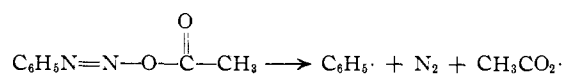


dehydrate 2,4-dinitrophenylhydrazine. Reaction in ether containing an equimolar amount of acrylonitrile changed the time for 40% nitrogen evolution from 62 min. to 106 min. The yield of benzene was reduced to 23%. No II could be isolated, although a small amount may have been formed. When dioxane was used in place of ether, benzene (46%), nitrogen (58%), and 1-dioxanyl acetate (22%) were formed. Treatment of another reaction mixture with 2,4-dinitrophenylhydrazine gave glyoxal 2,4-dinitrophenylhydrazone (36%).

N-Nitrosoacetanilide reacted in benzene to give 87% nitrogen, <1% carbon dioxide, and 72% biphenyl.⁴ Reaction under the same conditions except for the addition of a 10-mole excess of acrylonitrile increased the time required for 40% nitrogen evolution from ca. 90 to 290 min. No biphenyl was formed under these conditions. Decomposition in benzene containing a 10-mole excess of styrene increased the time for 40% nitrogen evolution to 146 min. Again biphenyl formation was completely suppressed. Finally, decomposition in the presence of a 10-mole excess of 2,6-di-*t*-butyl-*p*-cresol had very little effect on the rate of nitrogen evolution, but again no biphenyl was formed.

Previous mechanistic proposals for the reactions of I have involved rapid homolysis^{2a,b,5} after a slow rear-



angement of the N-nitroso compound. In aromatic solvents it has been suggested that further reaction of phenyl radicals and acetoxy radicals yields biphenyls and acetic acid. Many workers have recognized that the postulation of acetoxy radical formation without subsequent carbon dioxide formation requires very rapid reaction of the acetoxy radicals. In essence this anomaly has been rationalized by suggesting that biaryl formation involves a "cage reaction."^{2b,5}

The results reported here do not support this concept. The obtention of II and dioxanyl acetate is not in agreement with a simple dissociation mechanism.

(4) These yields are comparable to those reported by many investigators.

(5) R. Huisgen and G. Horeld, *Ann.*, **562**, 137 (1949).

Such a mechanism requires that a phenyl radical abstract an α -hydrogen from ether to give an α -alkoxy radical which then combines with an acetoxy radical. All of this must occur before the acetoxy radical can decarboxylate.⁶ The formation of II and dioxanyl acetate is readily explained by a mechanism involving induced decomposition of I. Attack by an α -alkoxy radical on I to give ester, nitrogen, and a phenyl radical is a very reasonable means of forming ester and perpetuating a chain reaction involving phenyl radicals. This mechanism readily explains the diminution in benzene yield in the presence of acrylonitrile.⁷ The effect of inhibitors on biphenyl yields is particularly striking and demonstrates that the course of the reaction is completely modified by these substances. In this connection it is important to note that nitrogen yields were not affected by the inhibitors. It seems reasonable to conclude that phenyl radicals and/or phenylcyclohexadienyl radicals, their addition product to benzene, are trapped before biphenyl formation can occur. These results certainly suggest that free phenyl radicals are involved in biaryl formation. A "cage reaction" should not be affected by an inhibitor.⁸ These observations suggest that the reaction of I in benzene involves induced decomposition rather than a "cage reaction."⁹ Clearly further work is required, and such is in progress.

(6) No more than 1% of carbon dioxide is formed during the decomposition in ethers.

(7) It is reasonable to assume that the monomer competes with the ether for phenyl radicals.

(8) It should be emphasized that two of the inhibitors decreased the rate of nitrogen evolution; thus it seems safe to conclude that the monomers are not reacting with N-nitrosoacetanilide or I. If this occurred, nitrogen formation would necessarily have to be faster than in the absence of inhibitor.

(9) Another piece of evidence which mitigates against a "cage reaction" and which has not been noted in this context is the essential absence of true "cage" product, phenyl acetate. Indeed, in a very careful investigation, T. Inukai, K. Kimura, O. Simamura, and T. Suehiro [*Bull. Chem. Soc. Japan*, **35**, 129 (1962)] showed that decomposition of methyl N-nitroso-*p*-acetamidobenz[¹⁴C]oate in benzene yielded only 0.046% of methyl 4-acetoxybenzoate.

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RECEIVED JUNE 11, 1964

BOOK REVIEWS

Chemical Analysis. Volume XIII. Alternating Current Polarography and Tensammetry. By B. BREYER and H. H. BAUER, School of Agriculture, Section of Agricultural Chemistry, The University of Sidney, Sidney, N.S.W., Australia. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1963. 228 pp. 15.5 × 23.5 cm. Price, \$12.00.

Despite their longtime recognition as basically valuable approaches to the study of moderately fast electrode processes, alternating current voltammetry (including polarography) and tensammetry, as distinct from bridge impedance methods, have been rather slow to command very widespread experimental interest among workers in this country. A good portion of this neglect might be ascribed as much to the slow development of a corpus of theory which could take acceptable account of the complex periodic relationships at the electrode surface, as to the experimental uncertainties and awkwardness of early instrumentation. Consolidation and extension of basic theory as well as recent improvements in experimental accuracy and convenience which have resulted from the successful use of new and improved types of instrumentation, such as operational amplifier circuitry, "lock-in" type phase discriminating ampli-

fiers, wave analyzers, etc., make it seem increasingly likely that a.c. voltammetry will elicit greater attention as an important investigational tool. Such expectation receives added strength with the appearance of this book by Breyer and Bauer which constitutes the first monograph review in this field. The book brings into long-needed focus a wide scattering of work which ranges over a twenty-two year period from the first measurements by Müller and co-workers around 1938, and it thus incorporates a good deal of the valuable exploratory effort of the early Australian school which appeared in journals that remain largely inaccessible to the average worker. Some 90 pages of the (228-page) text are devoted to introductory material and a review treatment of theory, including faradaic rectification, with some mention included of square-wave and radiofrequency polarography. Instrumentation is covered in the chapter following, and, on reading this, one is struck by the somewhat arresting fact that, except for the Mervyn-Harwell Square Wave Polarograph, most if not all of the classical a.c. polarographic instrumentation described in this chapter are of Japanese manufacture. Chapter 4 provides an extensive outline discussion of available information, much of which is qualitative, bearing on inorganic and organic applications of a.c. polarography, as well as a review of the

tensammetry of (mostly organic) substances which under such conditions do not participate in electron exchange. The fifth and last chapter of the book provides a description of some of the advantages which accrue to a.c. polarography and tensammetry in the elucidation of electrode processes.

"Alternating Current Polarography and Tensammetry" provides the reader with a good, if essentially noncritical, account of developments in these fields up to, as it turns out, about 1960. He is likely to come away, as did the Reviewer, with a small feeling of disenchantment from the fact that, despite its quite recent publication date, the book affords little suggestion of the important developments which occurred between 1960 and 1963 in the areas of instrumentation and a.c. harmonic voltammetry.

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Treatise on Analytical Chemistry. Part I. Theory and Practice. Volume 4. Edited by I. M. KOLTHOFF and PHILIP J. ELVING, with the assistance of ERNEST B. SANDELL, School of Chemistry, University of Minnesota, Minneapolis, Minn. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York 16, N. Y. 1963. 954 pp. 17 × 24 cm. Price, \$25.00.

To write a concise, critical, comprehensive, and systematic treatment of all aspects of classical and modern analytical chemistry would be a Herculean task, if not an impossible one, for any one person, so rapidly has analytical chemistry grown within the past twenty years. The alternative is to pool the techniques and skills of a large group of analysts who are specialists in their respective fields and to present their subjects in a systematic multi-volume work. This the editors of the "Treatise on Analytical Chemistry" are undertaking. When complete the Treatise will present a concise, critical, and comprehensive treatment of classical and modern analytical chemistry and is being published in three parts, each containing a number of volumes. It is not intended, however, to be such an exhaustive work as the "Handbuch der analytischen Chemie" by Fresenius and Jander. The analytical chemistry of the elements is covered in Part II, and Part III is devoted to analytical chemistry in industry.

Volume 4 of Part I consists of two sections (D-1 and D-2) and contains 15 chapters with 18 contributing authors. C. N. Reilley served as section advisor. Magnetic field methods of analysis are treated in Section D-1 and electrical methods of analysis in Section D-2. Topics covered in the respective chapters are: Chapter 38 (L. N. Mulay), "Analytical Applications of Magnetic Susceptibility"; Chapter 39 (N. F. Chamberlain), "Nuclear Magnetic Resonance"; Chapter 40 (F. W. Malpolder and R. A. Brown), "Mass Spectrometry"; Chapter 41 (S. Rubin), "Ion-Scattering Methods"; Chapter 42 (C. N. Reilley), "Fundamentals of Electrode Processes"; Chapter 43 (C. N. Reilley and R. W. Murray), "Introduction to Electrochemical Techniques"; Chapter 44 (P. Delahay), "Chronoamperometry and Chronopotentiometry"; Chapter 45 (N. H. Furman), "Potentiometry"; Chapter 46 (L. Meites), "Voltammetry at the Dropping Mercury Electrode (Polarography)"; Chapter 47 (R. N. Adams), "Voltammetry at Electrodes with Fixed Surfaces"; Chapter 48 (N. Tanaka), "Electrodeposition"; Chapter 49 (D. D. DeFord and J. W. Miller), "Coulometric Analysis"; Chapter 50 (I. Shain), "Stripping Analysis"; Chapter 51 (J. W. Loeveland), "Conductometry and Oscillometry"; and Chapter 52 (B. W. Thomas and R. Pertel), "Measurement of Capacity: Analytical Uses of the Dielectric Constant."

There are many schematic diagrams, figures, graphs, and tables that add much to the clarity and usefulness of the book. Many references are listed at the end of each chapter and total more than 2200. The book is well indexed (33 pp.) and in addition, each chapter is headed by an extensive and well-organized table of contents. Printing and paper are good, and the book has an attractive cloth binding.

Volume 4 of Part I maintains the high standard set by preceding volumes in the Treatise and is an authoritative and up-to-date reference work on magnetic field and electrical methods of analysis.

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June, 1964

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