Book Reviews

Catalysis of Organic Reactions. Edited by W. R. Moser. Marcel Dekker, New York. 1981.

This volume contains a compilation of papers from the Eighth Conference of the Organic Reactions Catalysis Society held in New Orleans June 2–4, 1980. It addresses in particular discoveries in chemical process technology and the impact of synthesis gas chemistry on fuels and chemicals. As such it contains material of different depth and scope. Some chapters are essentially an overview of commercial technology whereas others are comprehensive and contain mechanistic information in detail.

The first chapter by A. M. Brownstein is of an economic overview nature with principal emphasis on toluene as a replacement for benzene with styrene as an example and with synthesis gas for oxygenates. The oxygenates cited are acetic anhydride, ethylidene diacetate, and ethylene glycol. Prospects for synthesis gas-based olefin processes are also discussed. This chapter serves as a good "point-in-time" assessment, although changing supplies and availability of petroleum, gas, and coal feedstocks may invalidate the quantitative aspects.

Chapter 2 is concerned with selective oxidation processes, and outlines in detail the mechanism of Bi-Mo-oxides as catalysts for the selective oxidation of propylene to acrolein and ammoxidation to acrylonitrile. The third chapter is a short description of a Mobil ZSM-5 catalyst system for alkylation of benzene to ethylbenzene. The function of the intermediate pore size, spacioselective zeolite, and comparisons with other commercial processes are highlighted. The fourth chapter describes an alternate approach to styrene, the reaction of toluene and methanol over X-type zeolites with cesium cations. The influence of boron modification is also discussed. Spectrophotometric studies are included. In chapter 5, Chang, Lang, and Bell of Mobil Research and Development Corp. describe the influence of Shape Selectivity in zeolite catalysis on three reactions: aromatic hydrocarbon formation from methanol, the Prins reaction, and the acid-catalyzed condensation of acetone.

Chapter 6 describes calorimetric studies of the $C_2H_5AlCl_2/WCl_6$ olefin metathesis catalyst. While some conclusions concerning stoichiometry were drawn, these were insufficient for structure proofs or for mechanistic implications. Chapter 7 describes mechanistic studies which show that the sulfuric acid catalyzed oxidation of toluene produces derivatives of both formaldehyde and phenol. These are both desirable products, but further improvements in selectivity will be necessary for practical implementation. In chapter 8 synthetic oxometalloporphinates are described along with their reactivity for hydrocarbon oxidation and their relationship to cytochrome P-450. Chapter 9 gives a description of oxidation of organic olefin and alcohol substrates with nitro nitrosyl-ligated cobalt and palladium complexes. In chapter 10, F. Mares and S. E. Jacobson demonstrate the oxidation of olefins and ketones to epoxides and lactones, respectively, with dilute hydrogen peroxide in a triphase system. The solid was an arsonated polystyrene which was converted by hydrogen peroxide to the potent perarsonic acid. Chapter 11, somewhat an anomaly in this section, covers a compilation by R. C. Wade of uses of borohydrides as reducing agents in industrially significant reactions.

Part II surveys some aspects of new synthesis gas technologies. It begins with a chapter by K. Klier on the synthesis of C_1–C_4 alcohols with three types of heterogeneous catalysts. The first is the class of supported precious metals. The second, discussed in the most detail as it pertains to the author's own work, covers the Cu–ZnO-based methanol commercial catalysts. The third, which could hold considerable promise for the future, is composed of Cu/Co/M/A quaternary catalysts (M = Cr, Mn, Fe, e.g., A = alkali oxide). This chapter is particularly informative. In chapter 13, Rathke and Feder furnish kinetic data which is consistent with a coordinated formaldehyde intermediate in the CO/H_2 condensation to methanol, ethylene glycol, and methyl formate. This is an interesting paper for those concerned with oxygenate synthesis from synthesis gas. The next paper by Happel, Hinatow, and Bajars describes tracer techniques for delineating the mechanism of methanation over nickel and some nonmetallic catalysts.

The next two chapters are devoted to two different schemes for the homologation of methanol to ethanol. The first utilizes carbon monoxide and water with cobalt under *basic* conditions. The second is a unique scheme with iron pentacarbonyl and trimethylamine together with carbon monoxide rich synthesis gas. Both require relatively high pressures, a continuing problem with this desirable transformation. Selectivities are reasonable in both cases.

Two chapters are devoted to the commercially important hydroformylation reaction. Unruh, Christenson, Hughes, and Young of Celanese give a very detailed account of the effects of bidentate phosphines with rigid backbones on the rhodium-catalyzed reaction. Rates and selectivities are correlated with Hammett values. ^{31}P NMR studies were added, and a selective catalyst with three ligated phosphines is suggested. Pittman and Honnick found one of these phosphines, 1,1′-bis(diphenylphosphino)ferrocene, to be very effective for the hydroformylation of allyl alcohol to 4-hydroxybutanal. This aldehyde is desired as an intermediate in butanediol manufacture, but the normal hydroformylation reaction is plagued by isomerization to propanal, hydrogenation to propanol and the formation of high-boiling by-products.

Part III contains six chapters devoted to functional group hydrogenation. The nature of these papers are very diverse. One describes commercial applications of homogeneous hydrogenation catalysis. Others describe Raney nickel applications, both promoted and unpromoted. The paper on the industrial production of sugar alcohols is particularly informative.

The volume is of good quality and readable. The number of errors is very small. The index is somewhat short but adequate. Portions of it will appeal to those interested in industrial aspects of homogeneous and heterogeneous catalysis, but the wide diversity of topics will require a reader having a very wide range of interests.

Roy L. Pruett, *Exxon Research and Engineering Company*

Catalytic Aspects of Metal Phosphine Complexes. Edited by Elmer C. Alyea and Devon W. Meek. Advances in Chemistry Series No. 196. American Chemical Society, Washington, DC. 1982. x + 421 pages. $69.95.

This volume contains 24 of the papers which were presented at the June, 1980 Biennial Inorganic Symposium at Guelph, Canada, which was jointly sponsored by the Inorganic Divisions of the American Chemical Society and the Chemical Institute of Canada. The five subtopics of the symposium were ^{31}P NMR and the nature of the metal–phosphorus bond, the chemistry of bulky phosphine ligands, polydentate phosphines, the reactivity of transition-metal phosphorus compounds, and asymmetric synthesis. The articles vary in length (9–31 pages) and in scope from neatly packaged review articles to some previously unpublished specific research papers with detailed experimental sections. One of the latter articles which seems out of place with respect to style and content is an X-ray structural study complete with positional and thermal parameters, bond lengths and angles, and stereoscopic diagrams. As might be expected, about half of the articles deal with some aspect of rhodium phosphine chemistry. These include articles on asymmetric synthesis by Knowles et al., which describes some interesting new chiral tertiary phosphines with sulfone substituents thereby affording water-soluble catalysts (this article also includes specific experimental details), by Bosnich and Roberts, which outlines mechanisms and strategies of phosphine design for effective catalysts, by Brown, Chaloner, and Parker, which reviews mechanisms for hydrogenation of enamides and structures of intermediates in solution based on NMR evidence, and by Consiglio and Pino, which summarizes advances in asymmetric hydrocarbonylation and hydrocarbalkoxylation of alkenes. The homogenous hydrogenation with an interesting