with predictions for a *cis*-disubstituted octahedral tetracarbonyl complex. This infrared spectrum of III was invariant with time, whereas spectra of the isolated acetyl derivatives I or II varied rapidly with time as decarbonylation occurred. The proton resonance of the methyl group of III appears as two peaks of equal intensity at −5 and −13 c.p.s. in benzene. This splitting may arise from spin–spin interaction with the phosphorus-31 nuclei. Although manganese-55 ($I = {}^5/_2$) can theoretically cause spin–spin splitting in $CH_3Mn(CO)_5$ and in III, it appears not to do so in either case.

Further evidence for the equilibrium nature of this reaction was provided by two simple experiments. First, when carbon monoxide gas was bubbled into a benzene solution of III for 12 hr. at room temperature, nearly all of III was carbonylated. The p.m.r. spectrum of the resulting solution was identical with that obtained in the closed-tube reaction of $CH_3Mn(CO)_5$ with triphenylphosphine. That is, an equilibrium ratio of approximately 70% *trans*- and 30% *cis*-$CH_3COMn(CO)_4P(C_6H_5)_3$ was obtained (*cf.* ref. 2). Second, when a reaction mixture in a closed tube which had reached equilibrium at room temperature was heated to 45° for several hours, some of III was formed and the concentrations of each of the acyl isomers decreased, although there was little change in their relative concentrations.

Calderazzo[4] has indicated that he has also observed the formation of two acyl isomers in this system, although he apparently did not specify assignments for the acyl proton resonances.

Other studies of this type in these laboratories have shown that triphenylarsine gave almost exclusively *trans*-$CH_3COMn(CO)_4As(C_6H_5)_3$, whereas certain amines appeared to form exclusively *cis* derivatives.

(4) F. Calderazzo, private communication.

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Book Reviews

Thermal Methods of Analysis. Volume XIX. Chemical Analysis. A Series of Monographs on Analytical Chemistry and its Applications. By WESLEY WM. WENDLANDT, Department of Chemistry, Texas Technological College, Lubbock, Texas. Interscience Publishers, John Wiley and Sons, Inc., 605 Third Ave., New York, N. Y. 1964. x + 424 pp. 15.5 × 23.5 cm. $16.50.

The term "thermal methods of analysis" is defined by Professor Wendlandt to mean those techniques in which some physical parameter of a system is measured as a function of temperature, that property changing as a function of temperature so as to yield useful information concerning the chemical system. These techniques include the relatively long-known thermogravimetry and differential thermal analysis as well as the more recently developed methods of effluent gas analysis, pyrolysis, dynamic reflectance spectroscopy, thermodilametric analysis, and thermoluminescence. Although there have been a few books dealing with some of the individual thermoanalytical techniques, such as Duval's "Inorganic Thermogravimetric Analysis" and Smothers and Chiang's "Differential Thermal Analysis: Theory and Practice," this excellent book represents the first publication of a monograph dealing with the field as a whole and fills a long-felt need. Professor Wendlandt presents a critical review rather than a comprehensive survey of the literature of each thermal method. He wisely points out not only the advantages of each technique, but, just as importantly, discusses their limitations. The rapid growth in recent years in the use of these thermal methods of analysis has been stimulated by the increasing availability of commercial instruments designed to make these measurements. An especially valuable part of this book is the well-presented discussion and evaluation of all the apparatus commercially available at the time of publication.

After a general introduction to thermal methods of analysis in Chapter I, there follow three chapters dealing with thermogravimetry. Chapter II presents a discussion of the parameters, sources of error, and limitations of thermogravimetry; Chapter III is a review of both commercial and noncommercial instruments that have been developed; and Chapter IV is a discussion of the analytical applications of this technique. There are then three chapters devoted to differential thermal analysis, arranged in the same order as those about thermogravimetry. Chapter VIII is concerned with thermometric titrimetry, IX with pyrolytic techniques, X with dynamic reflectance spectroscopy, XI with thermal analysis, and XII with miscellaneous thermal methods which include thermoluminescence, oxyluminescence, dilatometry, electrical conductivity, and high temperature methods applied to infrared spectroscopy and X-ray diffraction.

This book is Volume 19 in Interscience's "Chemical Analysis Series" edited by P. J. Elving and I. M. Kolthoff. It is highly recommended not only to the analytical chemist but to any scientist who is using or contemplating using thermoanalytical techniques.

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