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Nucleophilic Attack of Hydroxide on a Mn^V Oxo Complex: A Model of the O−O Bond Formation in the Oxygen Evolving Complex of Photosystem II

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In photosynthesis by green plants, water is the source of the electrons that are finally used to convert carbon dioxide into biomass. In this process, which takes place in the oxygen evolving complex (OEC) of photosystem II, water is oxidized to molecular oxygen. The catalytic center of the OEC consists of a tetranuclear manganese cluster.[1] Despite numerous experimental and theoretical model studies, the actual mechanism for the formation of molecular oxygen is not clear.[2]

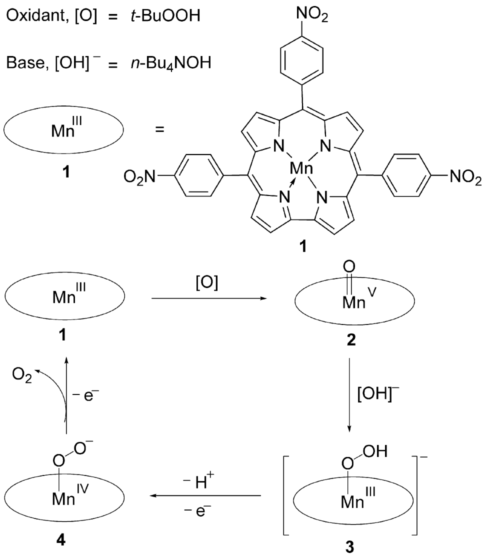
In principle, three different mechanisms have been suggested for the formation of the O−O bond: (a) nucleophilic attack of water or hydroxide on a formally Mn^V species, (b) radical coupling of two Mn^V oxo species, and (c) radical coupling of water (or hydroxide) with a bridging oxygen in the manganese cluster.[2]

Many attempts have been made to prepare Mn^V oxo complexes from species related to the OEC, but to date only circumstantial evidence for their existence has been obtained. The groups of both Crabtree and Brudvig[2e] and Pecoraro[2c] have provided evidence for Mn^V oxo intermediates related to the OEC that were very short-lived. However, both porphyrins[3] and corroles and some related complexes have been shown to give Mn^V oxo species with certain stability.[4] It therefore seemed interesting to prepare a reasonably stable Mn^V corrole complex and react this with hydroxide ion in order to see whether molecular oxygen could in fact be generated by such a species. Here we report the successful outcome of a study of this type using nitrophenylcorrole complex **1**.

In a previous study, we showed that both mononuclear and dinuclear "Pacman" Mn^{IV} corrole complexes could act as catalysts for electrochemical oxidation of water to molecular oxygen.[5] The dinuclear Mn complex was a more efficient catalyst than the mononuclear one, but the difference was moderate. It thus seems likely that a similar mechanism operates in both cases. This was verified by density functional theory calculations, which suggested that both complexes react via nucleophilic addition of water (or hydroxide) to Mn^V oxo species (Scheme 1).[6] In principle, a dinuclear Mn complex could react via oxygen−oxygen coupling, but this route was found to be energetically less favorable than nucleophilic attack.

In an attempt to get experimental evidence for a mechanism involving nucleophilic addition, we decided to study the reaction between a $Mn^V{=}O$ corrole species and hydroxide ion. The Mn^{III} corrole complex **1** was therefore first prepared in high yield (91%) by the reaction of 5,10,15-tris(4-nitrophenyl)corrole[7] with $Mn(OAc)_2 \cdot 4H_2O$ in refluxing DMF. This complex was dissolved in acetonitrile and treated at room temperature with a slight excess of *t*-BuOOH. A color change characteristic of conversion of a Mn^{III} to a Mn^V species occurred, as shown by the UV−vis spectra (Figure 1). Addition of an aqueous solution of $(n\text{-}Bu)_4NOH$ initiated rapid evolution of oxygen, as shown by mass spectrometry.

Scheme 1. Possible Mechanism of the Oxygen Evolution Cycle



The electronic absorption spectrum of complex **1** shows major peaks at 480 and 662 nm and a small peak at 418 nm (Figure 1a, solid line). In the corresponding hydroxide complex, the peak at 418 nm does not appear (Figure S1 in the Supporting Information). After addition of a small excess of *t*-BuOOH, the absorption peaks at 480 and 662 nm were replaced by a new strong peak at 420 nm (Figure 1a, dashed line). This spectrum is very similar to those previously reported for $Mn^V{=}O$ corrole complexes,[4a,c,8] suggesting that the $Mn^V{=}O$ complex was formed in our system. Next, 2 equiv of $(n\text{-}Bu)_4NOH$ were added to the mixture. Rapid oxygen evolution ensued, accompanied by the disappearance of the peak at 420 nm and the appearance of new peaks at 372, 455, and 605 nm (Figure 1a, dotted line). This spectrum suggests that a Mn^{IV} complex was initially formed in our experiment.[8,9] However, after a few minutes, the peaks at 372, 455, and 605 nm decreased and were replaced by new peaks at 484 and 666 nm (Figure

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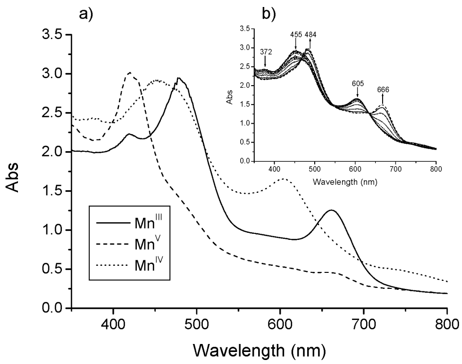

Figure 1. UV−vis spectral alterations for manganese corrole complexes in CH_3CN. (a) Mn^{III} corrole complex (solid); after addition of oxidant (dashed); after addition of base (dotted); (b) time-dependent UV−vis spectral alteration for the Mn^{IV} species.

1b). These spectral changes indicate that the Mn^{IV} species was gradually transformed into a Mn^{III} species.

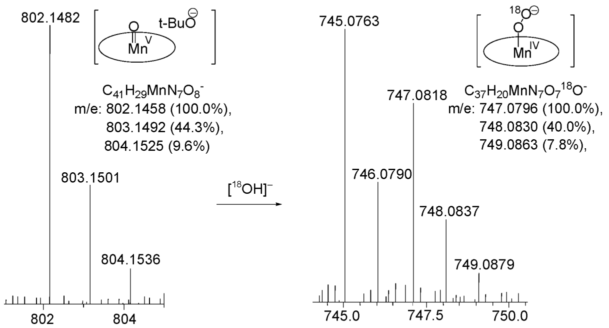

Figure 2. Oxygen isotope studies using HRMS.

The results could be confirmed by high-resolution mass spectrometry (HRMS) of the Mn corrole intermediates in the reaction (Figure 2 and Figures S2, S3, and S4). The mass spectrum of the starting Mn^{III} corrole complex **1** (negative mode, *m/z*) showed a strong peak at 758.0851, corresponding to $[M + HCOO]^-$ (Figure S2; calcd for $M = C_{37}H_{20}MnN_7O_6$, 758.0832). Upon oxidation with *t*-BuOOH, the Mn^{V}=O complex **2** ($M = C_{37}H_{20}MnN_7O_7$) was formed, as shown by both the appearance of a peak at 802.1482 (Figure 2, left; calcd for $[M + t\text{-BuO}]^-$, 802.1458) and the UV−vis spectrum (Figure 1). On addition of 2 equiv of alkali, a Mn^{IV} complex was rapidly formed, as shown by both UV−vis spectrum and the peak at 745.0780 in the mass spectrum attributable to Mn^{IV} complex **4** (Figure S3; calcd for $M = C_{37}H_{20}MnN_7O_8$, 745.0754 $[M]^-$). After another few minutes, the composition of the mixture changed, and the major observed peak was found at 730.0903, corresponding to the Mn^{III} complex $[\mathbf{1} + OH]^-$ (Figure S4; calcd 730.0883).

When these experiments were repeated using ^{18}O-labeled water, incorporation of ^{18}O into the peroxy intermediate **4** was observed by HRMS. There was thus a substantial increase of the peak at 747.0818 corresponding to ^{18}O-labeled **4** (Figure 2, right; calcd 747.0796 $[M]^-$).

The experiments were carried out using online gas analysis by mass spectrometry to measure the amount of oxygen generated (Figure 3). When hydroxide was added to oxo complex **2**, rapid oxygen evolution took place. The oxygen curves in Figure 3 show that only a small amount of $^{16,18}O_2$ was formed, corresponding to the content of ^{18}O in natural water (Figure 3, left). However, when ^{18}O-labeled water (10% ^{18}O) was used, ~8% $^{16,18}O_2$ was contained in the generated oxygen (Figure 3, right). This is approximately proportional to the $^{18}O/^{16}O$ ratio of the labeled water in the experiment and shows that the $^{16,18}O_2$ was formed by addition of ^{18}O hydroxide to the unlabeled Mn^{V}=O.

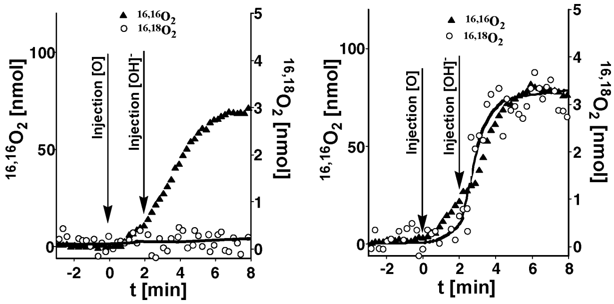

Figure 3. Oxygen isotope studies using online gas analysis by mass spectrometry: (left) without ^{18}O-labeled water; (right) with ^{18}O-labeled water. The solid lines are fits to the $^{16,18}O_2$ data (○).

The mechanism of water oxidation can thus be summarized in the following way: First, the Mn^{III} corrole complex **1** is oxidized to the Mn^{V} oxo complex **2**. Second, nucleophilic attack of hydroxide presumably gives initially the Mn^{III} hydroperoxy complex **3**. This is oxidized (e.g., by unreacted Mn^{V} oxo complex) to give the Mn^{IV} hydroperoxy complex, which after loss of a proton gives rise to the observed peroxy complex **4**. This either disproportionates with loss of oxygen or is oxidized to the corresponding Mn^{V} complex, which undergoes reductive elimination of oxygen to form the starting complex **1**. The main conclusion from this study is that O−O bond formation via nucleophilic attack of hydroxide on a Mn^{V} oxo oxygen has been experimentally demonstrated and is a viable mechanism for conversion of water into molecular oxygen.

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Supporting Information Available: Experimental preparation of **1**, UV−vis spectra of complex **1** upon reaction with hydroxyl, HRMS data for complex **1** and intermediate **4**, and the gas analysis setup. This material is available free of charge via the Internet at http://pubs.acs.org.

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