Water-Mediated Ru-Catalyzed Asymmetric Oxygen Atom Transfer Reaction Using Molecular Oxygen as an Oxidant

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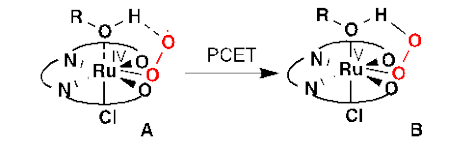
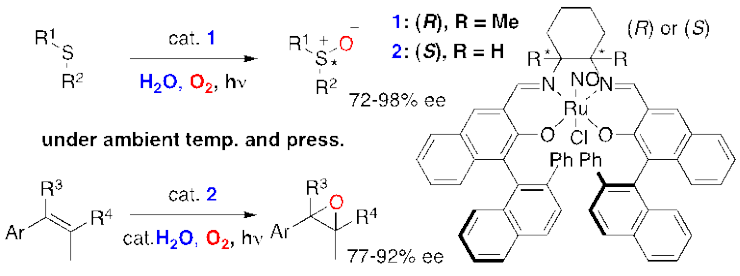
Oxidation reaction, especially oxygen atom transfer reaction, is an important tool for converting raw materials to useful compounds via oxygen functionalization. Thus, developments of catalytic, stereoselective, atom-efficient, and eco-friendly oxidation reactions are still strongly required. Atom efficiency and eco-friendliness of oxidation reaction largely depend on the oxidant used and molecular oxygen (O_2), in particular, atmospheric oxygen (air) is an ideal oxidant, because molecular oxygen is abundant, clean, and highly atom efficient. However, the known asymmetric aerobic oxidation reactions need addition of co-reductant, and/or heated or pressured conditions. Still, selective oxidation using O_2 as an oxidant under ambient conditions without co-reductant remains a challenging goal in organic synthesis. Hence we have been intrigued to the asymmetric oxidative oxygen atom transfer reaction with a metal complex as catalyst.

Recently, we found that ruthenium-salen complexes are capable of activating O_2 and catalyzing oxidation (dehydrogenation) of alcohols. The kinetic studies of this oxidation indicated that alcohol bound Ru(IV)-superoxide intermediate **A**, which is poorly reactive to nucleophilic substrates, was formed in the reaction. On the other hand, it is well known that, in enzymatic oxidation reaction, metal-superoxide species undergoes proton coupled electron transfer (PCET) to give electrophilic metal-hydroperoxide species by an electron- and proton-relay network. Thus, we considered that Ru(IV)-superoxide **A**, which has a metal-bound acidic alcohol or water, would be converted to Ru(V)-hydroperoxide **B** via proton-coupled electron transfer (Scheme 1) and transfer oxygen atom to external substrates such as sulfides and olefins.



Scheme 1

Based on these considerations, we investigated oxygen atom transfer reaction using air or O_2 with Ru-salen complex as a catalyst and achieved water-mediated catalytic asymmetric sulfoxidation and epoxidation using O_2 under visible light irradiation at ordinary temperature and pressure (Scheme 2).



Scheme 2