to be a "rapid and convenient guide" when a method is required for a limited number of analyses, when no investment in other than routine equipment or development time can be justified. It intends to provide enough information for the reader to decide which among the methods selected for presentation by the authors might be worth looking into further. The reader is referred to the literature for details of procedure and technique. All elements through number 94 are covered except for four lanthanides and five noble gases.

Methods for a given element are presented together, first in a "synoptic survey," with two or three lines sketching out each method, then in 10- to 20-line outlines. "Classical methods" (pre-1960 or so) are distinguished from "contemporary methods" (1959 through 1968), and only contemporary methods are outlined. The outline does not follow any strict paradigm, but generally contains indication of precision, sensitivity, interferences, reagents and instrumental requirements, as well as the principle of the method. There is ordinarily one reference for each method.

Success of the book can be evaluated in regard to three questions: (1) Does it provide enough information to enable the reader to pick out one or two methods most appropriate for him? Here the book is quite adequate, considering the brevity and restriction to titrimetric methods. A more useful book would include all methods an ordinary lab could use with little investment, especially spectrophotometric methods.

(2) Do the literature references enable the typical reader to find the details of a procedure? There are very many references to journals the typical chemist would not have access to. If one would like to titrate aluminum with EDTA, for example, he would have to locate *An. Real. Soc. Espan. Fis. Quim. (Madrid)*. (Three EDTA titrations of aluminum are detailed by Schwarzenbach and Flaschka in the second English edition of "Complexometric Titrations.") The book would be more useful if it included more references to other compendia of methods.

(3) Are the methods selected for description actually the best among the simple methods available? The book's emphasis on "contemporary" methods biases the selection against proven methods and makes selection on bases other than what is claimed by the literature that reports initial development of a method very difficult. Selection corresponds well with that of more specialized compendia, when fundamentals of the selected methods are compared, but does not correspond closely when details of methods are considered. So far as can be judged, selection of methods was done competently.

The need the book seeks to fill is a real need, and the book does a good job of filling it. Because the purpose of the book is narrow and practical, the prospective buyer must ask the practical questions, "is the need the book fills an important need for me?" A marginal plus is that, because much detail is omitted, the book makes surprisingly good browsing.

Jerrold C. Jayne, *California State University, San Francisco*

**Handbook of the Analytical Chemistry of Rare Elements.** By A. I. BUSEV, V. G. TIPTSOVA, and V. M. IVANOV. Translated by J. SCHMORAK. Ann Arbor-Humphrey Science Publishers, Inc., Ann Arbor, Mich. 1970. xii + 402 pp. \$21.00

It is nearly 50 years since A. A. Noyes and W. C. Bray wrote "Qualitative Analysis for the Rare Elements" as a record of an experimental investigation by them and their many collaborators—an investigation that extended over 30 years in three well-known chemistry departments. This great memoir is not mentioned in the book under review.

No definition of a rare element satisfies everyone. The present book recognizes about 60, among which the five rare gases are counted. But only 26 are actually treated therein provided the rare earths (REE) are regarded as one element, which seems fair

enough as only cerium receives much attention. Surprisingly, gold and the platinum metals are not discussed.

In the 21 pages of introductory material, important methods such as X-ray emission spectrography and methods involving radioactive species are mentioned and dismissed, not to reappear subsequently. Journals, books, and other publications that contain relevant material are listed, sometimes with brief description. Even here, though to a lesser extent than in the bibliographies that follow the sections devoted to the 26 elements treated, Russian sources receive major emphasis. We are thus given a welcome index to the Russian, but not to the world literature.

The sections just mentioned usually begin with a "micro Gmelin" that describes the element being considered, continues with ways by which it can be separated, and concludes with methods (mainly chemical and photometric) by which it can be determined. These sections are well done. Among the six appendices, the first (organic reagents), the second (masking compounds), and the third (isolation by solvent extraction) are particularly interesting.

Near-identity of chemical behavior among elements, so frustrating in determinations by chemical methods, is without significance in X-ray emission spectrography as Moseley himself showed for the rare earths, and Coster and (von) Hevesy demonstrated in 1923 for hafnium and zirconium. One might have predicted then that X-ray emission spectrography would become the method of determination satisfactory for more elements than any other on the day when suitable equipment became widely available. That day is in sight. When it arrives, the book under review is likely to join Noyes and Bray in almost unbroken library repose. Meanwhile, purchase is recommended.

H. A. Liebhafsky, *Texas A&M University*

**Chemical Reactions in Urban Atmospheres.** Edited by C. S. TUESDAY (General Motors Research Laboratories). American Elsevier, New York, N. Y. 1971. xiv + 287 pp. \$14.50.

This volume consists of papers presented at a symposium at the Editor's institution in mid-1969. There are 11 papers, all fairly lengthy, which both review previous literature and report the authors' research. Subsequent discussion of each paper is also reported, apparently nearly verbatim. There are good indexes and the traditional participant list. There is, for better or for worse, no group photograph.

The title of the volume is somewhat of a misnomer; there are numerous types of reactions in urban atmospheres that are never mentioned. Furthermore the majority of the results reported are not obtained in urban atmospheres, but in artificial model systems at high concentrations; the results may be valid at real concentrations in the open air, but the matter is in many cases unproven. A better title might be "Photochemical Studies Related to Urban Air Chemistry," since all the papers report on the photochemical portion of the entire complex of reactions that occur in polluted atmospheres.

The meeting was clearly a good one for those in the field. The pace was slow enough to permit the authors to synthesize, explain, detail misgivings, relate blind alleys, and request help from colleagues in understanding anomalous results. Discussion was extensive and informed (or uninformed discussion was deleted in editing). However, it is hard to read the list of attendees and refrain from wondering what about one-third of the audience learned. There are automotive engineers, a few control officials, and even a lobbyist. Is singlet oxygen meaningful to lobbyists (or their clients)?

For those directly concerned with more-or-less applied photochemistry, the volume should be extremely useful. Two adverse criticisms are possible. First and foremost, the delay of over two years between presentation and publication makes some of the papers obsolete. Only one author seems to have taken the opportunity to update the discussion. Second, and corollary to the first, the authors of necessity present their work up to the date of the symposium. There are numerous comments that "the work is being continued," or that "that is the next thing we will try." Very likely the final reports have already appeared; while it is unreasonable to expect the authors to rewrite their papers, it should have been possible to add a short supplementary bibliography, say, up to early 1971.

However, these are minor points. The list of authors and discussants is distinguished, including the majority of significant contributors to the field. The papers cover some aspect or other of every significant primary absorber of available solar energy. The book cannot be recommended as a handy reference volume for

air pollution control officers, but it clearly belongs in the libraries of all who aspire to understanding of atmospheric photochemistry.

James P. Lodge, *National Center for Atmospheric Research*

**Annual Review of Materials Science. Volume 1. 1971.** Edited by R. A. HUGGINS (Stanford University). Annual Reviews Inc., Palo Alto, Calif. 1971. ix + 420 pp. \$10.00.

This first volume of a new series on materials science consists of twelve articles written by recognized authorities within the field. They are critical appraisals of the status of different portions of materials science, with special emphasis upon recent progress and current trends. The approach is interdisciplinary in nature, since the organizational scheme places emphasis on the more general aspects of structure, characterization, phenomena, and properties related to the solids comprising the materials of engineering use, rather than in terms of the traditional academic fields of chemistry, physics, ceramics, metallurgy, polymer chemistry, etc.

Quite appropriately, the leading article is an extended and critical discussion of the current status and trends of research in the techniques for the structural characterization of materials by the use of electron microscopy in combination with electron diffraction and electron and X-ray emission spectroscopy. This article is followed by a short but significant one on the development and application of theoretical techniques to problems in materials science.

Other articles deal with the structure of defects in solids, structure of ideal clean solid surfaces, solid-state phase transformations, crystal growth, solid thin films, and anomalous properties of the vanadium oxides. A discussion on solution thermodynamics in metallic and ceramic solid systems represents the high-temperature chemical aspects of the work of materials scientists. Reviews of the current status of research on strengthening mechanisms in crystalline solids and on electronic and optical phenomena in semiconductors are also included. The final review constitutes a report on the status of corrosion science, as limited to corrosion of materials in aqueous solutions.

This volume effectively introduces the reader to the philosophy of the materials science approach. The series should be of considerable interest and benefit to researchers and graduate students in chemistry, physics, and engineering who are concerned with work related to materials.

Joseph A. Pask, *University of California*

**Polymerization at Advanced Degrees of Conversion.** By G. P. GLADYSHEV and K. M. GIBOV. Distributed by International Scholarly Book Services, Inc., Portland, Ore. 1971. v + 124 pp. \$13.00.

This book treats the subject of polymerization at high degrees of conversion. It is divided into three chapters. The first, "Advanced Polymerization," treats the theoretical background of this important but still not adequately treated subject. The theory of the gel effect, also known as the Trommsdorf effect, is explained in a clear and concise manner. Examples of supporting quantitative data are given. The chapter is concluded with a discussion of how free-radical polymerization processes at high degrees of conversion can be monitored through temperature variation and addition of inhibiting agents.

Chapter Two, "Experimental Study of Free-Radical Polymerization," offers a routine treatment of initiation rate, chain-transfer reactions, and some rather common measurement methods.

Chapter Three, "Methods of Study of Advanced Free-Radical Polymerization," describes the application of the methods mentioned in Chapter Two to the particular problem of polymerization at high degrees of conversion. Several calculations and estimations of rate constants conclude the book.

The book may be considered a sound and well-organized review of the fundamentals of this type of reaction. It can be recommended for graduate students who work in the area of kinetics. It is clearly written and very much to the point. For people in industry, the special asset of this book is its extensive bibliography. The drawback of this book is that the calculations of rate constants in Chapter Three are rather sketchy. Some more detail would have been desirable.

W. Poppe, *Amoco Chemicals Corporation*

**Solvent Extraction Reviews.** Edited by YIZHAK MARCUS (The Hebrew University). Marcel Dekker, Inc. New York, N. Y. 1971. x + 256 pp. \$19.50.

The seven reviews contained in the first volume of "Solvent Extraction Reviews" cover a wide variety of extraction-related topics

ranging from those of direct technological application (mixing equipment; industrial extraction of phosphoric acid) and the nuclear process industry (extraction of polonium and protactinium), to those of more general and theoretical interest (organic phase interactions of acidic organophosphorus extractants; mass transfer problems; kinetics of metal extraction by organophosphorus acids). As could be expected, the extractants most frequently treated are of the ubiquitous organophosphorus types.

The editor's commendable review goals to sort out "the essential from the transitory, to get to the bottom of conflicting claims, and to relate the conclusions to the results of other disciplines," however, are not easy to achieve, and the information available in the literature at times is insufficient to permit satisfying attainment of these objectives. Nonetheless, a distinct service is rendered in the review of conflicting claims, and areas for further studies are illuminated.

The prospective purchaser has the choice of obtaining the reviews either by subscribing to the semiannual review journal of the same name at \$17.50 per year or of buying the hard-cover book edition published annually from the journal with attendant author and subject indexes at \$19.50. The latter might be the better buy for institutional libraries at which only one version could be justified. A convenience associated with the author index is that it also includes references to text pages on which work is mentioned without accompanying author identification. A majority of the reviews contained in this volume also thoughtfully contained a nomenclature section to define the symbols used by the author.

The major advantage of this publication both to workers in the field and to newcomers is the service rendered in summarizing papers pertinent to the topics which have been published in quite a wide scattering of journals.

Kenneth C. West, *St. Lawrence University*

**Techniques of Chemistry. Volume I. Part IV.** Edited by A. WEISSBERGER and B. W. ROSSITER (Eastman Kodak Co.). Wiley, New York, N. Y. 1972. xi + 561 pp. \$27.00.

Volume I of "Techniques of Chemistry," entitled "Physical Methods of Chemistry," is the first of three volumes which are written to "... give the theoretical background for an understanding of the various methods and operations and describe the techniques and tools, their modifications, their merits and limitations, and their handling." Part IV of "Physical Methods of Chemistry" fulfills the objectives of the series and continues the high quality of its predecessor, the "Technique of Organic Chemistry Series."

Part IV considers the determination of mass, transport, and electrical-magnetic properties. This is not a how-to-do-it book for those unfamiliar with the techniques of the physical measurements discussed. Rather, the book is a collection of seven articles (chapters), which are to a large extent review articles. However, all the articles sketch the theory and the basic concepts relevant to the physical measurements. In some instances, detailed discussions are given of new or unfamiliar methods of measurement. There are a total of 1521 references, so that anyone unfamiliar with any given technique has available in this book a handy guide to more complete discussions of both theory and experiment.

In the first chapter, A. H. Corwin discusses balance design and the sources of error in weighing. Most of this discussion concerns the knife edge balance, and the elimination of errors through balance design and adjustment is stressed. N. Bauer and S. Z. Lewin give a thorough discussion of the determination of the density of liquids, solids, and gases. G. L. Beyer gives an extensive review of the methods of determination of particle size and molecular weight with the objective of enabling the reader to select from a very great variety of methods those that are best suited to his own needs. Experimental methods for studying diffusion in liquids, gases, and solids are discussed by P. J. Dunlop, B. J. Steel, and J. E. Lane. Stress is placed on the relatively recent and more popular methods. In most cases the theory is outlined, and in some cases the construction of cells is discussed in detail. W. E. Vaughan, C. P. Smyth, and J. G. Powles systematically explore the methods used for the measurement of dielectric constant and loss at various frequency ranges from below 60 Hz to above  $6 \times 10^{10}$  Hz. The theory of dipole-moment determination from dielectric-constant measurement and the uses of dipole-moment values are outlined by C. P. Smyth; the three main methods of measuring dielectric constants are discussed. In the last chapter, L. N. Mulay reviews the numerous methods which have been devised to measure magnetic susceptibility. The details of the experimental set-ups for the Gouy and Faraday methods are discussed.

Richard E. Wilde, *Texas Tech University*