Reversible O–O Bond Cleavage and Formation between Mn(IV)-Peroxo and Mn(V)-Oxo Corroles

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Abstract: Mn(IV)-peroxo and Mn(V)-oxo corroles were synthesized and characterized with various spectroscopic techniques. The intermediates were directly used in O–O bond cleavage and formation reactions. Upon addition of proton to the Mn(IV)-peroxo corrole, the formation of the Mn(V)-oxo corrole was observed. Interestingly, addition of base to the Mn(V)-oxo corrole afforded the formation of the Mn(IV)-peroxo corrole. Thus, we were able to report the first example of reversible O–O bond cleavage and formation reactions using in situ generated Mn(IV)-peroxo and Mn(V)-oxo corroles.

Dioxygen O–O bond-cleaving and bond-forming reactions occur at transition metal centers in a number of metalloenzymes. For example, heme and nonheme iron monooxygenases bind and activate O2 to generate high-valent iron-oxo intermediates via O–O bond cleavage of iron(III)-peroxo precursors, [Fe(III)-O2]9+. The O–O bond activation of iron–O2 adducts has for that reason been intensively investigated using synthetic iron porphyrins to elucidate mechanisms of the iron-oxo intermediate formation over the past several decades (e.g., heterolysis vs homolysis).2

In the case of the O–O bond formation, the photosynthetic conversion of water into dioxygen occurs at the oxygen-evolving complex (OEC) in photosystem II (PS II); a manganese(V)-oxo conversion of water into dioxygen occurs at the oxygen-evolving center derived from H2O2. The X-band EPR spectrum of 3 yielded several absorption bands at 435 and 590 nm within 1 min (Scheme 1, reaction A; Figure 1 and SI, Figure S2 for UV–vis spectral changes). The intermediate was stable enough to be characterized by various spectroscopic methods (~10 min at 10 °C). The electrospray ionization mass spectrum (ESI MS) of 2 exhibited a prominent ion peak at a mass-to-charge ratio (m/z) of 1090.8, which corresponds to the mass and isotope distribution pattern of [Mn(TFMPC)(O2)(CH3CN)(CH3OH)]7 (calculated m/z 1091.1; Figure 2a). The ESI MS of 2, prepared with D2O2 in D2O, showed the identical mass peak (SI, Figure S3), whereas 2, prepared with H318O2 in H316O, showed a mass peak at m/z 1094.8, which corresponds to [Mn(TFMPC)(18O2)(CH3CN)(CH3OH)]7 (Figure 2a, inset). The 4 mass unit increase upon the substitution of 16O with 18O indicates that 2 contains an O2 unit derived from H2O2. The X-band EPR spectrum of 2 exhibited a broad signal at g ∼ 4 (Figure 2b and SI, Figure S4 for EPR spectra taken during reactions), which we assign to a high-spin S = 3/2 Mn(IV) with a strong zero-field splitting.6 Taken together, the spectroscopic data provide strong evidence that 2, generated in the reaction of 1 and H2O2 in the presence of base, is a high-spin Mn(IV) complex bearing an O2 ligand, [Mn(IV)(TFMPC)(O2)]7.

Scheme 1

Figure 1. UV–vis spectra of 2 (solid blue line), 3 (solid red line), after addition of acid (20 equiv of HClO4) to 2 (dashed green line), and after addition of base (20 equiv of TMAH) to 3 (dashed black line).
When measured in CH₃CN at complex, Mn(IV)-peroxo complex, repeated several times without showing a significant decrease of base (Scheme 1, reactions C and D); this reversible cycle could be marked with * are from solvent.

Figure 2. (a) ESI MS spectrum of 2. Inset shows isotope distribution patterns for ²¹⁸O (left) and ²¹⁶O (right). The mass peaks at m/z 1017.1 and 1048.1 correspond to [Mn(TFMP)(CH₃O)] and [Mn(TFMP)-CH₂O]²⁻, respectively. (b) EPR spectrum of 2. Inset shows a parallel mode X-Band CW-EPR spectrum of the starting Mn³(II)(TFMPC) complex. Also, see SI, Figure S4.

We then synthesized a Mn(V)-oxo corrole complex, 3, by reacting 1 with 2.0 equiv of iodosylbenzene (PhIO) in CH₃CN at 10 °C (Scheme 1, reaction B; Figure 1 and SI, Figure S5 for UV−vis spectral changes). The ESI MS of 3 exhibited a prominent ion peak at m/z 1002.1, whose mass and isotope distribution pattern corresponds to Mn(TFMP)(O)(O) (calculated m/z 1002.1; Figure 3a).

When 3 was prepared with isotopically labeled PhIO in the presence of H₂¹⁸O, a mass peak corresponding to Mn(TFMP)(¹⁸O) appeared at m/z 1004.2 (calculated m/z 1004.1; Figure 3a, inset). 3 is EPR silent (SI, Figure S4), suggesting a diamagnetic d² (S = 0) species as has been reported for other Mn(V)-oxo corrole and corrolazine complexes. The resonance Raman spectrum of 3, measured in CH₂CN at −40 °C with 442-nm laser excitation, displays an isotope sensitive band at 957 cm⁻¹ upon introduction of ¹⁸O (Figure 3b). The observed isotopic shift of −37 cm⁻¹ with ¹⁸O substitution is in close agreement with the value calculated for a Mn−O diatomic oscillator (−42 cm⁻¹). The calculated force constant for the 957 cm⁻¹ mode by a simple Hook’s law is 6.7 mdyne/Å, which is consistent with triply bonded Mn−O bonds in Mn(V)-oxo complexes. Taken together, the spectroscopic data demonstrate that 3 is a Mn(V)-oxo corrole with a Mn−O triple bond, Mn⁵(O)(TFMP).

Remarkably, a reversible conversion between the Mn(IV)-peroxo and Mn(V)-oxo corroles was observed upon addition of acid and base (Scheme 1, reactions C and D); this reversible cycle could be repeated several times without showing a significant decrease of the absorption bands corresponding to the products. First, the Mn(IV)-peroxo complex, 2, was converted to the Mn(V)-oxo complex, 3, upon addition of HClO₄ (Scheme 1, reaction C); the full formation of 3 was confirmed by the UV−vis and EPR spectra of the resulting solution (Figure 1 and SI, Figure S4). In addition, 2 was converted to 3 by addition of benzoyl chloride (data not shown). It has been well-documented that the reactions of metal-peroxo species, including Mn(III)-peroxo porphyrins, with benzoyl chloride lead to formation of their corresponding high-valent metal-oxo species. However, the O−O bond cleavage mechanism of the putative Mn(IV)−OOH intermediate is not yet clear at this moment (see Scheme 2 for O−O bond homolysis vs heterolysis).

Nevertheless, to our knowledge, this is the first demonstration of the analogous conversion of a Mn-peroxo corrole to a Mn-oxo corrole upon protonation.

Figure 3. (a) ESI MS spectrum of the complex 3. Inset shows isotope distribution patterns prepared with PhIO (left) and PhO²⁻ (right). (b) Resonance Raman spectra of 3 prepared with PhO²⁻ (black line) and PhO²⁻ (red line), and the difference spectrum of 3-¹⁸O−3-¹⁸O (blue line). The peaks marked with * are from solvent.

In the O−O bond formation reaction, addition of base to the Mn(V)-oxo complex, 3, produced the Mn(IV)-peroxo complex, 2, quantitatively (Scheme 1, reaction D; Figure 1). The formation of 2 was further confirmed by taking EPR and ESI MS of the resulting solution; a broad signal at g ≈ 4 was observed in the EPR spectrum (SI, Figure S4). In ESI MS experiments, 2 prepared in the reaction of Mn(V)¹⁸O and ¹⁶OH− contained an ¹⁶O¹⁸O group (SI, Figure S6). Similarly, 2 prepared in the reaction of Mn(V)¹⁸O and ¹⁶OH− contained an ¹⁸O¹⁶O group (SI, Figure S6). These results demonstrate that the peroxo ligand in 2 was generated by the O−O bond formation between the Mn-oxo moiety in 3 and the hydroxide ion, followed by a deprotonation of a hydroperoxo ligand by another hydroxide ion (Scheme 2). However, there is an electron missing in the proposed mechanism, and this is probably due to a greater stability of a Mn(V)-peroxo corrole species under the reaction conditions.

In conclusion, we have synthesized and characterized new Mn(V)-peroxo and Mn(V)-oxo correles and used them in O−O bond cleavage and formation reactions. We have also shown the first example of reversible O−O bond cleavage and formation between high-valent metal-oxo and metal-peroxo species. Future studies will be focused on understanding mechanistic aspects involved in the O−O bond cleavage and formation processes.

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Supporting Information Available: Experimental details and Figures S1−S6. This material is available free of charge via the Internet at http://pubs.acs.org.

References


