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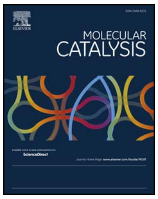

Non-redox metal ions accelerated oxygen atom transfer by Mn-Me_3tacn complex with H_2O_2 as oxygen resource

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ABSTRACT

This work demonstrates a novel strategy that the introduction of non-redox metal ions as Lewis acids to the classic dinuclear manganese complex $[Mn_2^{IV}(\mu\text{-}O)_3(Me_3tacn)_2](PF_6)_2$ can greatly promote the alkene epoxidation efficiency under mild conditions with H_2O_2 as the solely terminal oxidant because of its economic and environmental advantages. When $[Mn_2^{IV}(\mu\text{-}O)_3(Me_3tacn)_2](PF_6)_2$ was used as the catalyst in the absence of Lewis acids, only 16.4% conversion of cyclooctene with 6.2% yield of epoxide was obtained and the obvious decomposition of H_2O_2 was observed. However, the oxygen transfer efficiency of the catalyst was sharply improved with 100% conversion and 90.2% yield of epoxide under identical conditions when the non-redox metal ion, such as Sc^{3+}, was introduced to the catalytic system. The novel strategy was successfully applied to the epoxidation reactions of different types of alkenes. Through UV–vis, FT-IR, EPR and CV characterizations, it was evidenced that the non-redox metal ions with high positive charge as Lewis acids could dissociate the sluggish dinuclear Mn-(μ-O)$_3$-Mn core and the open-loop dinuclear manganese complex, HO-Mn^{III}-(μ-O)-Mn^{IV} = O or O = Mn^{IV}-(μ-O)-Mn^{IV} = O, was proposed as the active species, which was capable of the alkene epoxidation process. This work illustrated an alternative protocol to manipulate the reactivity of those sluggish catalysts by the introduction of non-redox metal ions and provided clues to understand the role of non-redox metal ions in metalloenzymes and heterogeneous catalysts.

Introduction

Manganese complexes have attracted considerable attentions because of its significant roles in a series of biological metabolisms and chemical oxidation processes, such as the oxygen evolution complex (OEC) of photosystem II (PSII) in water oxidation and the synthetic Mn catalysts in the oxo functionalization of hydrocarbons. The synthetic dinuclear manganese(IV) complex $[Mn_2^{IV}(\mu\text{-}O)_3(Me_3tacn)_2](PF_6)_2$ (as shown in Scheme 1, Me_3tacn is 1,4,7-trimethyl-1,4,7-triazacyclononane) [1], and its derivatives have been revealed to be efficacious catalysts for the oxidation of a broad range of organic functional groups in the presence of carboxylic acids as additives, using both homogeneous [2–30] and heterogeneous [18,31–35] analogues, including olefin epoxidation [2–15] and dihydroxylation [4–6,16–18], alcohol oxidation [11,19–22], sulfide and sulfoxide oxidation [9,21,23–25], and alkane activation [8,26–28]. Studies on these manganese complexes disclosed that Mn-Me_3tacn is a good system for developing model compounds of manganese-containing biologically important enzymes.

It is noteworthy that almost no oxidation reaction can be observed in the absence of carboxylic acid in all cases mentioned above. The carboxylic acids as additives are essential to suppress the unwanted catalase-like decomposition of hydrogen peroxide and achieve high catalyst productivity and selectivity. Although the acids have been proposed to form adducts with the Mn complex, the precise nature of the active intermediate and the role of the carboxylic acids remain unclear.

Alternatively, non-redox metal ions have been realized to play significant roles in various oxidation processes. For instance, it is well known that certain non-redox metal ions are contained in the oxidative reaction of metalloenzymes such as the oxygen evolution of Photosystem II in which Ca^{2+} is one essential component of the active Mn_4O_5Ca center [36–41], and many non-redox metal ions are frequently employed as additives in heterogeneous catalysts to modify the reactivity and stability of the redox catalysts [42–46]. Therefore, non-redox metal ions offer another feasible strategy for regulating the reactivity of redox metal ions through its bridge or ligation with the metal oxo functional groups in a number of homogeneous reactions [47–60].

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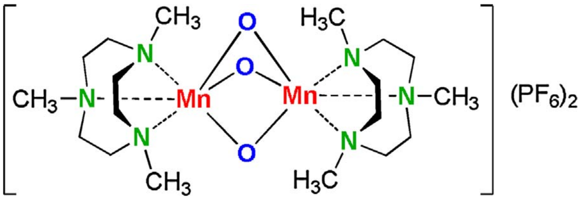

Scheme 1. Chemical structure of $[Mn_2^{IV}(\mu\text{-}O)_3(Me_3tacn)_2](PF_6)_2$ catalyst.

Addressing the functional roles of non-redox metal ions is highly related to the mechanism of both metalloenzymes in nature and multimetallic catalysts in chemical oxidation, and their roles have attracted considerable attentions in both the biological and chemical communities [36–76].

In our previous works, the effective strategy of introducing non-redox metal ions as Lewis acids was widely applied to modulate the reactivity of transition metal catalysis including manganese, iron, palladium, vanadium, ruthenium and osmium complexes in versatile homogeneous reactions, such as hydroxylation, N-dealkylation, C—C coupling, dehydrogenation, isomerization and epoxidation [61–76]. Recently, we have communicated the first example that the addition of non-redox metal ions can greatly improve the oxygen atom transfer efficiency in catalytic epoxidation by dissociating the dinuclear $Mn^{III}\text{-}(\mu\text{-}O)_2\text{-}Mn^{IV}$ complex which is very sluggish for olefin epoxidation [74–76]. We further compared the promotion effect of Lewis acid with that of Brønsted acid and found that they showed very similar reaction pathway and promotion effect. However, the organic oxidant, $PhI(OAc)_2$, was used in these cases, while all other oxidants including H_2O_2 were not efficient, giving sluggish performance. For economic and environmental reasons, catalytic olefin oxidations based on H_2O_2 are preferred over traditional stoichiometric oxidations because of its low cost, high atom efficiency and environmentally benign by-product (water) [77–80].

In the previous reports by other groups, it was found that H_2O_2 was sharply decomposed by the classic dinuclear manganese complex, $[Mn_2^{IV}(\mu\text{-}O)_3(Me_3tacn)_2](PF_6)_2$, in the acetonitrile solution [10,23,81]. Although the unwanted manganese-catalysed self-destruction of H_2O_2 could be suppressed by the application of acetone as the reaction solvent, this proposal was not acceptable for large-scale synthesis because of the risk of generation of explosive cyclic peroxides. These findings provide a challenge for us to explore whether the wasteful catalase-like decomposition can be suppressed by the introduction of non-redox metal ions serving as Lewis acids with acetonitrile as the solvent.

Encouraged by the classic Mn-Me_3tacn complexes and the effective strategy of introducing non-redox metal ions, herein, we have investigated the oxygen atom transfer reaction of alkene catalysed by the dinuclear manganese(IV) complex $[Mn_2^{IV}(\mu\text{-}O)_3(Me_3tacn)_2](PF_6)_2$ with H_2O_2 as the solely terminal oxidant in the promotion of non-redox metal ions. Compared with the effect of carboxylic acids in abundant reports, the introduction of non-redox metal ions as Lewis acid can also induce the remarkably promotional effect by dissociating the dinuclear $Mn\text{-}(\mu\text{-}O)_3\text{-}Mn$ core in the epoxidation reaction and better efficiency is observed in the case of Lewis acids with higher positive charge. The primary mechanism in catalytic process was further explored and the open-loop dinuclear manganese complex was proposed as the key active species to be capable of the alkene epoxidation process. This work demonstrates a novel strategy to improve the catalytic reactivity of some μ-oxo-bridged complexes and inspires us to explore novel catalysts for current challenges and societal demands.

Experimental section

Chemicals

All chemicals were commercially available and used without further purification unless otherwise indicated. The non-redox metal salts, such as sodium trifluoromethanesulfonate (NaOTf), magnesium trifluoromethanesulfonate ($Mg(OTf)_2$), scandium trifluoromethanesulfonate ($Sc(OTf)_3$), ytterbium trifluoromethanesulfonate ($Yb(OTf)_3$) and yttrium trifluoromethanesulfonate ($Y(OTf)_3$) came from Accela ChemBio Co., Ltd or Alfa Aesar. Other trifluoromethanesulfonates including $Ca(OTf)_2$, $Ba(OTf)_2$, $Zn(OTf)_2$ and $Al(OTf)_3$ were purchased from Aladdin or Shanghai Dibai Chemical Company. The alkenes, such as cyclooctene, cyclohexene, norbornene, styrene, 1-hexene and 1-dodecene, and their corresponding epoxides were obtained from Aldrich, Alfa Aesar or TCI (Shanghai) Development Co., Ltd. Ammonium hexafluorophosphate was purchased from Alfa Aesar. Common solvents, H_2O_2 (30% aqueous solution) and inorganic manganese salt, $MnCl_2{\cdot}4H_2O$, came from Sinopharm Chemical Reagent Co., Ltd. The ligand, 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3tacn), and its corresponding dinuclear manganese(IV) complex, $[Mn_2^{IV}(\mu\text{-}O)_3(Me_3tacn)_2](PF_6)_2$, were synthesized according to the previous literature procedures [82–84], and the chemical structure of $[Mn_2^{IV}(\mu\text{-}O)_3(Me_3tacn)_2](PF_6)_2$ is displayed in Scheme 1.

Characterization equipment

Gas chromatography-mass spectrometry (GC–MS) analysis was conducted on an Agilent 7890A/5975C spectrometer. FT-IR spectra were collected on a Bruker VERTEX70. UV–vis spectra were obtained on an Analytik Jena Specord 205 UV–vis spectrometer. Electron paramagnetic resonance (EPR) experiments were performed at 130 K on a Bruker A200 instrument, with a center field of 3352.488 G, frequency of 9.395 GHz, power of 19.44 mW, modulation amplitude of 2.00 G and receiver gain of 1.00×10^3. The content of Mn ion was determined by atomic absorption spectroscopy (AAS) analysis with an Analyst 300 Perkin Elmer. Mass spectra (MS) were measured in negative mode in the range m/z 50–3000 by a Bruker SolariX 7.0T spectrometer (ESI-MS). Elemental analysis (EA) was performed on a Vario Micro cube. Cyclic voltammetry (CV) were conducted with a CS CorrTest electrochemical workstation equipped with glassy carbon as both working and counter electrodes and saturated calomel as the reference electrode. Electrochemical data were collected in dry acetonitrile with 0.1 M tetrabutylammonium perchlorate as the supporting electrolyte.

Reaction procedure

General procedure for non-redox metal-ions-accelerated alkene epoxidation by the dinuclear manganese(IV) complex

The solution of 5 mL of acetonitrile containing 0.1 M alkene, 1 mM dinuclear manganese(IV) complex and 2 mM non-redox metal salt as Lewis acid was cooled in an ice water bath (273 K). Then 1.5 mmol H_2O_2 (30% aqueous solution) was added to the mixture solution to initialize the reaction. The reaction mixture was magnetically stirred at 273 K in the ice water bath for 2 h (set intervals for kinetics study). The yield of epoxide and the conversion of alkene were quantitatively analyzed by GC using the internal standard method. Control experiments using the dinuclear manganese (IV) complex or different non-redox metal salts alone as the catalyst were performed in parallel under identical conditions. All the reactions were conducted at least in triplicate and the average data were applied in the results and discussion section.

Results and discussion

Non-redox metal-ions-accelerated effect in alkene epoxidation

The promotional effect with non-redox metals on epoxidation was initially conducted with cyclooctene as the typical substrate and $[Mn_2^{IV}(\mu\text{-}O)_3(Me_3tacn)_2](PF_6)_2$ as the catalyst, during which H_2O_2 was applied as the solely terminal oxidant. The catalytic epoxidation experiments in the promotion of trivalent metals like Al^{3+} and Sc^{3+} were investigated at different reaction temperatures as shown in Table S1.