

Another mode of reaction is suggested by the formation of phenyl disulfide (80%) and triphenylphosphine oxide (75%) from **1** and triphenylphosphine. Thus, we are investigating further the difference between direct attack on **1** and reactions of **2**.

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spectra and Dr. P. A. Wadsworth performed the high-resolution mass spectral study.

(10) Work was performed at Shell Development Co., Emeryville, Calif.

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Book Reviews

Organic Syntheses via Metal Carbonyls. Volume I. Edited by IRVING WENDER, Pittsburgh Coal Research Center, Bureau of Mines, U. S. Department of the Interior, Pittsburgh, Pa., and PIERO PINO, Istituto di Chimica Organica Industriale, Università di Pisa, Pisa, Italy. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1968. xi + 517 pp. 16 × 23 cm. \$18.95.

This book can be strongly recommended to those interested in the chemistry of transition metal carbonyls and their derivatives or in stoichiometric or catalytic syntheses involving metal carbonyls.

The first chapter, by F. Calderazzo, R. Ercoli, and G. Natta, comprises over half the book (272 pp) and is the best account of the general chemistry of metal carbonyls yet in print. The methods of preparation, structures, and chemical properties are given, and the references are well chosen and up to date. The treatment includes many types of substituted carbonyls, hydrido carbonyls, halogeno carbonyls, phosphine carbonyls, etc.

Chapter 2, by W. Hübel, is an equally satisfying treatment of the great variety of organometallic compounds obtained from the interaction of carbonyls and acetylenes, while the next chapter by C. Hoogzand and W. Hübel is complementary in that it describes the cyclic polymerization of acetylenes by metal carbonyl compounds.

There is then an excellent account by R. F. Heck of the preparation properties and use specifically of cobalt carbonyl hydride, alkyls, and acyls and their use in organic syntheses, such as the carboxylation of epoxides or the acyldiene synthesis.

Finally a substantial chapter by A. Rosenthal and I. Wender deals with the very extensive application of the OXO or hydroformylation reaction to unsaturated compounds with carbon-nitrogen and nitrogen-nitrogen bonds in reactions such as cyclization reactions of Schiff bases, azo compounds, oximes, etc.

In all chapters much useful information on preparations, reactions, and spectra is collected in extensive tables. The indexes, both author and subject, are satisfactory.

In short "Organic Syntheses via Metal Carbonyl" is an authoritative book of interest to a wide spectrum of chemists.

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Chemistry of Dissociated Water Vapor and Related Systems. By M. VENUGOPALAN and R. A. JONES, Royal Military College of Canada, Kingston, Ontario. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1968. xviii 463 pp. 16 × 23.5 cm. \$19.50.

This timely book fills the need for a long-awaited survey of the chemistry of dissociated water and other oxyhydrogen systems. It is the outgrowth of a lengthy article published by the authors a couple of years ago in *Chemical Reviews*. *A priori* one would not imagine that this topic alone could fill a book of over 450 pages; but here it is, and without too much redundancy at that.

After a brief introduction outlining the historical development of the subject, some 60 pages (Chapter 2) are devoted to the various ex-

perimental methods for dissociation and excitation of gas streams, the trapping techniques, and finally the analytical methods, mostly physical: spectroscopy, diffraction, calorimetry, etc. Inevitably, a good deal of this material has already been reviewed elsewhere, in particular, in the monograph "Formation and Trapping of Free Radicals," A. M. Bass and H. P. Broida, Ed. (Academic Press, New York, N. Y., 1960). This would not be too serious were it not for the fact that the authors, as kineticists, are not familiar with most of these techniques. As a result their perspective is often distorted if not downright erroneous. For instance, on page 40, the X-ray and electron diffraction methods are related to surface structure studies, which certainly is not the case here. Then, on page 50, this reviewer is credited with the development of an isothermal ice calorimeter (in fact, it was a diphenyl ether calorimeter), and the instrument is said to have been equilibrated at -196° , a most difficult and useless task, to be sure.

Chapter 3 deals at length with the dissociation in electrical discharges at low pressures of various oxyhydrogen systems: water and hydrogen peroxide vapor, atomic hydrogen reacted with molecular oxygen or ozone. It also contains a section on the condensed products from these systems (about which, more later), and another one on reaction mechanisms. The other methods of dissociation, namely thermal, photochemical, electron impact, and radiolysis, are dealt with adequately in Chapter 4. In this, as in other chapters, attention has been focused mainly on gas-phase reactions so as to keep the size of the survey within reasonable limits.

Chapter 5 is concerned with the reactions between the two elements in question, whether it be in explosions, flames, photochemical (sensitized or not), radiochemical, and electrical discharges, both at low and ordinary pressures. Over 200 individual references are quoted in this chapter alone (well over 1000 in the whole book), and 100 basic reactions are discussed. The sixth and penultimate chapter covers, with some repetition, the properties of individual atoms and free radicals as well as their chemical reactions. The kinetics of some 15 systems, either binary or with third bodies, are summarized.

Last, and least in size, Chapter 7 is a review of the still very controversial question of the superoxides of hydrogen, H_2O_3 and H_2O_4 . At that stage the authors depart from their stated policy of presenting the facts and conflicting views objectively. On reading this chapter, and previous sections on the same topic, one would think that they hold a brief to defend the cause of the superoxides. All opposing evidence is disputed or minimized, whereas every favorable argument, no matter how far-fetched, is presented down to the least minutiae (*cf.* in particular pp 128-158). One is reminded here of that meticulous critic who was said to "use gold scales to weigh fly-specks." This is not the place to point out all the inaccuracies encountered in that connection. This reviewer must, however, mention at least one since his own work is at stake. On page 132 one reads: "It is known that replacing hydrogen with deuterium in H_2O_2 results in a shift of the 0-0 vibration to shorter wavelengths." Now, this is contrary not only to the facts (the authors should have checked their reference) but also to the theory of spectroscopy.

It is unfortunate that the authors took this attitude on what is, after all, a minor point in the whole topic. It detracts seriously from

the value of an otherwise successful endeavor. The book ends with detailed author and subject indexes. It is remarkably free from misprints and other errors. The physical presentation is first class. The price seems high, but not too much above the recent trend.

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