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Book review

Advances in catalytic activation of dioxygen by metal complexes, L. Simándi ed., Kluwer, Dordrecht, 2003, pp. 352, Euro 148, US$145, GB £93, ISBN: 1-4020-10745.

Oxygen and hydrogen peroxide are readily-available, clean oxidants and are increasingly being favoured in "green" chemistry. However, their reactivity makes control of the reaction products a challenge. In this context, it is of interest to examine and to try to imitate the metalloenzymes that catalyse specific oxidations with oxygen. Such metalloenzymes include oxidases, peroxidases, monooxygenases and dioxygenases. Most of them contain heme or nonheme iron, and/or copper. They provide fascinating examples of inorganic reaction mechanisms, often involving radicals. The diversity and structures of more and more of these enzymes are being revealed. In parallel, biomimetic chemistry is producing compounds that emulate aspects of the metalloenzyme structure and function. The oxygen-dependent metalloenzymes provide fresh insights for the design of chemical catalysts. Of course, in designing industrial catalysts chemists do not have to be confined, as is biology, to neutral aqueous solution and to ambient temperatures and pressures. Moreover, they can use metal ions and ligands that are, as far as we know, absent from the biosphere. They are more concerned with long-term stability of the catalysts, which metalloenzymes cannot provide.

This collection of six reviews, which constitutes volume 26 of the series *Catalysis by Metal Complexes*, provides an overview of the past ten years of the growth of the chemistry of oxygen at metal complexes. During that time there have been enormous developments in understanding the biological catalysts, some of which were described in volume 19 of this series (edited by Funabiki and published in 1997). The focus here is on new developments in catalysis by inorganic (sometimes biomimetic) complexes. It encompasses a wider range of metals – manganese, cobalt (Simándi), ruthenium (James group), gold (Hill group), as well as iron (Funabiki) and copper (Karlin group).

An update on chemistry of the nonheme iron oxygenases, and recent chemical efforts to emulate their reactivity, is summarized in the chapter by Funabiki. The oxygenases containing heme- and nonheme-iron are able to attack alkanes and refractory aromatic molecules by the reductive activation of dioxygen. Often these enzymes employ a secondary reductant such as an oxoacid to generate a reactive Fe^{IV}=O or Fe^{III}-peroxo species. This type of reaction is difficult to control under homogeneous conditions and in any case represents a waste of resources. Clearly it would be advantageous to have catalysts with the reactivity of the iron complexes but without the need for the reductant. The gold complexes described by Boring, Geletii and Hill, though aimed at less refractory targets such as the sulfoxidation of thioethers, were designed with this in mind. The different mechanisms for oxidation of alcohols are reviewed by Sheldon and Arends. Whereas, the oxidations with early transition metals (V, Mn, Cr, Ti, Mo) take place via high-oxidation-state oxo- or peroxo-metal species, the later transition metals use a hydrido-metal mechanism. The range of catalytic possibilities is expanded by using further elements. It is intriguing to consider what possible chemistry might have emerged naturally had biology had access to such elements during evolution. Indeed, some of this chemistry may well be our there in the field, yet undiscovered.

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