Book reviews

Photoprocesses in Transition Metal Complexes, Biosystems and Other Molecules. Experiment and Theory

Elise Kochanski (ed) Kluwer, Dordrecht, 1992 £97.00 ISBN 0 7923 1936 2

This volume forms part of the NATO Advanced Science Institutes Series C on the mathematical and physical sciences, and is a compilation of the papers presented during the NATO Advanced Institute held at Aussois, France, between 1 and 13 September 1991. The purpose of the meeting was to bring together leading scientists from diverse areas of expertise, to promote cooperative links and to demonstrate how the various techniques and methodologies developed for specific applications may find utility in other areas. The book can be divided into three general themes: (1) theoretical aspects of photophysics and photochemistry, (2) the photo-induced chemistry of metal-containing systems, and (3) protoprocesses of biological importance.

The theoretical topics covered in the book include an introduction to the general principles of photophysics which describes the fundamental laws of molecular spectroscopy. This paper, presented by A. Tramer, outlines the origins of the selection rules for electronic transitions and reviews the vaious relaxation processes for excited-state species. It provides an excellent basis upon which to assimilate the contents of the subsequent papers on electron-transfer processes (R. A. Marcus and P. Siddarth), calculation of the excited-state lifetimes for small molecules, and relativistic effects in molecular calculations (S. D. Peyerimhoff).

The section on the photo-induced chemistry of metal-containing systems is introduced by a paper by J. J. Turner describing the various spectoscopic techniques used in this field. This provides a useful guide to the limitations and advantages of the cryogenic versus the time-resoved techniques. Following this, Professor Turner's survey of the photo-induced chemistry of Cr(CO)₆ itemizes the numerous questions remaining unanswered for this system. The stereochemical and catalytic aspects of the photochemistry of organometallic metal carbonyl compounds are discussed by F.-W. Grevels, who describes reactions of metal carbonyl photogragments with olefins. Of particular interest here is the use of such systems in photo-induced olefin isomerization, hydrogenation and hydrosilation reactions. This paper describes how careful analysis of the production of various $M(CO)_x(olefin)_y$ compounds from the parent carbonyl compounds can provide an insight into the efficiency of the various photochemical processes involved in their production.

Over the years, many photochemical reactions have been explained in terms of simple molecuar-orbital diagrams. Electronic transitions from the ground state to some higher-energy orbital have been proposed to explain why in some instances homolytic cleavage of a particular bond occurs, while heterolytic cleavage is observed in other cases. The chapter by A. Veillard entitled 'Photochemistry of organometallics: quantum chemical approach' describes the use of CI (Configuraton Interaction) to explain why some systems exhibit concurrent photochemistry, a phenomenon not easily explained by the molecular-orbital approach. This chapter also describes how the construction of potential-energy and state-correlation diagrams can be used to gain a better understanding of the mechanisms of organometallic photochemistry. Many examples of how this methodology has been applied are presented.

The remainder of the book is concerned with energyor electron-transfer process. The topics covered range from simple molecular systems such as those described by Stufkens, van der Graaf, Stor and Oskam, who describe the photochemisty of (CO)₅M'M(CO)₃(α-diimine) (M, M' = Mn, Re) and its relation to electrontransfer chain catalysts. The principle reason why such systems are of interest is that they exhibit a rich photochemistry which is in contrast to most other metal carbonyl compounds containing di-imine ligands. A chapter by Balzani, Campagna, Denti and Serroni describes how ruthenium and osmium complexes with various di-imine-type ligands can be used to build supramolecular systems for the purpose of energy capture and subsequent energy migration to a specific reaction centre. The photophysics of energy and electron transfer in bimetallic systems is described in a paper by Scandola, Bignozzi, Chiorboli Indelli and Rampi, and the effect of solvent, distance and conformation effects in electron transfer processes is discussed in a chapter by Verhoeven, Paddon-Row and Warman. The final four chapters deal with electrontransfer processes in biological systems or models of biological systems. Schneider's paper on the 'Spectroscopy of biliproteins and energy transfer in photosynthetic antenna complexes' outlines the various spectroscopic techniques which have been applied to investigate energy transfer in photosynthetic antenna pigments, whilst Mathis describes the conversion of light into chemical energy in biological systems. Finally, a paper by Sessler, Capuano, Kubo, Johnson, Magda and Harriman describes the use of synthetic models for elucidating the pathway-dependent mechanisms of long-range electron-transfer processes.

Whilst it is hard to find much to criticize in any of the individual contributions to this volume, it is difficult to envisage at whom the book is aimed. The concept of holding a meeting of this type is an excellent one, with the primary benefit coming to the participants. However, it must be added that a scientist wishing to broaden the experimental base being applied to a particular problem might not necessarily consider volumes such as this to be their primary source of inspiration.

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Chemistry of Iron

J. Silver (ed)
Blackie Academic and Professional, Glasgow, 1993
306 pp. £69.00.

This book is intended to provide a general introduction and overview to the main areas of current interest in iron chemistry and to direct readers from a variety of scientific backgrounds to prime literature sources for in-depth studies. It is written at a level which is claimed to be suitable for use by graduates in chemistry, biochemistry, physics, geology, materials science and biology. It probably is the first, as the editor claims, to provide a comprehensive review of the important chemistry of iron in both its elemental and combined forms. Other works devoted to specific aspects of iron chemistry, e.g. the monographs by Koerner von Gustorf et al. on the organic chemistry of iron (1978, 1981) have of course been available for some time and are now rather out of date.

The book is divided into eight chapters, each of which is written by authors who are active in the subject. A general introduction to iron chemistry (J. Silver) is followed by chapters on industrial chemistry of iron and its compounds (F. J. Berry), inorganic chemistry of iron (E. Sinn), organo-iron compounds (P. L. Pauson), spectroscopic methods for the study of iron chemistry (B. W. Fitzsimmons), biological iron (J. G. Leigh, G. R. Moore and M. T. Wilson), models

for iron biomolecules (A. K. Powell) and iron chelators of clinical significance (R. C. Hider and S. Singh). Over 200 pages are devoted to organo-iron complexes and biological aspects, perhaps reflecting the current level and emphasis of interest in these areas. In view of this, I suspect that geochemists, materials scientists and metallurgists will find the book of rather more limited use than (for example) organometallic chemists, biochemists and clinical biologists.

The chapter on organo-iron compounds (96 pages), which is probably of most interest to the readers of Applied Organometallic Chemistry, contains sections on iron carbonyls, cyclopentadienyl iron complexes. $\eta^1 - \eta^6$ hydrocarbon complexes, miscellaneous complexes and practical applications of organo-iron compounds. This is a comprehensive, well-written review which provides a welcome up-to-date addition to the literature. In contrast, I feel that the brief chapter (11 pages) on spectroscopic methods for the study of iron chemistry—essentially Mössbauer spectroscopy seems somewhat out of place in a book of this kind, particularly so when considerably more than half of it is devoted to the theory of a well-established technique and only three pages contain examples involving iron chemistry. The chapters on biological aspects are interesting and well written; even though closely related reviews have appeared elsewhere (see references to Chapter 6), the accounts given here do provide an excellent overview of the field.

Considering that this is a multi-author work, the editor has done a good job in integrating and linking the contents of the various chapters and in ensuring a reasonably consistent style throughout. There are some inconsistencies, for example the references to some chapters include titles, some do not and others contain a mix of the two. Typographical errors are few, although I did note a rather unfortunate one concerning the 'pyrophobic' nature of finely divided iron. However, these are small points which detract little from the conclusion that (with the inclusion of a number of 1992 references) the book provides an up-to-date overview of the chemistry of iron in a single volume which also serves as an excellent source of reference.

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