Unexpected ligand lability in condition of water oxidation catalysis

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ABSTRACT

In the search for rational design of improved water oxidation catalysts, enhanced catalytic activities were reported for single site Ru catalysis with Ru-iodide coordination. As these complexes are not initially capable of proton coupled electron transfer (PCET) and Ru=O formation, a proposal was put forward on the generation of catalytically active 7-coordinate Ru species. We tested this hypothesis by EPR and X-ray spectroscopy and found that $[Ru^{II}(bpy)(tpy)I]^+$ only serves as a precursor for the formation of $[Ru^{IV}(bpy)(tpy)=O]^{2+}$. Upon oxidation with excess of Ce^{IV} the Ru—I bond quickly dissociates with the formation of $[Ru^{III}(bpy)(tpy)H_2O]^{3+}$ and $[Ru^{IV}(bpy)(tpy)=O]^{2+}$ complexes. The catalytic steady state was composed of 95% $[Ru^{IV}(bpy)(tpy)=O]^{2+}$ species. Thus, introducing the Ru—I bond into initial catalysts does not serve to improve catalyst design. This manuscript also shows how EXAFS can directly probe transition metal–halogen interaction for in situ catalysis.

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1. Introduction

Ru based complexes are widely used in homogeneous catalysis [1,2]. Some of them exist in a form which contains a Ru–halogen bond in the catalyst precursor or in the active form of the catalyst. When such complexes are dissolved in coordinating solvents or added to reaction mixtures, it is sometimes difficult to establish the dynamics of halogen exchange. For diamagnetic complexes, NMR can be used to monitor the resonance of organic ligands and draw conclusions about the halogen ligands' exchange with solvent [3] but this technique is not applicable for paramagnetic Ru^{III}, Ru^{IV} and Ru^V complexes and their intermediates. Here we show that X-ray absorption spectroscopy (XAS) can serve as a very sensitive and direct probe of the metal–halogen binding as well as report on the overall electronic structure of the Ru center.

This study focuses on analyzing the water oxidation mechanism in single site Ru based catalysts for artificial photosynthesis. The realization of artificial photosynthesis carries the promise of abundant and clean solar fuels. However, the process requires an efficient and durable water oxidation catalyst. Mononuclear Ru-based water oxidation catalysts are currently under active investigation in an effort to uncover the fundamental principles controlling their catalytic activity [3–13]. A mononuclear Ru-based catalyst usually contains polypyridine ligands and one water molecule coordinated with Ru. The role of ligands in

catalytic water oxidation by mononuclear ruthenium complexes is summarized in a recent review by Zeng and coworkers [14]. Molecular Ru containing complexes remain the prime choice for mechanistic studies as series of complexes are available with varying redox potentials, ligand environment and catalytic activities. Thus, a detailed analysis of these complexes will help to understand overall principals controlling the catalytic water oxidation and result in design of more active molecules with higher stability.

In single site Ru catalysts, a water molecule bound to Ru^{II} is capable of proton coupled electron transfer (PCET) when both electron and proton are removed from the catalyst during oxidation to prevent charging of the complex. This process produces the oxidized $Ru^{IV}=O$ and $Ru^V=O$ species [8,15–18]. However, some water oxidation catalysts have been reported which are seemingly incapable of PCET as they lack a ligand suitable for deprotonation, such as water [3,19]. For instance, [Ru(bpy)(tpy)I]I catalyst lacks an H_2O bound to Ru but evolves more oxygen than the parent $[Ru^{II}(bpy)(tpy)H_2O]^{2+}$ complex [3]. This calls for an investigation of potential reasons for improved catalysis. The importance of steric strain on reactivity has been noticed for complexes with no water ligand on Ru [19]. To explain these unexpected observations the expansion of Ru coordination sphere to 7 has been proposed to accommodate water as a 7th ligand and allow for PCET and catalytic activity leading to O—O bond formation [3,5]. Formation of 7-coordinated species was also implicated in water oxidation catalysis by $Ru^{II}(X)_2L$ type complexes (where H_2L is 2,2′-bipyridine-6,6′dicarboxylic acid and X can be monodentate ligand such as 4-picoline) [20,21].

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In this study we investigate claims of 7-coordinated Ru intermediate in [Ru(bpy)(tpy)I]I and the potential role of this new pathway for design of better catalysts of water oxidation. Our spectroscopic EXAFS (Extended X-ray Absorption Fine Structure) analysis has shown that in the catalytic cycle, a 7-coordinate Ru intermediate is not a major species. Instead, the $[Ru^{IV}(bpy)(tpy){=}O]^{2+}$ species was observed as catalytic steady state intermediate. Thus, the inclusion of halogen atoms in the Ru coordination sphere instead of H_2O molecules will unlikely result in a new class of catalysts with significantly improved reactivity. Our results also illustrate significantly different behavior for Ru—I and Ru—Cl bonds under appropriate conditions for water oxidation. Ru—Cl interaction is retained under strongly oxidizing conditions over the investigated period of time and the complex is not catalytically active. This observation reinforces the finding that $[Ru^{IV}(bpy)(tpy){=}O]^{2+}$ is a prerequisite of catalytic activity.

2. Experimental

2.1. Sample preparation

Throughout this study the $[Ru^{II}(bpy)(tpy)I]^{+}$ (bpy = 2,2′-bipyridine, tpy = 2,2′; 6′,2″-terpyridine) complex was used as a I^{-} salt. Note that all experiments with $[Ru^{II}(bpy)(tpy)I]I$ salt dissolved in water should be performed immediately (within 2 min) to avoid any exchange of Ru—I with water. For optimal experimentation the $[Ru^{II}(bpy)(tpy)I]I$ solution was aliquoted into small plastic tubes and frozen for further use. $[Ru^{II}(bpy)(tpy)\,H_2O]Cl_2$ is obtained by incubation of $[Ru^{II}(bpy)(tpy)Cl]Cl$ in water for 24 h. Ultrapure (Type 1) water (resistivity 18.2 MΩ cm at 25 °C, TOC 4 μg/L) was used for solutions. All samples were prepared in 0.1 M HNO_3 pH 1.0 (Catalog No. 225711 from Sigma Aldrich). Oxidant solutions were prepared fresh daily by dissolving $Ce(NH_4)_2(NO_3)_6 \cdot 4H_2O$ in 0.1 M HNO_3. A Cary 300 Bio UV–Vis spectrophotometer (Varian Inc.) was used to monitor UV–Visible spectra (5×10^{-5} M concentration). Solutions for the preparation of electron paramagnetic resonance (EPR) samples were bubbled with argon to displaced dissolved oxygen.

2.2. EPR measurements

Low-temperature X-band EPR spectra were recorded by using a Bruker EMX X-band spectrometer equipped with an X-Band CW microwave bridge. The sample temperature was maintained at 20 K, unless otherwise indicated, by the use of an Air Products LTR liquid helium cryostat. Spectrometer conditions were as follows: microwave frequency, 9.65 GHz; field modulation amplitude, 10 G at 100 kHz; microwave power, 31.70 mW. Standard EPR sample tubes were filled with sample through all of the resonator space, a septum was placed on top and sample space was evacuated to prevent oxygen condensation. Whenever relative signal intensities are discussed, measurements were conducted on the same day and under the same conditions to allow direct comparison of the signal intensities. Field calibration was checked versus a DPPH (2,2-diphenyl-1-picrylhydrazyl) standard.

2.3. Oxygen (O_2) evolution measurements

Oxygen evolution was measured with a PC-operated Clark type polarographic oxygen electrode from Oxygraph System (Hansatech Instruments Ltd.). The sample was housed within a hermetic borosilicate glass reaction vessel, thus preventing penetration of any atmospheric oxygen. Calibration was carried out by the measurements of the signal from O_2-saturated water in an open reaction vessel. Sodium dithionite, an oxygen depleting agent, was added to the water, and the drop in the signal was related to the solubility of oxygen in water at room temperature (276.26 μmol/L). The glass vessel was thoroughly washed with water and then 0.8 mL of 0.55 mM Ru solution in water was added. A defined number of Ce^{IV} equivalents (usually 20 equiv in 1 M HNO_3) were carefully added by means of a Hamilton syringe into the chamber through a plunger screw, and oxygen evolution was measured as a function of time. The dilution of Ce^{IV} solution was adjusted to 10:1 to allow for final pH = 1.

2.4. Ru K-edge X-ray absorption spectroscopy measurements

Ru K-edge XAS spectra were collected at the Advanced Photon Source (APS) at Argonne National Laboratory on the BM-20 beamline at incident photon energy 23 keV and average current of 100 mA. The radiation was monochromatized by a Si(1 1 0) crystal monochromator. The intensity of the X-rays was monitored by three ion chambers (I_0, I_1 and I_2) filled with 70% nitrogen and 30% argon and placed before the sample (I_0) and after the sample (I_1 and I_2). Ru metal was placed between the I_1 and I_2 and its absorption was recorded with each scan for energy calibration. Plastic (Lexan) EXAFS sample holders (inner dimensions of 12 mm × 3 mm × 3 mm) filled with frozen solutions were inserted into pre-cooled (20 K) cryostat. The samples were kept at 20 K in a He atmosphere at ambient pressure. Data were recorded as fluorescence excitation spectra using a Ge 13-element energy-resolving detector. Solid samples were diluted with BN powder in a 1:5 ratio, pressed between mylar tape, and measured in the cryostat in transmission mode. In order to reduce the risk of sample damage by X-ray radiation, 80% flux was used in the defocused mode (beam size 1 × 8 mm) and no damage was observed in multiple scans. The samples were also protected from the X-ray beam during motor movements by a shutter synchronized with the scan program. Additionally, low flux measurements (only 10% of beamline flux) were done on reactive intermediates to demonstrate the same EXAFS results. No more than 5 scans were taken at each sample position at any condition.

Ru XAS energy was calibrated by the first maxima in the derivative of the ruthenium metal XANES (X-ray Absorption Near Edge Structure) spectrum (22,117 eV). EXAFS scan with 10 eV steps in the pre-edge region (21,967–22,102 eV), 1-eV steps (22,102–22,117 eV) through the edge and 0.05 Å^{-1} steps from k = 2.0–16 Å^{-1} were used. As reference compounds for high Ru oxidation states, Ru^{IV} and Ru^{V}, Ru^{IV} oxide and tetra-n-propylammonium bis-2-hydroxy-2-ethylbutyrato(oxo) ruthenate(V) [22] were used.

2.5. Extended X-ray Absorption Fine Structure (EXAFS) data analysis

The Athena software was used for data processing [23]. The energy scale for each scan was normalized using a ruthenium metal standard, and scans for same samples were added. Data in energy space were pre-edge corrected, normalized, deglitched (if necessary), and background-corrected. The processed data were next converted to the photoelectron wave vector (k) space and weighted by k^3. The electron wave number is defined as $k = [2m(E - E_0)/\hbar^2]^{1/2}$, where E_0 is the energy origin or the threshold energy. The k-space data were truncated near the zero crossings (k = 3.90–15.20 Å^{-1}) before Fourier transformation. The k-space data were transferred into the Artemis Software for curve fitting. To fit the data, the Fourier peaks were isolated separately, the peaks were grouped together, or the entire (unfiltered) spectrum was used. The individual Fourier peaks were isolated by applying a Hanning window to the first and last 15% of the chosen range, leaving the middle 70% untouched. Curve fitting was performed using ab initio-calculated phases and amplitudes from the FEFF8 program from the University of Washington [24]. Ab