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Aerobic asymmetric oxygenation catalysis: a well forgotten... future?

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Aerobic dioxygen, the cheapest oxidant with the highest active oxygen content, has so far remained underrepresented in selective, including stereoselective, oxidation catalysis. This article surveys the milestones in the area of catalytic asymmetric oxidations of organic molecules leading to formation of new C–O or X–O bonds, reported in the last decades. The existing catalyst systems are outlined, and technical as well as fundamental difficulties that hamper widespread adoption of dioxygen into asymmetric oxygenation catalysis are discussed.

Keywords: asymmetric catalysis, dioxygen, green chemistry, mechanism, transition metal complexes.

Introduction

Earth acquired its oxidative atmosphere about 2.8–2.5 billion years ago after cyanobacteria started producing dioxygen by means of photosynthesis.[1] From then on, the atmosphere has remained one of the indispensable sources of life, responsible for the oxidative metabolism of the majority of currently living organisms. Nowadays, the atmosphere of Earth contains 20.95% (by volume) of dioxygen, comprising *ca.* 1.185×10^{18} kg of dry dioxygen,[2] which is available virtually at no cost for our physical needs and industrial demands. Moreover, with its high active oxygen content of 50 or 100% (depending on the process), dioxygen, affording water as the only oxidation co-product,[3] is the most advantageous oxidant in terms of the environmental requirements. The problem of dioxygen utilization has attracted close attention of catalytic chemists,[4–10] acknowledged by the recent special issue of *Chemical Reviews* 'Oxygen Reduction and Activation in Catalysis'.[11]

At the same time, in asymmetric oxygenation catalysis, the use of dioxygen has so far been rather limited.[12,13] The fundamental reasons for this situation can be best realized through the prism of biomimetic approach in oxidation catalysis. Processes involving the oxidation of organic compounds (epoxidation, hydroxylation, sulfoxidation, *etc.*) with dioxygen are exergonic under ambient conditions. However, direct reaction of dioxygen having triplet ground state ($^3O_2$) with spin-paired organic molecules is spin-forbidden, which requires either photoinduced conversion of triplet dioxygen to the reactive singlet state ($^1O_2$), or participation of suitable metal-based catalysts (and, possibly, co-reductant) to form reactive metal-oxygen (oxo, peroxo, alkyl-, acylperoxo, *etc.*) species. In either case, the catalyst system should be capable of both activating triplet dioxygen molecule and transferring the oxygen atom(s) to the substrate(s) in a selective manner.

In living organisms, various chemo-, regio-, and stereoselective oxidative transformations are conducted by metalloenzymes, *viz.* oxygenases, under mild conditions with high (typically, complete) selectivity. This has been an inspiration for the emergence of biomimetic approach in catalysis focused on mimicking the catalytic behaviour of naturally occurring metalloenzymes, mostly monooxygenases, *e.g.* cytochrome P450,[14,15] with synthetic transition-metal-based catalyst systems, aiming at understanding the mechanisms of their catalytic action and reproducing their exceptionally high efficiency and selectivity.

The mechanisms of action of natural oxygenases have been extensively studied. Scheme 1 outlines the cycles of monooxygenases of the cytochrome P450 superfamily (that catalyze a number of C–H hydroxylation reactions)[16] and dioxygenase (naphthalene dioxygenase),[17] illustrating the necessity of the reducing cofactors such as NADPH, NADH. Without getting deep into detail of mechanisms of dioxygen activation by metallic centres of enzymes,[18,19] the simplistic scheme of an aerobic oxidative process, mediated by a monooxygenase enzyme, can be presented as in Scheme 2, top. In living cells, the

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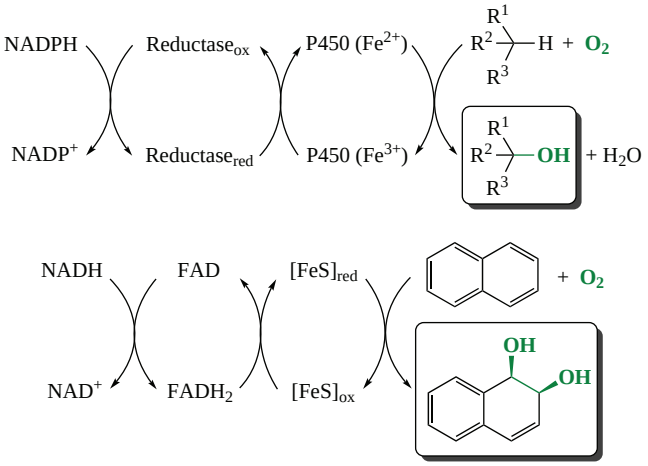
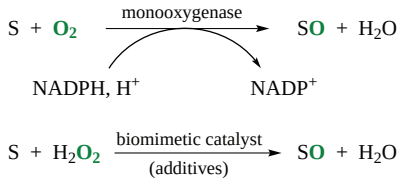


Scheme 1 Generalized catalytic cycles of the cytochrome P450 (top) and of naphthalene 1,2-dioxygenase (bottom). FAD is flavin adenine dinucleotide.

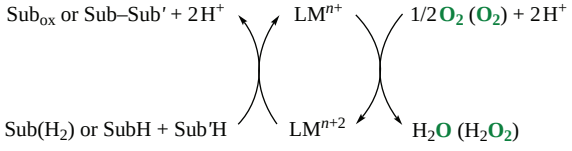


Scheme 2 Formal scheme of substrate (S) aerobic oxygenation in the presence of monooxygenase enzyme (top), and mimicking this reaction using a single oxygen-atom donor oxidant H_2O_2 (bottom).

co-reductant after oxidation in the course of the reaction to nicotinamide adenine dinucleotide phosphate, $NADP^+$, is readily recycled elsewhere in the organism. However, from the synthetic chemistry perspective, the need in stoichiometric (and, typically, high-molecular-weight) co-reductant is a serious drawback (the co-reductant is thought of as 'sacrificial reductant'), depreciating the overall process efficiency. Moreover, dioxygen activation with the aid of synthetic co-reductants typically involves free radical species that may initiate non-catalyzed radical-driven non-stereoselective reactions with the substrate, deteriorating the chemo- and stereoselectivity.

That is why the majority of biomimetic monooxygenase-type catalyst systems reported to date have relied on the common single oxygen-atom donor two-electron oxidants, such as H_2O_2 and alkylhydroperoxides, peroxycarboxylic acids, iodosylarenes, *etc.* (Scheme 2, bottom). In fact, such synthetic catalyst systems mimic only the oxygen-to-substrate transfer, leaving the second major enzyme function, dioxygen activation,[18,19] beyond the research focus.

Alternatively, many catalyst systems designed exploit 'oxidase'-type ping-pong mechanism consisting of two redox reactions, namely (1) oxidation of an organic molecule with the catalyst and (2) oxidation of the reduced catalyst with O_2 (Scheme 3).[20] This opens the possibility of avoiding a sacrificial co-reductant employed in monooxygenase-type reactions that proceed *via* reductive activation of O_2. However, the scope of asymmetric catalytic reactions of these types is largely



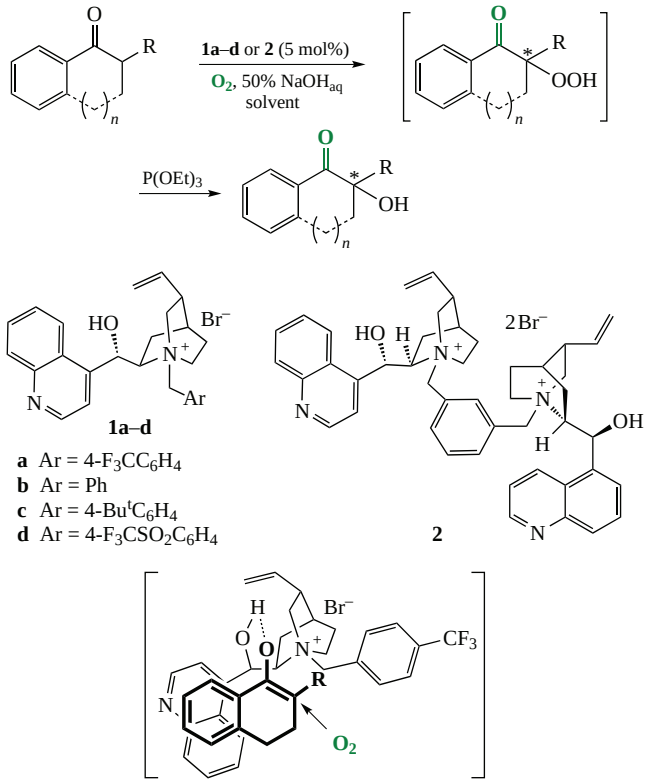
Scheme 3 Simplified representation of 'oxidase'-type aerobic oxidation mechanisms in catalysis.

restricted to C–C and C–heteroatom bond forming (coupling) reactions or oxidative kinetic resolutions,[21–23] excluding oxygenations.

This contribution is not intended to summarize the state-of-the-art of aerobic asymmetric oxidation catalysis which is documented elsewhere.[12,13,21–23] Instead, we selectively survey catalyst systems (either metal based or organocatalytic) capable of conducting different aerobic asymmetric oxygenation processes ('oxygenase catalysis')[7] that, in our opinion, have had milestone fundamental significance and/or hold considerable promise for the future. The mechanisms of catalytic action and dioxygen activation, if available, are presented, and remaining challenges and opportunities are discussed.

Asymmetric hydroxylations

Designing catalytic processes for chemo- and stereoselective hydroxylation is an attractive goal.[24] Such approaches can be used to introduce functional (hydroxy) group into complex organic molecules, thus revolutionizing the existing methods of synthesis of biologically active molecules and pharmaceuticals. In 1988, Shiori with co-workers reported the first aerobic catalytic asymmetric process of this kind, namely, α-hydroxylation of 2-alkyltetralones and 2-alkylindanones (Scheme 4).[25] The reaction was mediated by chiral phase-transfer organocatalyst, cinchona alkaloid derived quaternary ammonium chloride salts of the type **1** (5 mol% catalyst loading), with **1a** ensuring the best results (55–98% yield and up to 27–79% *ee*). The reaction proceeded within 5–48 h at room temperature in 50% aqueous NaOH solution, which served to deprotonate the substrate and so initiate molecular oxygen capture. The net α-hydroxylation of the carbonyl compound in fact occurred *via* hydroperoxidation of the tertiary C–H group, with subsequent *in situ* reduction of the intermediate hydroperoxide to the desired α-hydroxy carbonyl compound



Scheme 4 Organocatalytic asymmetric aerobic net α-hydroxylation of carbonyl compounds (top) and the structures of phase-transfer catalysts. Proposed substrate–catalyst ion pairing in the course of oxidation of cyclic ketones in the presence of chiral organocatalyst of the type **1** (bottom, in square brackets).

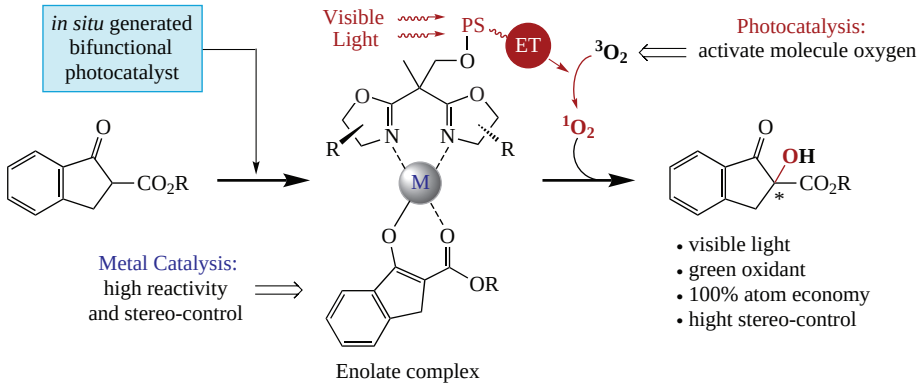


Figure 1 Asymmetric photooxygenation of β-keto esters in the presence of metal-based bifunctional photocatalyst (PS is photosensitizer). Reprinted with permission from ref. 36, © American Chemical Society, 2017.

with an excess of $P(OEt)_3$. The asymmetric induction was proposed to originate from the ion pairing between the substrate and the chiral catalyst, assuming the oxidation of the enolate form of the substrate (see Scheme 4, bottom).[25]

Since the milestone contribution by Shiori and co-workers, other phase-transfer catalysts of this kind have been reported.[26–35] Designing more elaborate dimeric catalyst **2** (see Scheme 4) allowed for achieving generally higher enantioselectivities (62–98% *ee*) in the oxidation of 2-alkyltetralones and 2-alkylindanones within 18–72 h at 10 °C.[35] Catalyst **2** also mediated the oxidation of various acyclic ketones with moderate to high enantioselectivities (up to 88% *ee*).

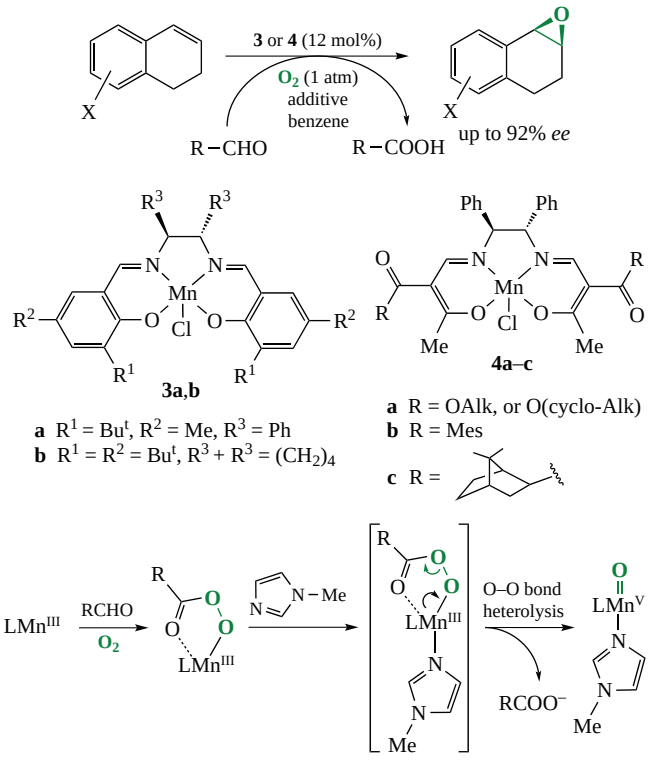
With amino acids as catalysts, aerobic asymmetric oxygenations of this kind could arguably serve as a model for direct incorporation of molecular oxygen into carbonyl compounds suggesting a possible prebiotic scenario to furnish sugars.[27] The involvement of singlet oxygen $^1O_2$ in the reaction requiring external (*e.g.* ambient) irradiation was presumed,[27,31] while in the dark the reaction did not proceed. The practical drawbacks of the catalyst systems based on chiral quaternary ammonium salts as above have been the relatively low catalytic efficiencies, long reaction times, narrow substrate scope, and the need for external co-reductant. However, by applying LED irradiation, the reaction time could be reduced to 30–60 min at 2.5 mol% catalyst loading.[33] More recently, metal-based (Figure 1)[36] and metal-free[37,38] bifunctional catalysts (combining the substrate-binding site and the photosensitizer) or catalytic combinations (metal based catalyst plus organic photosensitizer)[39] for the photoinduced aerobic α-hydroxylation of cyclic β-keto esters in up to 97% yield and 99% *ee* were developed, that, in addition, required no external co-reductant for the reaction to occur. It is of note that in the bifunctional catalyst systems reported in refs. 36 and 39, the metal center played the role of Lewis acid catalyst rather than participated in dioxygen activation.

To date, the area of aerobic α-hydroxylations of carbonyl compounds as above, which was historically the first example of aerobic catalytic asymmetric net oxygenation process, has remained active. Despite the existing limitations (such as rather specific substrates and so far unacceptably high catalyst loadings), catalytic processes of this kind represent an attractive synthetic route to chiral α-keto alcohols and further progress in this direction is expected. At the same time, asymmetric aerobic organocatalytic oxidations other than α-hydroxylations of carbonyl compounds have been scarce, in fact restricted to organocatalytic epoxidation in the presence of sacrificial reductant.[13,40]

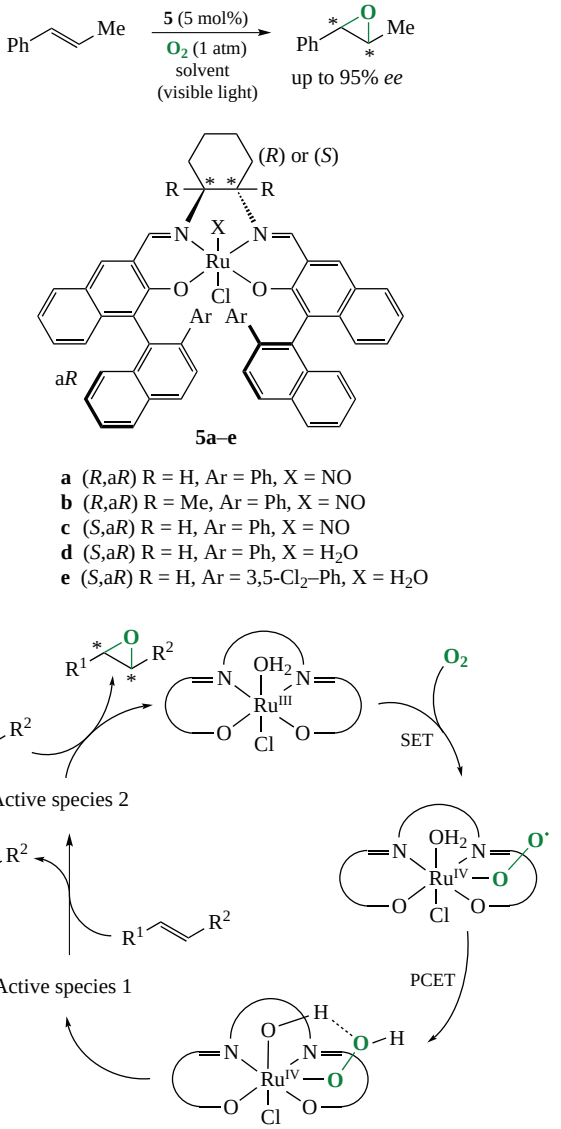
Asymmetric epoxidations

Chiral epoxides are considered as useful (stable yet readily reactive) intermediates in fine organic synthesis capable of reacting with nucleophiles to afford products of epoxide ring cleaving with excellent stereospecificity. In early 1990s, Mukaiyama with co-workers reported the first aerobic asymmetric epoxidation of olefins, catalyzed by manganese salen[41,42] and β-keto iminato[43–45] complexes of the type **3** and **4**, respectively (Scheme 5). Mukaiyama's discovery was undoubtedly a breakthrough; catalyst systems of this kind were shown to afford chiral epoxides in up 92% *ee*. The reaction mechanism was proposed, involving the formation of high-valent oxomanganese intermediate (see Scheme 5, bottom).[46,47] Moreover, analogous manganese based catalyst systems for the aerobic asymmetric (up to 79% *ee*) oxidation of alkylaryl sulfides to sulfoxides have been developed.[48,49] However, the practical drawbacks, such as the need in 3–4 fold excess of aliphatic aldehyde (as sacrificial reductant), and poor catalytic efficiency (which required high catalyst loadings, typically 12 mol%), substantially restricted further progress of catalyst systems of this kind. Complexes of other metals did not show comparable levels of enantioselectivity.[12,13]

Later, Katsuki with co-workers developed a family of Ru–salen complexes of the type **5** (Scheme 6).[50,51] Complexes



Scheme 5 Manganese-based catalyst systems for the aerobic asymmetric epoxidation of olefins, and proposed formation of active species of epoxidation (bottom).



Scheme 6 Ruthenium-based catalyst system for the aerobic asymmetric epoxidation of olefins. Proposed epoxidation mechanism (bottom): SET is the single electron transfer step, PCET is the proton-coupled electron transfer step.

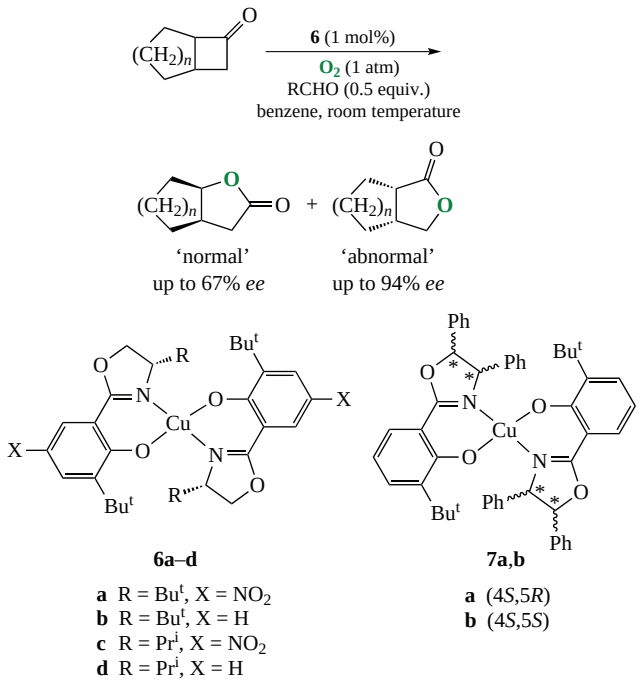
5a–**c** were capable of mediating asymmetric epoxidation of conjugated olefins with O_2 under visible light irradiation in the presence of water, which presumably served as the proton source. The role of visible light was to promote the axial NO ligand dissociation. In contrast, the water-coordinated counterparts **5d** and **5e** efficiently operated without irradiation,[51] epoxidizing conjugated olefins with air at 25 °C or with O_2 at 0 °C with high enantioselectivities (up to 95% *ee*). Remarkably, Katsuki's Ru–salen catalyst systems required no sacrificial reductant; on the other hand, their shortcoming was the use of expensive metal and the sophisticated ligand bearing elements of central and axial chirality. Taking into account the need in high catalyst loadings (5 mol%), this significantly depreciated the practical potential of such catalyst systems.

At the same time, in addition to epoxidations, Ru–salen based catalysts successfully conducted the asymmetric sulfoxidation of alkyl aryl sulfides (in up to 94% *ee*),[50] as well as the aerobic oxidative kinetic resolution of secondary alcohols (demonstrating high selectivity factors k_{rel}, in some cases approaching 25–60),[52] thus operating as a valuable mimic of natural oxygenases (possibly dioxygenases). We have to note, however, that the nature of the true oxygen-transferring active species, as well as the detailed reaction mechanism, has remained obscure as yet. Katsuki's hypothetical mechanism, assuming the formation of two different active oxygen-transferring species (with Ru in different oxidation states), over one catalytic turnover (see Scheme 6, bottom), looks unlikely, taking into account the excellent epoxidation and sulfoxidation enantioselectivities that point to a single stereoselectivity-determining step and hence single oxygen-transferring species. Unfortunately, after Katsuki's untimely decease, enantioselective catalyst systems of this kind did not progress any more.

Asymmetric Baeyer–Villiger oxidations

Until early 1990s, asymmetric Baeyer–Villiger-type oxidation reactions, allowing for one-step asymmetric synthesis of chiral lactones, could only be achieved with the aid of biocatalysts (either purified enzymes or whole-cell systems).[53] However, in 1994 Bolm and co-workers proposed the first synthetic catalyst system for this reaction, relying on chiral copper oxazoline catalysts of the type **6** (Scheme 7).[54] The authors used pivalaldehyde (0.5 equiv.) as sacrificial co-reductant; catalyst **6a** exhibited the best results in terms of enantioselectivity converting racemic 2-phenyl-cycloalkanones to the corresponding chiral lactones having up to 69% *ee* in moderate yields (21–65%). Subsequently it was demonstrated that **6a** also catalyzed the oxidation of cycloalkyl-appended cyclobutanones with dioxygen (see Scheme 7) affording two isomeric γ-lactones, major 'normal' and minor 'abnormal' products.[55] The 'abnormal' lactone was formed with higher enantioselectivity (up to 94% *ee*). A number of substrates were screened, with the highest *ee* values reported for bi- and tricyclic cyclobutanones. Modified copper oxazoline complexes of the type **7** were tested by others but showed lower enantioselectivity.[56]

Unfortunately, Bolm and Schlingloff did not examine the mechanism of dioxygen activation, as well as of stereoselective oxygen transfer to the substrate. The authors only suggested that the role of the chiral metal complex consisted in ensuring the proper diastereofacial control in the course of the Crigee intermediate formation.[55] To date, Cu–oxazoline complexes have remained the only example of synthetic catalysts for asymmetric Baeyer–Villiger oxidations; further progress in this area (including large-scale synthetic applications) entirely relied on biocatalytic approaches.[57,58]

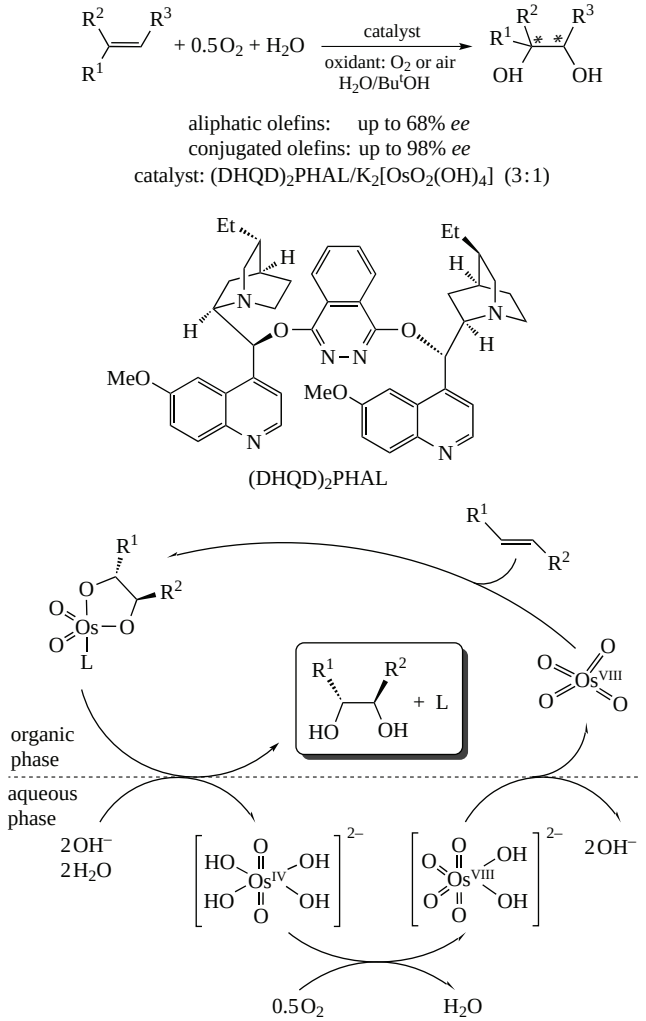


Scheme 7 Copper-based catalyst system for the aerobic asymmetric Baeyer–Villiger oxidations.

Asymmetric *syn*-dihydroxylation of olefins

In 1999, with the backdrop of industrial importance of 1,2-diols, including chiral 1,2-diols that were valuable intermediates for pharmaceuticals and agrochemicals on the one hand, and the success of Sharpless osmium tetroxide mediated asymmetric *syn*-dihydroxylation of olefins on the other hand,[59] Beller with co-workers reported another milestone example of aerobic asymmetric catalytic oxygenation process.[60,61] Namely, using *in situ* formed chiral catalyst (0.5–2.0 mol% of $K_2[OsO_2(OH)_4]$ salt combined with 1.5–6.0 mol% of $(DHQD)_2PHAL$ chiral ligand, Scheme 8), the authors achieved enantioselective *syn*-dihydroxylation of olefins in a mixture of aqueous buffer (pH 10.4) and Bu^tOH under the atmosphere of O_2 at 50 °C. The reaction demonstrated good substrate conversions (53–100%) within 16–24 h, affording 1,2-diols of terminal aliphatic olefins in up to 68% *ee* and of conjugated olefins in up to 98% *ee*.

It was established that both oxygen atoms from the O_2 molecule were used productively in the oxidation, with one of the oxygen atoms of the resulting diol apparently stemming from water molecule. To overcome the problem of further nonselective oxidation of the diol, an organic solvent was added so that a second liquid phase was formed under the reaction conditions. Subsequently, the authors adapted the catalyst system for using air (20 bar) instead of oxygen gas (1 bar). The catalytic cycle was proposed (see Scheme 8, bottom), which, though, remained speculative without experimental proof. Given the potentially high practical promise, the authors advertised[61] further adaptation



Scheme 8 Osmium catalyzed enantioselective *cis*-dihydroxylation of olefins and the proposed catalytic cycle (bottom).

of the reaction to industrial needs; unfortunately, the latter did not follow.

Conclusions and outlook

The catalyst systems surveyed above represented groundbreaking advancements in due time that gave great hopes and paved the way for further progress of catalytic asymmetric oxygenations. However, to date, the area has remained very far from maturity. The parent catalyst systems in most cases did not develop a lot – this is particularly true for the metal-based catalyst systems described above. The intrinsic limitations of these systems, such as poor catalytic efficiency, high consumption of expensive metals (for Ru and Os based systems), the need in sacrificial co-reductant (for Mn based systems), low yield and *ee* of the target product (*i.e.* 'normal' lactone in Cu–oxazoline based system), *etc.*, have not been obviated – which resulted in gradual decline of interest to their further development. In case of organocatalytic or bifunctional systems for aerobic asymmetric hydroxylation the situation looks somewhat better: their progress in 30 years has been evident (the new generations of catalysts combine the active site and the photosensitizer, require lower catalyst loadings, do not need external reductant), and research is ongoing. However, their major drawback – the narrow substrate scope (limited to α-alkyl substituted carbonyl compounds) – has persisted to date.

The significance of asymmetric catalysis was acknowledged by the 2001 Nobel Prize in Chemistry to W. S. Knowles, R. Noyori, and to K. B. Sharpless – 'for his work on chirally catalysed oxidation reactions'.[62] The last two decades witnessed an explosive progress in this area; crucially, significant efforts were focused on the drive toward greener and cleaner catalyst systems, essentially, *via* the use of environmentally benign reagents.[63] However, the progress largely swerved from the aerobic road, giving credit to hydrogen peroxide as a more fruitful 'green' terminal oxidant. Widespread involvement of atmospheric dioxygen into (asymmetric) oxygenation processes, especially C–H oxygenations, continues to be a tempting but elusive goal which, we believe, could be rightfully added to the list of 'Holy grails' of modern chemistry.[64] To date, there have been no realistic biomimetic models of natural hydroxylases capable of activating dioxygen on the metal center and chemo- and stereoselectively transferring oxygen atom to the substrate C–H bond.[12,63,65] In fact, any progress in aerobic asymmetric oxygenations could be potentially highly rewarding for oxidation catalysis as well as for biomimetic chemistry. We are eager to witness groundbreaking achievements in both areas and hope to contribute to those to the best of our ability.

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