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Thermal stability of $[Mn(III)(O)_2Mn(IV)(H_2O)_2(Terpy)_2](NO_3)_3$ (Terpy = 2,2′:6′,2″-terpyridine) in aqueous solution

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ABSTRACT

The chemistry of oxidizing water to dioxygen in photosynthesis is catalyzed by a Mn_4Ca cluster in PS II. A synthesized Mn(III/IV)-oxo dimer compound, $[Mn(III)(O)_2Mn(IV)(H_2O)_2(Terpy)_2](NO_3)_3$ (Terpy = 2,2′:6′,2″-terpyridine) is able to catalyze the conversion of water to dioxygen. In this work, we investigated the thermal stability of this Mn(III/IV)-oxo dimer in the range of 20–85 °C. The decomposition of the Mn(III/IV)-oxo dimer in aqueous solution at ~60 °C occurred involving a change in Mn valence. Values of the activation energies for the first fast step with a lifetime of 3.5 ± 0.5 min and in the following slow step with lifetime of 19 ± 4 min were determined to be 68 ± 10 kJ/mol, and 82 ± 16 kJ/mol, respectively. We speculate that the thermal inactivation of PS II may also be associated with a Mn valence change in the Mn_4Ca cluster. Unexpectedly, the thermal decomposition of the Mn(III/IV)-oxo dimer was found to generate a Mn-containing precipitate that retained catalytic oxygen-evolution activity. The solid Mn-containing material is not manganese dioxide as judged by EPR, FTIR, elemental analysis, and atomic absorption spectroscopy. The novel Mn-containing precipitate, tentatively assigned as a Mn-oxo oligomer, is thermally stable and may be a unique material for fabricating catalytic materials in solar fuel production.

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1. Introduction

The chemistry of oxidizing water to dioxygen involves multi-electron and proton transfer reactions and is conducted at room temperature, normal pressure and at neutral aqueous conditions in photosynthetic organisms. This important reaction is catalyzed by a Mn_4Ca cluster in the oxygen-evolving complex (OEC) of photosystem II (PS II) [1]. The structure and oxidation state of the Mn_4Ca cluster was investigated by X-ray crystallography [2–4], electron paramagnetic resonance (EPR) [5–7], Fourier transform infrared (FTIR) [8,9], and X-ray absorption spectroscopy [10,11], and computational methods [12]. However, the precise chemical structure of the Mn_4Ca cluster in PS II is not completely known.

The structure information of the Mn_4Ca cluster in PS II provides a solid foundation for functional investigation of photosynthetic water-oxidation chemistry. For example, on the basis of the structural data on the Mn_4Ca cluster, five types of Mn-containing complexes have been synthesized to mimic the process of breakdown of water to oxygen in PSII [13–17]. These compounds are demonstrated to be able to catalyze the conversion of water to dioxygen, serving as PSII functional models [18].

Thermal denaturation of the PS II complex was investigated by differential scanning calorimetry (DSC) [19,20]. The thermal reaction may involve a reaction of the Mn complex with hydroxide ions, which are oxidized to peroxide or superoxide, and results in the reduction and release of Mn. Recent studies of the effect of temperature on PSII revealed that the target of the temperature jump from 25 °C to 47 °C is the Mn_4Ca cluster [21,22]. The disassembly of the Mn complex of PSII by a temperature jump from 25 °C to 47 °C experienced three distinct phases. Firstly, the oxygen-evolution activity was lost. This phase also involved the release of Ca but the overall structure of Mn complex remained largely intact. Subsequently, two Mn(III) or Mn(IV) ions in the native complex were reduced to Mn(II) and released. The two unreleased Mn ions formed a di-μ-oxo bridged Mn(III/III) dimer complex. Finally, the tightly-bound Mn(III/III) unit was slowly reduced and released. However, due the complexity of PSII, which contains more 20 polypeptides and more than 250 cofactors, the details of the thermal disassembly process in PS II is not completely understood.

The mixed-valence Mn(III/IV)-oxo dimer compound, $[Mn(III)(O)_2Mn(IV)(H_2O)_2(Terpy)_2](NO_3)_3$, is the first functional model

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Abbreviations: DSC, differential scanning calorimetry; EPR, electron paramagnetic resonance; FTIR, Fourier transform infrared; MES, 2-(N-morpholino)ethanesulfonic acid; Mn(III/IV)-oxo dimer, $[Mn(III)(O)_2Mn(IV)(H_2O)_2(Terpy)_2](NO_3)_3$; OEC, oxygen evolution complex; Oxone, potassium peroxymonosulfate, $KHSO_5$; PS II, photosystem II; Terpy, 2,2′:6′,2″-terpyridine; TES, 2-{[tris(hydroxymethyl)methyl]-amino}ethanesulfonic acid.

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oxygen-evolution complex of PS II [16]. It is able to catalyze oxygen evolution in the presence of several oxidants such as hypochlorite [16,23], Ce^{4+} ion [24] and oxone [25]. The mechanism of its catalytic reaction in water oxidation was well studied [23,26–28]. In this work, the effect of elevated temperature on the functional PSII model complex, a mixed-valence Mn(III/IV)-oxo dimer compound, was investigated over the range of 25–85 °C by UV–Vis absorption spectrometry, atomic absorption spectrometry, oxygen evolution measurements, FTIR, and EPR methodologies. The results provide novel insights into the structure and mechanisms of the water-oxidation chemistry of the functional PSII model complex.

2. Experimental

2.1. Synthesis of Mn(III/IV)-oxo dimer

The Mn(III/IV)-oxo dimer, $[Mn(III)(O)_2Mn(IV)(H_2O)_2(Terpy)_2](NO_3)_3$, was synthesized according the procedures reported previously [25] Oxone (potassium peroxymonosulfate, $KHSO_5$) solutions were made in acetate buffer (pH 4.50, 0.23 M HAc/Ac^-). All solutions were prepared using doubly deionized water.

2.2. Heat treatment of the Mn(III/IV)-oxo dimer

Three kinds of pH buffers (0.50 M) were prepared as follows: 2-(N-morpholino)ethanesulfonic acid (MES) buffer for pH 5.00–7.00, Na_2HPO_4 buffer for pH 6.00–8.00, and 2-{[tris(hydroxymethyl) methyl]amino}ethanesulfonic acid (TES) buffer for pH 8.00–10.00. Because there is no appropriate buffer at the low pH range, the solutions of the Mn(III/IV)-oxo dimer at pH 2.00 to 4.50 were prepared by addition of hydrochloric acid (pH 1.00 and 2.00). The pH value was determined and verified at the beginning and end of the thermal reactions by a pH meter. Typically, the solid Mn(III/IV)-oxo dimer was dissolved in water, diluted to 1.0 mM in test tubes containing different pH buffers, and placed in the water bath at 25–85 °C maintained at a constant temperature by a circulated thermostat. The rate of heating was approximately 1 °C per minute.

2.3. UV–Vis absorption spectroscopy

UV–Vis spectra were recorded on a HP 8425A Diode Array spectrophotometer. Typically, 100 μl aliquots of each sample were taken from the test tube at temperature intervals of 5 °C, and UV–Vis spectra were measured. For experiments at a fixed decomposition temperature, the UV–Vis spectra of the samples were obtained at the different time intervals. A 1.0-cm path length cuvette was used to collect the spectra. When the effect of dissolved oxygen on the transformation temperature of the Mn(III/IV)-oxo dimer was examined, filtered helium or nitrogen gas was bubbled into the solution to remove the dissolved oxygen prior to heating and a stream of gas was kept 1.0 cm above the solution during the entire heating process. To test the effect of excess terpyridine ligand on the reaction, an appropriate amount of terpyridine/acetonitrile solution was added to the Mn(III/IV)-oxo dimer solution to ensure a 1:1 M ratio of Mn(III/IV)-oxo dimer to terpyridine.

2.4. Oxygen evolution measurements

The oxygen-evolution activity of the Mn(III/IV)-oxo dimer after heating to the elevated temperatures was determined at 20 °C by a Clark-type electrode (Ranker Brothers, Ltd). In a typical experiment, 30 μl of the heat-treated solution of Mn(III/IV)-oxo dimer was added to a 2.0 ml solution of oxone by a syringe. All oxygen evolution rates were determined from the initial rate of the recorded slope.

2.5. EPR measurements

Aliquots of Mn(III/IV)-oxo dimer solutions were frozen in liquid nitrogen after heating to the elevated temperatures. EPR spectra of frozen samples were collected at 7 K with an X-band Bruker Biospin Elexsys E500 spectrometer equipped with an Oxford ESR-900 liquid helium cryostat. Typical instrument settings were the following: modulation amplitude = 20 G, modulation frequency = 100 kHz, and microwave power = 0.5 mW.

2.6. Atomic absorption spectrometry

The amount of Mn in the precipitate and supernatant that resulted from heating the solution of Mn(III/IV)-oxo dimer was determined by using a Perkin-Elmer Analyte 100. In brief, the samples were prepared by the following procedure. The mixture of solution and precipitate that formed after heating the solution of the Mn(III/IV)-oxo dimer at ~80 °C was transferred from a test tube to a 50 ml centrifuge tube. The precipitate was centrifuged and washed three times with water. The supernatant was diluted to 50.00 ml with 2% nitric acid. The washed precipitate was dissolved using 2.00 ml of aqua regia (concentrated hydrochloric acid:concentrated nitric acid = 3:1) and diluted to 50.00 ml with 2% nitric acid.

3. Results

3.1. Thermal decomposition reaction of the Mn(III/IV)-oxo dimer

The UV–Vis spectra of the Mn(III/IV)-oxo dimer at different temperatures with intervals of 5 °C in the range from 25 °C to 85 °C are shown in Fig. 1. The UV spectroscopy change indicated two transformation steps. The absorbance at 400 nm gradually increased when the temperature was increased from 25 °C to 60 °C, indicating that the Mn(III/IV)-oxo dimer was transformed into another species. Because the Mn(IV/IV)-oxo dimer species has a strong absorption peak at 400–440 nm [26], the increase in absorption at these wavelengths upon heating may be due to conversion of the Mn(III/IV)-oxo dimer to the Mn(IV/IV) species. The increase at 300 nm is likely due to the dissociation of the terpy ligand from the Mn-oxo dimer compound. We also observed that a further increase in temperature caused the absorption peak at 400–440 nm to decrease accompanied by the formation of a brown precipitate. We conclude that the thermal decomposition of the Mn(III/IV)-oxo dimer occurs in two phases during the heating process. The first phase occurred at temperatures below 60 °C, possibly due to formation of an intermediate with a valence change in Mn, followed by the second phase above 60 °C in which the intermediate decomposed.

3.2. EPR measurements of the Mn(III/IV)-oxo dimer during the heating process

Fig. 2 shows the EPR spectra of frozen solutions of the Mn(III/IV)-oxo dimer collected over time during the heating process. The native Mn(III/IV)-oxo dimer sample in acetate buffer shows a 16-lines signal in the range of 2800–4100 G, which is characteristic for the Mn(III/IV) mixed-valence species. When the solution was heated at 75 °C, the 16-line EPR signal was decreased by a factor of 90% within 10 min. This indicates that the Mn(III/IV)-oxo dimer is converted by heating into an EPR silent species, such as the