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Book reviews

Homogeneous Catalysis by Metal Complexes. Volume I: Activation of Small Inorganic Molecules. Volume II: Activation of Alkenes and Alkynes, by M.M. Taqui Khan and Arthur E. Martell; Academic Press, New York, 1974. Vol. I, xi + 422 pages, $42.00; Vol. II, xi + 195 pages, $23.00.

This two volume work attempts to review the activation of small gas molecules by metal complexes. Volume I (900 refs.) contains 5 chapters (individually referenced) dealing with H_2, O_2, N_2, CO, and NO; Volume II, containing one set of 312 references, concerns activation of alkenes and alkynes in 6 chapters, dealing with π-bond migration, the oxo reaction, hydrosilation, oxidation of alkenes and alkynes, and multiple insertion reactions (oligomerization and polymerization). Both volumes have author and subject indexes. The presentation is basically a good balance between a mechanistic and descriptive approach, but unfortunately the books are very disappointing.

The stated "exhaustive" account of such a vast topic in two volumes is clearly an impossible claim; however, the major weaknesses are the out-dated coverage and an alarming number of scientific inaccuracies. The work is said to have developed over a long period: the literature to 1969 is reasonably surveyed (not exhaustively) but later coverage is scant. Excessive use of "recently", commonly referring to 1961-66 literature, emphasizes the failing.

There is no mention of asymmetric synthesis or supported homogeneous catalysts. Other omissions include: the studies of Perutz in the section on natural oxygen carriers; the use of organophosphinecobalt carbonyls for hydroformylation catalysts; considerable data on oxidative addition of H_2 to d^8 systems; important 1968-69 work on hydrosilation; Burnett's findings on the reaction of $HCo(CN)_5^{3-}$ with butadiene (which differs from the presented views of Kwiatek).

Some examples of incorrect scientific statements are: the interaction of heme units in hemoglobin oxygenation *decreases* the binding energy as the four groups are successively oxygenated; the $RhCl(PPh_3)_3$ catalyst *does not* hydrogenate ethylene; there is *no* evidence for stepwise transfer of hydrogen atoms using the $RhCl(PPh_3)_3$ catalyst; the hydrogenating activity for $PtCl_2L_2/SnCl_2$ systems *increases* with π-acceptor ability of L. Ru^{II} nitro complexes are incorrectly called nitrito complexes; the reaction of O_2 with some Co^{II} nitrosyls gives nitro complexes and not nitrates; the decline in acetylene hydration rate using Ru^{III} catalysts at higher chloride is *not* due to formation of substitution inert species; the activating effect of substituents on the hydrogenolysis of benzyl alcohols using $HCo(CO)_4$ is said to be not understood, while the original paper presents a plausible explanation in terms of carbonium

intermediates; cuprous salts are incorrectly said to activate H_2 by homolytic cleavage only; rhodium-catalyzed substitution processes using H_2 are discussed only as involving Rh^{III} hydrides and not the more established Rh^{I} intermediates; the autocatalytic stage of the CO reaction with Rh^{III} is *not* termolecular; the hydrogens in structure 29 cannot be *trans*; the species $Rh_2(SnCl_3)_4Cl_2$ said to be a Rh^{III} complex is an anionic Rh^{I} complex; the early confusion over the $Co(N_2)(PPh_3)_3$ and $HCo(N_2)(PPh_3)_3$ complexes is not recognized.

The number of typographical errors, mistakes in formulas, references, authors, etc., is unbelievably high. The use of "nitric acid" instead of "nitric oxide" on the inside cover is unfortunately a harbinger of things to come. "Morikawa" in the text becomes "Morkawa" in the reference, and "Morkowa" in the author index; in a list of four cationic carbonyls, three are shown as neutral and one of these is $PtClH(PPh_3)_2$! The list is endless. Attempts to follow up details on topics led me to many frustrating experiences. A mechanism suggested by the authors for the reaction of $Ru(NH_3)_5H_2O^{2+}$ with N_2 has been discussed by Page et al. in a paper referred to elsewhere in the chapter for some kinetic data; the reference given (157) starts M. Clive, I. Elson, J. Itzkovitch . . . instead of C.M. Elson, I.J. Itzkovitch . . . .

Further, the volumes are expensive at about 10 cents per side, especially when there has been little effort to conserve space. For example, Table VII (Vol. I), reporting the hydroxylation of 24 organics, covers 8 pp; space-consuming structural formulas are often used for simple oxidative addition and related reactions, such as eqns. 133, 134, 169 in Vol. II; more than one reaction scheme showing the same mechanistic principle are often given, when a cross reference would be equally effective; the structure of $IrCl(CO)(PPh_3)_2O_2$ showing only the O—O bond length does not merit half a side; the 15 page coverage of Ru^{II} nitrogen complexes could be presented much more concisely.

The term "aralkyl" used for a mixed aryl—alkyl derivative was new to this reviewer.

The extensive coverage given to model and natural hydroxylation and oxidase systems is very similar to the chapter contributed by the same authors to Eichhorn's "Inorganic Biochemistry", Vol. 2. Elsevier, 1973.

Some of the reported unpublished findings of Taqui Khan et al. were of considerable interest, and should be more well-documented in the journal literature; for example, the syntheses of $RuClH(AsMePh_2)_3O_2$, $RuCl_2(AsMePh_2)_2(N_2)(O_2)$, and $Mn(N_2)Cl(diphos)_2$; the $RuCl_2(AsPh_3)_3O_2 + H_2$ reaction to give H_2O_2 and $RuClH(AsPh_3)_3$; and the conversion of N_2/H_2 mixtures to NH_3 using various platinum metal chlorides in aqueous HCl in the presence of reducing agents such as Sn^{II}, Ti^{III}.

In summary then, this reviewer has to conclude that new and seasoned workers contemplating further studies in the extensive area of homogeneous catalysis will need to refer to more updated and specialized reviews.

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Electronic Structure and Magnetism of Inorganic Compounds, Volume 3, A Specialist Periodical Report, P. Day, Senior Reporter, The Chemical Society, London, 1974, xi + 431 pages, £14.00.

This is the third volume under the indicated title and includes chapters on electronic spectra (Day), natural and magnetic optical activity (R.G. Denning), ning), magnetic susceptibilities (A.K. Gregson), and photoelectron spectroscopy (A. Hamnett and A.F. Orchard). The coverage includes all types of inorganic materials but does not encompass organometallics, whose electronic properties are summarized in a separate Specialist Periodical Report. Although the preface contains the expected disclaimer that the literature coverage is not complete, there seems to be little if anything falling within the purview of this report and published in 1972 that has escaped the roving eye of the reporters. A check of two subjects with which this reviewer is quite familiar revealed no omissions in literature citations. Indeed, the collection of relevant literature is not merely adequate, but is microscopically exhaustive to the point of citations from obscure journals, including, for example, a review of stereoselectivity of metal complexes in Portuguese! Each chapter is well written and includes brief semi-interpretative discussions of what the authors consider more important and interesting work, followed by tabulations of references on other systems not discussed. Throughout there are well selected figures from the literature, and a full author index is furnished.

This reviewer is now an enthusiastic devotee of Specialist Periodical Reports, and this admirable volume is no exception. These Reports will shortly include some 34 titles. For those uninspired by the prospect of seeking out needed published work of several or more years ago via the *Chemical Abstracts* method, these Reports offer an alternative and conspicuously less tedious approach. The full set of Reports is a must for any chemical or science library and the price of this and most other volumes (~$15-20) places them in the range of the invidual researcher.

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Introduction to Modern Liquid Chromatography; by L.R. Snyder and J.J. Kirkland, Wiley-Interscience, New York/Londen, 1974, xv + 534 pages, £9.00.

Readers of this journal who do not reside in North America may not be aware of the continuing education program sponsored by the American Chemical Society, through which a series of "Short Courses" of 2-3 days length on topics of current chemical interest is offered at various locations in the U.S.A. to practicing chemists to aid them in keeping abreast of some

of the latest developments in the field. One of the most popular of these short courses is the one on liquid chromatography, taught by the authors of this book. Here, they have attempted to present in written form the topics usually covered in the course along with other supplementary materials useful in the practice of LC.

The book consists of thirteen chapters and six appendices. After a general introduction, basic concepts and the control of separation are considered. Equipment currently in use is next discussed with particular emphasis on detectors and columns. There follow separate chapters on each of the four basic LC techniques, liquid—liquid, liquid—solid, ion-exchange, and gel chromatographies. Suggestions for selecting a particular LC method are then given. The book closes with a chapter on large scale separations (by J.J. DeStefano) and a brief discussion of several other topics. Throughout, there is a good balance between theory and practical applications. There are many suggestions which should prove helpful to any chemist wishing to use this separation technique. A particularly useful example is the suggested scheme for systematically changing various parameters to effect a given separation.

One can always find things to criticize. Since this book is produced directly from a typed manuscript, the figure captions are in the same format as the main text; this sometimes causes a momentary confusion in reading, especially when turning a page. A few typographical errors were noted. Also, one should remember that much of the information on specific instrumentation and column packings, while extremely useful now, will rapidly become somewhat dated as newer equipment and materials become available.

Organometallic chemists have long used chromatography as a standard laboratory technique. They have not yet made extensive use of the modern equipment which has become commercially available in the last five years. This probably accounts for the fact that, of all the literature references listed, only one is readily identifiable as involving an organometallic system. As more chemists become aware of the separations and purifications that can readily be attained by these methods, more applications to organometallic chemistry are to be expected. This book will serve as an excellent guide to those who wish to explore these possibilities.

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