Coordination Chemistry Reviews 257 (2013) 3030–3050

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Review

Metal-catalyzed asymmetric sulfoxidation, epoxidation and hydroxylation by hydrogen peroxide

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0010-8545/$ – see front matter
http://dx.doi.org/10.1016/j.ccr.2013.05.010

ARTICLE INFO

Article history:
Received 27 February 2013
Accepted 9 May 2013
Available online 18 May 2013

Keywords:
Hydrogen peroxide
Metal complex
Asymmetric sulfoxidation
Asymmetric epoxidation
Asymmetric dihydroxylation
Metalloporphyrin

ABSTRACT

The development of environmentally benign reactions is an important goal in synthetic organic chemistry and chemical engineering. However, catalytic enantioselective oxidations using transition-metal complexes are limited when the oxidant is hydrogen peroxide. The two main difficulties of using hydrogen peroxide in the presence of transition metal complexes are the homolytic cleavage generating OH radicals and the catalase reaction with formation of dioxygen. The current applications of asymmetric sulfoxidation, epoxidation, dihydroxylation of alkenes and hydroxylation will be herein reported. Use of non-heme systems will be presented. The possibility of asymmetric oxidation catalyzed by metalloporphyrins will also be discussed.

1. Introduction

Oxidation catalysis is an important domain of chemical research. Numerous applications exist nowadays in the fine chemical industry. The nature of the terminal oxidant is often crucial for the efficiency of oxidation reactions, and typical oxygen-transfer reagents include alkyl hydroperoxides, iodosylbenzene, peroxycarboxylic acids, hypochlorite, dioxygen and oxone. Despite significant efforts to utilize H_2O_2 in asymmetric oxidation catalysis, only a few general systems work well with this abundant, environmentally benign, atom-economical and relatively safe oxidant [1,2]. However hydrogen peroxide is probably the best terminal oxidant after dioxygen with respect to environmental and economic consideration [1,3]. It is also very attractive because its solubility in water and many organic solvents is quite large. As a result, oxidation systems that use hydrogen peroxide in conjunction with catalytic amount of cheap, relatively non-toxic metals such as iron, and to a less extent manganese, are highly desired for application in pharmaceutical area. Despite significant efforts to utilize H_2O_2 in asymmetric oxidation catalysis, only a few general systems are efficient with this environmentally benign oxidant [2]. The only side-product when using hydrogen peroxide as oxidant is a water molecule. However, the two main difficulties of using hydrogen peroxide in the presence of transition metal complexes are the homolytic cleavage generating OH radicals and the catalase reaction with formation of dioxygen [4].

Recently, however, there has been a revival in developing original and efficient system in asymmetric catalysis [5]. Thus we have now the development of new generations of metal complexes which are able to selectively catalyze various oxidation reactions. In this review the focus is on promising asymmetric oxidation systems using hydrogen peroxide as oxidant and metal-based catalysts. Organic catalysts designed for asymmetric oxidation may also operate with hydrogen peroxide [2,6–8] but they are beyond the scope of this review. Direct use of hydrogen peroxide as primary oxidant, in the Baeyer–Villiger oxidation has also been reported [9]. However, only a few catalysts are used in combination with hydrogen peroxide as the oxidant for enantioselective reactions [10–12]. Consequently, this reaction will not be developed in the present review, there are excellent reviews on this topic [9,13,14].

2. Asymmetric sulfoxidation

The selective oxidation of sulfides to sulfoxides has attracted much attention over the years after the pioneering work of Kagan and coworkers [15] and Modena and coworkers [16]. Hydrogen peroxide, however, has to be used in a controlled manner, due to the possibility of an over-oxidation reaction since possible formation of sulfones is also observed in various reactions as by-products [17]. This formation may suggest the existence of a kinetic resolution process during the course of the reaction. To investigate this aspect, the time dependence of the asymmetric process should be studied in more details. Sulfoxides also constitute chiral synthons in organic synthesis for the preparation of biologically active compounds [18]. They also serve as chiral auxiliaries [19]. There are recent and excellent reviews on this topic [17,18,20–23].

2.1. Iron systems

Among all the methods described so far [17], the asymmetric oxidation of sulfides by metal catalysts is one of the most attractive routes to optically active sulfoxides, and quite recently, even non-toxic and inexpensive iron complexes have been developed successfully, using hydrogen peroxide as oxidant [24–26]. Recent results will be separated in two parts: non-heme systems and iron porphyrin catalysts.

2.1.1. Non-heme systems

The iron complex $[FeO(pb)_4(H_2O)_2]ClO_4$ (pb = (−)-4,5-pinene-2,2′-bipyridine) was reported in 1999 by Fontecave and coworkers [27,28] as catalyst for the sulfide oxidation with hydrogen peroxide with yields ranging from 45 to 90%, but the enantioselectivity was only modest (ee = 40%) (Scheme 1). The catalytic properties of the mononuclear complex were compared with those of its related dinuclear analogue. Each system generates specific peroxo adducts but the latter was more reactive and enantioselective than its mononuclear counterpart [29].

Since then several examples of asymmetric oxidation of sulfides using H_2O_2 catalyzed by non-heme chiral iron complexes have been reported by Bolm and coworkers (Scheme 2) [18,24,25,30]. Despite the remarkable application of the chiral iron complexes with H_2O_2, the rather low reaction yields and the moderate enantioselectivities remained problematic. These limitations, however, could be overcome by the use of additives such as benzoic acid derivatives or their lithium salts [24]. After a comprehensive screening of carboxylic acids, *p*-methoxybenzoic acid or the corresponding lithium carboxylate was found to be the most efficient additive in this transformation. The use of this additive dramatically improved the reaction yields as well as the enantioselectivities [25]. An iron-catalyzed asymmetric sulfide oxidation was the key step in the synthesis of the non-steroidal anti-inflammatory drug sulindac (Fig. 1) [31]. Both enantiomers of the chiral product can be prepared with 92% ee in good yield.

Applicable asymmetric oxidation of sulfides using a Fe(salan) complex/aqueous hydrogen peroxide system was also reported in water by Egami and Katsuki [26]. Remarkably, the reactions were carried out in water using a chiral iron catalyst without a surfactant and higher enantioselectivity was observed in water than in methanol. After optimization, the reaction proceeds with high enantioselectivity (87–94% ee) (Scheme 3) [32].

The enantioselective oxidation of thioanisole to methyl phenyl sulfoxide has been recently realized by using new iron(III)