

BOOK REVIEWS

ORGANIC HIGH PRESSURE CHEMISTRY W.J. le Noble (Editor), Elsevier, 1988, 500 pp, \$168.50

The high pressure variable in all aspects of chemistry is now almost as well established as that of temperature, both as a probe into molecular behaviour and as a means towards desired synthetic ends. Bill le Noble has for many years past been an effective advocate of this technique and this book is to be welcomed as an account of the latest state of the art in numerous of its manifestations. It is a multi-author work in 14 chapters each written by an acknowledged expert in his field and begins with a sage account of the practicalities of ΔV^* measurement. Exner contributes a useful account of additivity in molar volumes setting out the limits to which reaction volumes can be computed. Hamann's chapter contains a most comprehensive review of the involvement of pressure and volume in the thermodynamics of rates and equilibria. The question of the inclusion or not of a compressibility term in the expression for activation volume is clearly aired. Activation volumes have been expressed as useful additional probes into incidence of quantum mechanical tunnelling during hydrogen transfer reactions and this aspect is critically treated by Sasaki and Osugi. Subsequent chapters are devoted to the interpretation of activation volumes of specific reaction types; stereoisomerisations, pericyclic reactions, 'anionic reactions' and carbocation involvements. Each is very comprehensive and up to date. For instance, Whalley's fascinating solvolytic work at very high pressures (30 kbar!) presented in symposia, is included ahead of publication in the journals as is Jenner's data on pressure effects in ene reactions. A short chapter by Rahm on applications in the field of organometallic chemistry contains valuable information in this little-explored field and the section on synthesis (Jurczak) reviews the scope of this large field of application which needs a separate volume to be comprehensive. Indeed, a more detailed appraisal of synthetic high pressure chemistry awaits this author's own edited volume due in the near future. Synthetic chemists by now should be aware of the potential of high pressures in all manner of addition reactions and it is clear that many groups are acquiring the necessary equipment. The association between photochemistry and high pressures is less well investigated but a timely review of photochemical and photophysical applications follows. The shifting of energy levels by pressure and the subsequent changes in quantum yields and rate constants, provides a valuable probe into the mechanics of radiation transfer and other primary processes. The comprehensive nature of the book permits an inclusion of biochemical systems and their relationship with high pressure by Heremans; enzymes, not surprisingly, show pressure-dependent rates and denaturation processes, the causes of which at a molecular level pose a considerable problem in interpretation but may have far-reaching applications (boiled eggs can be prepared at room temperature under high pressure!). The book concludes with some pretty examples of the uses of activation volumes in the carbene field and conclusions by the editor.

This book is highly recommended to be read by all organic chemists and will surely be found to contain something for everyone. Full text references are provided and

adequate author and subject indexes are appended. Being a multi-author publication there are a few drawbacks however. The style of each chapter varies widely and the type-written photocopied format means that consistent editing was not possible to remove the rather quaint English in certain chapters. Some topics such as the effects of pressure on solvation are not treated explicitly and only sparsely mentioned in one or two chapters. The price furthermore, will not be attractive to the individual buyer and it is to be hoped that this does not deter libraries from stocking a copy.

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FREE RADICALS: METHODOLOGY AND CONCEPTS

Edited by Catherine Rice-Evans and Barry Halliwell

Richelieu Press, London, 1988. 556 pages

This volume records the papers presented during the December, 1987 meeting of the Society for Free Radical Research: held at the Royal Free Hospital School of Medicine. A wide range of topics, all related to the biology of free radicals, are well discussed in this carefully edited book; whose major focus is the peroxidation of polyunsaturated lipids.

T.F. Slater, in a thoughtful introduction, inquires how one can distinguish between free radicals as the primary agents of cell damage, or as a secondary reflection of damage imposed by non-radical mechanisms. The answer, of course, is that it is not easy. Thus, the elevation of plasma conjugated dienes in certain disease states was taken to signify increased lipid peroxidation, but the abundance of conjugated fatty acids in fried foods and in dairy products introduces a note of caution. Parallel measurements of conjugated dienes and of alkyl hydroperoxides in rat liver showed that the former exceeds the latter by 20- to 40-fold and that both are elevated during Vit E deficiency. What is the non-hydroperoxide conjugated diene? One possibility is conjugated diene alcohols produced by the action of glutathione peroxidase on the corresponding hydroperoxides.

Halliwell *et al.* discuss the production of powerful oxidants, such as the hydroxyl radical, by the iron-catalyzed reduction of H_2O_2 by O_2^- . Knowledge of this process, but not of the catalytic role of Fe(III), is nearly two decades old and it is appropriate that the major concern of this chapter is the description of methods which can be used to measure the production of hydroxyl radical both *in vitro* and *in vivo*. Aromatic hydroxylation is one of the methods discussed and this theme is further developed by Singh and Hider, who use a 3,5-disubstituted nitrobenzene which can be hydroxylated by $HO\cdot$, but which cannot give rise to the easily oxidized and metal-chelating catechols. Since $HO\cdot$ reacts rapidly with virtually all organic compounds, there is almost no limit to the methods which can be derived to detect and measure it: as demonstrated by Babbs and Gale who use the conversion of dimethyl sulfoxide to methylsulfinate as their method of choice.

In living cells, as in modern societies, the replication and transformation of information claims a large share of total effort and stores of information represent a

potential Achilles' heel. Free radical attack on DNA is thus an important topic and it was explored by Dizdaroglu, who detected and identified many products generated from the attack of hydroxyl radical on DNA. Interesting, in view of the current argument about the production of hydroxyl radical by activated phagocytes, is his observation that DNA exposed to activated neutrophils yields products characteristic of attack by hydroxyl radical.

Conversion of unstable radicals to stable radicals, in the technique called spin-trapping, has added greatly to our ability to detect and characterize these fleeting intermediates. Sophisticated methods often set pitfalls for the unwary. Mason and Morehouse identify many potential artifacts and thus provide the sophistication needed for meaningful use of spin trapping; while the chapters which follow describe applications to important biological problems.

In a section devoted to lipid peroxidation, Lands describes a very sensitive enzymic assay for lipid hydroperoxides which depends upon their ability to activate fatty acid oxygenases (lipoxygenases). He applies this method to biological samples and discusses the potential effects of the "peroxide tone" on the biosynthesis of eicosanoids. Steinberg and his coworkers have implicated oxidation of the lipids of blood plasma low density lipoproteins (LDL) in atherogenesis. For this reason the chapter by Esterbauer *et al.*, on the products generated during the oxidation of LDL, is particularly interesting.

I am afraid that this review has already flouted the virtue of brevity and we have not even mentioned several sections of this book such as those which deal with *Chemiluminescence*, or with Metal Ions and Radical Reactions. Suffice it to say that both the neophyte and the expert will benefit from reading it from cover to cover. I know that I have so benefitted.

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THE ROLE OF OXYGEN IN CHEMISTRY AND BIOCHEMISTRY

Ed. W. Ando and Y. Moro-oka, Elsevier, Amsterdam, 1988.

(Studies in Organic Chemistry, 1988, vol. 33)

This book is a collection of 86 papers from the International Symposium on, "The Activation of Dioxygen and Homogeneous Catalytic Oxidations", at Tsukuba, Japan in July 1987. It includes papers by each of the 25 invited speakers and two of the six plenary lecturers and the presentations from the poster sessions. It is a pity that four of the plenary lectures, which were the key-note talks at the conference, were not included.

The papers are grouped under three headings:

1. Singlet oxygen, photo-oxygenation and nonmetallic oxidations (Part A).
2. Metal-catalysed oxidations (Part B).
3. Biological oxidation – Enzymes and enzyme models (Part C).

Part D reports the views of five round-table discussion panels on, singlet oxygen and photo-oxygenation; non-metallic oxidations; metal catalysed oxidations, enzymes and enzyme models; and lipid peroxidation and oxygen toxicity. The main aims of the panels were to summarise the recent progress in their field and to identify areas and targets for future research. These summaries provide a useful and informative overview of the conference and delineate clearly the direction needed for an interdisciplinary approach to understanding Chemical and Biochemical oxidations. It would perhaps have been more sensible to sub-divide the papers into five sections, one for each round table discussion, rather than three. The book would have also been more "reader-friendly" if it had included an author index (and possibly a subject index). The symposium programme (Part E) is no substitute for these indices.

The material in this book covers the wide range of oxygen chemistry bringing together the theoretical, synthetic, analytical and mechanistic aspects of the field. The contributions report recent work from Universities and Research Institutes and a few from Industry. Perhaps inevitably from the location for the conference, the poster session and consequently the whole book is dominated by contributions by Japanese chemists.

The content of Part A shows the breadth of singlet oxygen, photo-oxygenation and non-metallic oxidation chemistry and provides up to date views on the variety of reactive oxygen species that can be utilised as oxidants. It is interesting to note the way this active field has developed and, more importantly, to see how it will progress. In the latter respect, the summaries of the future goals are informative, challenging and stimulating.

Part B reports the significant progress in metal-catalysed oxidation of most classes of organic compound. Although the papers cover a large number of different transition metals, the round-table discussions identify Fe, Mn and Ru for special attention. Some of the papers in this section relate closely to those on enzyme models in Part C. Indeed this point is reinforced by the summaries of the panels on metal-catalysed oxidations and on enzymes and enzyme models. The challenge for the future remains; can the enzyme models be developed into viable and economic metal-catalysed industrial or laboratory processes?

Part C covers enzyme models for cytochrome P450 and horseradish peroxidase and to a lesser extent lipid peroxidation, oxygen toxicity and enzymic oxygenations. Central to this work is the nature of the active oxidants in the enzymes and their models. For example, with metalloenzymes are they high valent metal oxo species or perhaps, as suggested for heme enzymes, the controversial iron(II) and iron(III) oxene complexes?

The book provides plenty of food for thought for the expert and for the reader who wishes to be brought up to date with recent progress in oxygen chemistry. If the progress that has been made over the last few years is maintained we can look forward to the future with great interest.

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