

Review

Amphoteric reactivity of metal–oxygen complexes in oxidation reactions

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ABSTRACT

Mononuclear metal–oxygen species, such as metal-superoxo, -peroxo, -hydroperoxo and -oxo complexes, are key intermediates involved in dioxygen activation and oxidation reactions catalyzed by a variety of metalloenzymes and their biomimetic compounds. Dioxygen is an electrophile or electron acceptor, but not a nucleophile or electron donor. However, when dioxygen is bound to metal complexes and metal–oxygen species are formed, such as metal-superoxo, -peroxo, -hydroperoxo, alkylperoxo, and -oxo complexes, the metal–oxygen intermediates react as nucleophiles and electron donors as well as electrophiles and electron acceptors. This review is intended to focus on such an amphoteric reactivity of the metal–oxygen complexes in electrophilic and nucleophilic reactions. Both the electronic and steric effects of the ligands have finely tuned the reactivity of metal–oxygen complexes in both the electrophilic and nucleophilic reactions. The amphoteric reactivity of metal–oxygen complexes can also be tuned by binding of redox-inactive metal ions acting as Lewis acids and also by binding of Brønsted acids.

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1. Introduction

Electron donors are reducing agents (reductants) as well as nucleophiles [1–4]. Nucleophiles are often the most effective as negatively-charged anions, and they are also referred to sometimes as Brønsted and Lewis bases or in terms of their softness on the hard and soft acids and bases (HSAB) scale [5–8]. The contrasting descriptions have also been applied to electrophiles and oxidants in reference to their behaviors as electron acceptors and acids. Many molecules have amphoteric properties as nucleophiles (electron donors and bases) and electrophiles (electron acceptors and acids) [1–4]. A typical example of the amphoteric reactivity is water that acts not only as a nucleophile (electron donor, reductant and base) for oxygen evolution by water oxidation [Eq. (1)] but also as an electrophile (electron acceptor, oxidant and acid) for hydrogen evolution by water reduction [Eq. (2)] [9–16]. In contrast, dioxygen normally acts only as an electrophile and an electron acceptor, since it is very difficult to be oxidized [17–24]. Once dioxygen is oxidized to dioxygenyl radical cation (O_2^+) photochemically or thermally [25–28], O_2^+ becomes an extremely strong oxidant capable of oxidizing even N_2 [29–35].



When dioxygen is bound to metal complexes, however, they can act not only as electrophiles and electron acceptors but also as nucleophiles and electron donors [36–45]. Mononuclear metal–oxygen species, such as metal-superoxo, -peroxo, -hydroperoxo, and -oxo complexes, are key intermediates involved in dioxygen activation and oxidation reactions catalyzed by a variety of metalloenzymes including cytochrome *c* oxidases in respiration and the oxygen evolving complex in Photosystem II [46–63]. In the realm of electrophilic oxidative reactions, the high-valent metal-oxo chemistry has been well established in the electrophilic reactions, such as in hydrogen atom transfer (HAT) and oxygen atom transfer (OAT) reactions [64–74]. However, manganese(V)-oxo complexes of corrolazine with axially coordinated anionic donors have been reported to act as both an electrophile and a nucleophile in the sulfoxidation of thioanisoles with electron donating and withdrawing substituents, respectively [75]. In contrast, metal-peroxo complexes exhibit nucleophilic reactivities in enzymatic and biomimetic systems (e.g., aldehyde deformylation) [37,38,76–98]. The amphoteric reactivity of metal-peroxo complexes has been reported to be tuned by binding of redox-inactive metal ions acting as Lewis acids [99].

The amphoteric properties of the metal-superoxo [36–38,100–123] and -hydroperoxo complexes [122–133] have been also unveiled in HAT, OAT, and nucleophilic deformylation reactions. Similarly, metal-alkylperoxo complexes, such as a nickel(II)-alkylperoxo complex, exhibit amphoteric reactivity towards the electrophilic oxidation of triphenylphosphine (PPh_3), carbon monoxide (CO) and nucleophilic deformylation of aldehyde [134]. The reactivity of copper(II)-alkylperoxo complexes has also been examined in both electrophilic [135–138] and nucleophilic reactions [139]. In addition to the mononuclear reactive species, homo- and heterodinuclear bis(μ -oxo) complexes show both electrophilic and nucleophilic reactivities [140–143]. As described above, electrophilic and nucleophilic reactivity of metal–oxygen complexes has so far been discussed separately. Thus, the amphoteric reactivity of various metal–oxygen complexes has yet to be reviewed and discussed together.

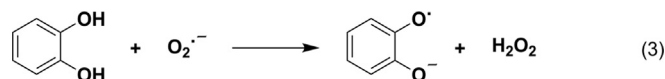
This review is intended to focus on recent findings of amphoteric reactivities of metal–oxygen complexes, such as metal-superoxo, -peroxo, -hydroperoxo, -alkylperoxo, and -oxo com-

plexes. We have also shown that how the ligand architecture of metal complexes modulate their amphoteric properties in electrophilic and/or nucleophilic reactions. The mechanisms of the electrophilic and nucleophilic reactions are discussed as well.

2. Metal-superoxo complexes

2.1. Amphoteric reactivity of superoxide

Superoxide ion (O_2^-) acts as an oxidant, an electron acceptor and electrophile in various oxidation reactions [17,144–150] as well as a nucleophile in nucleophilic addition and substitution reactions [151–156]; therefore, superoxide ion exhibits an amphoteric reactivity. A typical example of the reactivity of O_2^- as an oxidant is shown in the oxidation of catechol by O_2^- [Eq. (3)], in which O_2^- is reduced to H_2O_2 [145]. In contrast to the oxidation reaction by O_2^- , the nucleophilic reaction of O_2^- is not necessarily associated with the change in the oxidation state. For example, the nucleophilic attack of O_2^- on the polarized $C^{\delta+}$ carbon of CH_3Cl results in the substitution of Cl^- by O_2^- that acts as a Lewis base rather than a reductant with no redox reaction [Eq. (4)] [151,152]. O_2^- also acts as an electron donor to reduce stronger oxidants to yield O_2 [157,158]. In superoxide dismutases (SODs), O_2^- acts as both an electron donor (reductant) and an electron acceptor (oxidant) with protons to produce O_2 and hydrogen peroxide [Eq. (5)] [159–164].



2.2. Iron-superoxo complexes

Superoxide ion produced in enzymatic reactions is usually bound to metal complexes and resulting metal-superoxo complexes mainly act as an electrophile in HAT reactions in various enzymatic reactions such as Isopenicillin *N* synthase (IPNS) [165–167], 2-hydroxyethylphosphonate dioxygenase (HEPD) [168], and 1-aminocyclopropane-1-carboxylic acid oxidase (ACCO) [169–171]. In homoprotocatechuate-2,3-dioxygenase (HPCD), an iron(II)-superoxo complex is generated after electron transfer from a bound catecholate to O_2 via the iron(II) center [172].

Several iron(III)-superoxo intermediates have been suggested to act as nucleophiles in enzymatic reactions [173–175]. Specifically, in the α -ketoglutarate (α -KG) dependent dioxygenases, a postulated Fe^{III} -superoxo intermediate (I in Scheme 1) is proposed to form from a bicyclic species (II in Scheme 1) via a nucleophilic attack of the uncoordinated O atom on C2 of α -KG, followed by the O–O bond cleavage to yield an Fe^{IV} -oxo intermediate (III in Scheme 1) [173]. In the next step, the Fe^{IV} -oxo intermediate abstracts a hydrogen atom (H-atom) from the substrate, yielding an Fe^{III} -OH complex and a substrate radical (IV in Scheme 1). Then, a fast “oxygen rebound” occurs between the Fe^{III} -OH complex and the substrate radical, yielding the hydroxylated product and the Fe^{II} center (V in Scheme 1) [173]. By the same token, an iron(III)-superoxo intermediate is also proposed to act as a nucleophile in the pterin-dependent hydroxylases, by attacking an electrophilic carbon atom of the tetrahydropterin co-substrate [174,175].

A variety of metal-superoxo complexes with different metals and ligands have been synthesized and characterized, and they

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