cis-Dihydroxylation and Epoxidation of Alkenes by Manganese Catalysts - Selectivity, Reactivity and Mechanism
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Oxidation reactions are among the most elementary of organic transformations and are essential in chemical industry.1 Whereas complete oxidation of hydrocarbons with (atmospheric) oxygen yields carbon dioxide and water (i.e. combustion), partial and selective oxidation of hydrocarbons introduces functional groups and yields useful products and intermediates.2,3 Even if the (initial) product of such an oxidation is not of immediate use, the formation of, for example, an alcohol from an alkane or epoxide from an alkene offers a handle to introduce selectively other functional groups and/or attach other building blocks and in doing so, quickly build up molecular complexity.

Oxidative transformations include the oxidation of alkenes to their corresponding epoxides and diols (or into dicarbonyl compounds via C=C bond cleavage), selective C-H bond activation and the oxidation of alcohols to aldehydes, ketones or carboxylic acids (Figure 1).4,5 Stain removal from cloths and the bleaching of paper pulp are also examples of important oxidation processes, which operate by oxidizing the staining compounds by oxygen or via electron transfer and thereby reducing their absorption of visible light.6

Despite considerable advances in recent years, major challenges remain in oxidation chemistry. The need for increased atom efficiency demands the use of oxidants, which do not generate stoichiometric amounts of by-products. From an environmental and atom economy perspective, the two most desirable oxidants to use are molecular oxygen (O2) and hydrogen peroxide (H2O2).1a Selectivity is another key issue. In order to develop a useful process, the introduction of oxygen atom(s) to the substrate should occur only at the desired position(s) in the molecule, otherwise a complex mixture of (by)products is obtained. Furthermore, the product formed should not be oxidised further (i.e. overoxidation should not happen).

Although catalysts are needed to activate O2 or H2O2, their role is not simply to allow the use of these oxidants under ambient conditions. The most important role of these catalysts is to activate the oxidants in such a way as to ensure that only the desired oxidative transformation will occur. This holds for the chemoselectivity (e.g. alkene vs. alkane
oxidation), regioselectivity (e.g. internal vs. external alkenes) and enantioselectivity of the reaction. Moreover, the catalyst should be cheap, (potentially) available at large scale and be non-toxic. Furthermore, the catalyst should show high activity and be robust, to enable its application at low concentration and give constant performance over prolonged periods.

The research described in this thesis focuses on the development of new protocols for the clean and selective cis-dihydroxylation and epoxidation of alkenes and on the mechanistic understanding of these processes. Complexes based on Mn-tmtacn (where tmtacn = \(N,N',N''\)-trimethyl-1,4,7-triazacyclononane, see Figure 3.1, Chapter 3) have proven to be effective in both bleaching applications and for the activation of \(H_2O_2\) towards the oxidation of alkenes. As a first-row transition metal manganese is relatively non-toxic (in fact it is an essential trace element). However, as for many manganese based complexes, catalase-type activity is usually observed when employing Mn-tmtacn. Many groups have therefore used additives to suppress this wasteful decomposition of \(H_2O_2\). However, the precise role of these additives and the mechanism by which the Mn-tmtacn based catalysts operate was understood only poorly.

The approach taken during the research described in this thesis is to combine the information gathered from varying reaction conditions systematically (e.g. catalyst precursor, pretreatment procedures, solvent) and their influence on the performance of the catalyst (substrate conversion, product formation and selectivity in time) with the intriguing solution chemistry of Mn-tmtacn, which was explored with a broad range of spectroscopic techniques. The key for the optimisation of catalytic performance and the fundamental improvements made in understanding the mode of action of these manganese-based catalysts is the interaction and feedback between those two approaches.

Chapter 1 provides a broad overview of the more synthetically useful enantioselective catalytic systems for both the epoxidation and cis-dihydroxylation of alkenes reported to date. Although many enantioselective epoxidation catalysts have been developed, the terminal oxidants used are generally not atom-efficient. Regarding enantioselective cis-dihydroxylation, the only synthetically useful catalysts are based on Os, which is both expensive and toxic.

Since active oxygen causes oxidative stress in vivo, enzymes, called catalases, are involved in the safe decomposition of \(H_2O_2\), affording cellular protection. In Chapter 2 the relationship between the dinuclear manganese-containing catalase enzymes and oxidation catalysts is reviewed and discussed.

Chapter 3 starts with an overview of the additives used in Mn-tmtacn based catalysis. The discovery of the suppression of the catalase-type activity of the Mn-tmtacn catalyst by the use of carboxylic acid additives at co-catalytic level is described. The factors controlling the activity and selectivity of this newly developed catalytic system are explored. By judicious choice of the carboxylic acid additive, the selectivity towards either cis-dihydroxylation or epoxidation can be tuned under otherwise similar reaction conditions.
Chapter 4 describes the solution chemistry of the Mn-tmtacn family of complexes. The focus is on the various µ-oxo and/or µ-carboxylato bridged manganese dimers and their interconversion. A range of physical techniques (including NMR, ESR, UV-Vis and FT-IR spectroscopy, mass spectrometry and electrochemistry) has been applied to determine the dependence of the nature of the non-carboxylato bridging ligands of the manganese dimers on the redox state of the manganese centers and presence or absence of carboxylic acids and/or water in the reaction medium.

Chapter 5 explores both the factors responsible for the lag period and the species present in solution during the catalytic cis-dihydroxylation and epoxidation of alkenes by the catalytic system described in Chapter 3. Analysis of the effects of variation in reaction parameters on both the behavior and stability of Mn-tmtacn complexes and on the catalytic performance, together with isotopic labeling studies, led to new insights into the mechanism by which this powerful catalyst operates.

In Chapter 6 the generality of the mechanism proposed for the Mn-tmtacn catalysed oxidation of alkenes in the presence of carboxylic acid additives is discussed in relation with the systems and additives used by other groups. The results suggest strongly that again dinuclear carboxylato bridged complexes are key to catalytic activity.

Chapter 7 describes the development of the first catalytic enantioselective cis-dihydroxylation catalyst based on manganese using H₂O₂ as oxidant.

In Chapter 8 the results of the research described in this thesis are discussed in relation to the requirements for new oxidation catalysts discussed above. Focus is on the major issues encountered, solutions and possibilities for future developments.

References


Although IUPAC recommends to use names such as acetato, carboxylato, oxido and hydroxido for anionic ligands, in this thesis the more prevalent and older trivial names such as ‘oxo’ and ‘hydroxo’ are used.