

Book Reviews

The Biological Chemistry of the Elements. The Inorganic Chemistry of Life

By J.J.R. Fraústo da Silva and R.J.P. Williams, published by Clarendon, Oxford, 1991, 561 pp.

A nicely developed text, in which information from a number of scientific domains, such as biology, botany, biochemistry and inorganic chemistry, has been put together successfully. Reading is made easier by a plain language and by the rich documentation of tables and figures. As bioinorganic chemistry is emerging as a new, challenging field of interest for chemists, we feel that this book could be profitably read by all those involved in the area. We would also recommend it to all people with a biological profile (medicinal chemists, pharmacists ...) and to high-school students, who may reap a considerable benefit from this book.

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Energetics of Organometallic Species

Edited by J.A. Martinho Simoes, NATO ASI Series – Series C: Mathematical and Physical Sciences – Vol. 367, published by Kluwer, Dordrecht, Netherlands, 1992, ISBN 0-7923-1707-6.

A broad view of the thermochemistry of organometallic compounds is given in this book. It starts with the historical developments, outlined in the first chapter by H. Skinner, a pioneer in the field, and moves towards the state-of-the-art techniques and applications. The role of theoretical chemistry as a useful tool in understanding and complementing experimental information is emphasized, providing yet another approach to the subject.

In Chapter 2, G. Pilcher discusses combustion calorimetry as applied to organometallic compounds, emphasizing its limitations, while in the following chapter T. Marks *et al.* illustrate the usage of reaction-solution calorimetry to study metal–ligand bond energies in f-element complexes and its implications for reactivity. Specific problems have led several researchers to develop new techniques. In this regard, new insights into C–H activation are offered by the elegant studies of W. Jones *et al.*, which describe thermodynamic versus kinetic factors competing in the η^2 -arene complexation. The determination through equilibrium studies of the Rh–C

dissociation enthalpies in Rh–porphyrin complexes (B. Wayland) contributes to a better understanding of the underlying reactivity. The presence of a very short lived species requires the use of other techniques and, as an example, the application of photoacoustic calorimetry has been successfully demonstrated by Burkey in his study of Si–H activation by metallic carbonyls. Electrochemical methods have also been used in relation to thermochemistry. These are described in Chapters 8 and 9, dealing with organic and organometallic radicals, and written by Wayner and Tilsets, respectively. The importance of referring all thermochemical data to the gas phase is stressed by Carson, who contributes with an experimental way of determining sublimation enthalpies, needed when transferring results from solution. That this can be relatively well approached in several cases by estimation is shown in the chapter written by Chickos *et al.* Studies made on the gas phase, however, do not imply these corrections and an example is provided by Walsh's description of how to derive thermodynamic quantities from kinetic measurements of elementary reactions in silanes. The next chapters are very useful for practicing chemists who need thermochemical data but cannot obtain them experimentally. Indeed, very practical tools, based on the ideas of transferring bond enthalpies, are discussed and shown to work effectively in many situations, by Connor and also by Martinho Simoes.

We now come to the part of the book dedicated to modern gas-phase techniques. Different methods and types of equipment are employed to study a variety of compounds and the relative problems by Richardson (bonding and solvation energetics for organometallic gas-phase molecules and ions), Stevens-Miller and Miller (gas-phase acidities of transition metal hydrides), Squires *et al.* (energy thresholds for CO dissociation in metal carbonyl anions) and Armentrout *et al.* (ion beam studies of the energetics of diatomic species). Beauchamp *et al.* make a survey of this field emphasizing the instrumentation, the experiments and the relevance of theoretical studies in understanding the mechanisms of organometallic reactions. A necessarily brief section dedicated to the contribution of theoretical methods completes the book. Ziegler reviews the application of Density Functional Theory to organometallic chemistry problems, while Blomberg describes the use of

sophisticated *ab initio* quantum chemical techniques to obtain the energetics of several organometallic reactions. While the nature of the method precludes its application to large systems, it is of interest in very small systems which can be experimentally accessed through the state-of-the-art gas-phase methods.

This book could be very useful to experimental organometallic chemists for it gives a good coverage of the problems which can be handled by thermochemical means. Not only is it emphasized how relevant this type of information is in order to understand the chemical reactivity of organometallic species, but information of immediate utility to estimate thermochemical parameters is also provided.

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