

## References

- 1 M. E. Baumgärtner and Ch. J. Raub, *Platinum Metals Rev.*, 1988, 32, (4), 188
- 2 P. E. Skinner, *Platinum Metals Rev.*, 1989, 33, (3), 102
- 3 Johnson Matthey, *European Appl.* 358, 375; 1989
- 4 R. Le Penven, D. Pletcher and W. Levason, *J. Appl. Electrochem.*, 1992, 22, 415
- 5 Many texts cover FT NMR spectroscopy, see J. W. Akitt, "NMR and Chemistry", 2nd Edn., Chapman and Hall, 1983; R. K. Harris, "Nuclear Magnetic Resonance Spectroscopy", Longmans, 1986
- 6 P. S. Pregosin, *Coord. Chem. Rev.*, 1982, 44, 247
- 7 R. G. Kidd and R. J. Goodfellow in "NMR and the Periodic Table", eds. R. K. Harris and B. E. Mann, Academic Press, London, 1978
- 8 R. J. Goodfellow in "Multinuclear NMR", ed. J. Mason, Plenum Press, New York, 1987
- 9 P. S. Pregosin in "Transition Metal NMR", Elsevier, Amsterdam, 1991
- 10 T. G. Appleton, J. R. Hall and S. F. Ralph, *Inorg. Chem.*, 1985, 24, 4685

## Dioxygen, a Versatile and Useful Oxidant

### Catalytic Activation of Dioxygen by Metal Complexes

L. I. SIMÁNDI, Kluwer Academic Publishers, Dordrecht, 1992, 396 pages, ISBN 0-7923-1896-X, Dfl. 220.00, U.S. \$128.00

This book, which constitutes Volume 13 in the series "Catalysis by Metal Complexes", reviews the ways in which metal complexes activate molecular oxygen for the catalytic oxidation of organic compounds under mild conditions, and related oxidation reactions. It is said that this area of study is developing rapidly, but the references given are rather older on average than one would expect in support of such a claim. Research on the topic is being stimulated by potential applications in organic synthesis and by the resemblance between purely chemical processes and enzymic systems.

Transition metal dioxygen complexes are frequently involved in these oxidation reactions, and for this reason the opening chapter describes the major features of their structure, equilibria and formation kinetics. The remaining chapters describe the oxidation reactions of eleven broad classes of organic compound. Most of the metals involved are from the transition series and platinum group metals systems feature most prominently in the chapters on catalytic oxidation of saturated hydrocarbons, alkenes, alcohols and various nitrogen-, phosphorus-, and sulphur-containing organics.

Some of these reactions have potential for commercial use, although in many cases the activities and/or selectivities are not yet satisfactory. Dimeric rhodium(II)acetate,  $\text{Rh}_2(\text{OAc})_4$ , is an active catalyst for hydrocarbon oxidation by molecular oxygen at atmospheric pressure and 25°C. Oxidative aromatisation of cyclohexadienes is general using this system and can be efficient, for example, 1-methoxy-1,4-cyclohexadiene gives anisole in 98 per cent yield under these conditions.

The best known example of a commercial application in this field is the catalytic oxida-

tion of alkene derivatives, including ethylene itself, in the presence of palladium-copper systems, but the mechanism of this Wacker reaction is via the attack of water on the co-ordinated alkene, and involves no dioxygen complex. With rhodium catalysts, the reactivity of the superoxoligand is in some cases sufficient to abstract a hydrogen atom from a hydrocarbon, as is the case with a cyclooctene-rhodium-(I)-superoxo complex. The actual transfer of a co-ordinated dioxygen ligand to a co-ordinated olefin has been demonstrated for  $[(\text{diene})\text{RhO}_2]_2$  complexes, with diene = 1,5-cyclooctadiene or norbornadiene.

Complexes of rhodium and iridium catalyse the dehydrogenation of alcohols to aldehydes and ketones, producing gaseous hydrogen or transferring hydrogen to suitable acceptors like olefins. Dioxygen does not act as acceptor in these systems. An example is the dehydrogenation of isopropanol to acetone at 82.5°C in the presence of  $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ .

Dibenzylamine is catalytically dehydrogenated to N-benzylidene benzylamine with dioxygen in the presence of  $\text{Ru}(\text{PPh}_3)_3\text{Cl}_2$  (80°C in toluene); by-products are benzaldehyde and benzonitrile. Both rhodium and iridium complexes have been used to catalyse the formation of phosphine oxides from tertiary phosphines using dioxygen; and Ru(II) in dimethylsulphoxide is an active catalyst for the oxidation of dialkylsulphides by molecular oxygen.

Overall, the book is a useful source of information on the topic of catalytic activation of dioxygen by metal complexes and related organic oxidation reactions, and in this context gives examples where platinum metals can be used for selective oxidation/dehydrogenation reactions.

D.T.T.