## Unraveling the Mechanism of Water Oxidation by Ruthenium-Oxo Complexes

Casseday Richers

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The oxidation of water to dioxygen and protons represents one half the watersplitting reaction:

 $2 H_2 O \longrightarrow O_2 + 2 H_2$ 

This reaction is important in photosynthesis, and as a possible non-hydrocarbon-based source of hydrogen gas.<sup>1</sup> Although a few catalysts are known for this reaction, relatively little is understood about the mechanism.<sup>2-4</sup> The discovery of a molecular catalyst, cis,cis- $[(bpy)_2(H_2O)Ru^{III}ORu^{III}(H_2O)(bpy)_2]^{4+}$  ([3,3]; bpy = 2,2'bipyridine) has provided a platform from which to carry out mechanistic investigations into the oxidation of water by ruthenium oxo complexes (the symbol [a,b] will refers only to the oxidation states of the two ruthenium and not to specific molecules which may vary in proton content and overall charge)..<sup>5</sup>

Crystal structures for both [3,3] and [3,4] indicate very little interaction between the two *cis*-aqua ligands. The crystal structure for [3,3] is shown in Figure 1.<sup>4</sup>



Figure 1: crystal structure for [(bpy)<sub>2</sub>(H<sub>2</sub>O)Ru<sup>III</sup>ORu<sup>III</sup>(OH<sub>2</sub>)(bpy)<sub>2</sub>]<sup>4+</sup>

Bond distances of 1.87 and 2.136 Å were observed for the Ru-( $\mu$ -O) and Ru-OH<sub>2</sub> bonds, respectively. A bridging angle of 165° was observed for the Ru-O-Ru group and a torsional angle of 66° was observed between the two *cis*-aqua ligands. The arrangement of atoms resulted in a distance of ~4.72 Å between the two *cis*-aqua oxygen atoms. The relatively short Ru-O distance for the  $\mu$ -oxo ligand indicates multiple bonding. The crystal structure for [3,4] revealed Ru-( $\mu$ -O) bond distances of 1.83 and 1.85 Å.<sup>4</sup> The bridging angle was 170° and the torsion was 117°. The distance between *cis*-aqua oxygen atoms was ~5.55 Å.

Cyclic voltammetry and pulse polarography experiments on [3,3] suggest that oxidation of the ruthenium dimer proceeds by successive one-, and two-electron

oxidations.<sup>6</sup> At pH 5, oxidation of [3,3] produces [3,4], which subsequently oxidizes to [4,5], and eventually forms [5,5]. The oxidation states of the two ruthenium atoms were assigned based on similarities observed with more stable osmium analogues and are supported by later studies.<sup>7</sup> Direct determinations of the oxidation states by coulometry could not be carried over because the higher oxidation states are unstable, presumably due to water oxidation. The [4,4] oxidation state is never observed and is predicted to be unstable at all pH values. A plot of redox potentials versus pH is given in Figure 2.



 $[3,3] \xrightarrow{-e^-} [3,4] \xrightarrow{-2e^-} [4,5] \xrightarrow{-e^-} [5,5]$ 

Figure 2: Redox Potential vs pH; Oxidation Scheme at pH = 5.

In general, the redox potentials increase with decreasing pH. At pH values less than 2.2, [4,5] becomes unstable with respect to disproportionation and the oxidation of [3,4] becomes a three-electron process.

An alternative mechanism for the oxidation of [3,3] to [5,5] is shown in Figure 3.<sup>8</sup>

$$[3,3] \xrightarrow{-e^-} [3,4] \xrightarrow{e^-} [4,4] \xrightarrow{-2e^-} [5,5]$$

## Figure 3: Oxidation Scheme proposed by Hurst and co-workers.

Evidence for the [4,4] and [5,5] oxidation state is obtained from titrations the moreoxidized dimers, with  $Os(bpy)_3^{3+}$ . Additional support for the [4,4] state comes from mixing experiments which show that only one product is formed upon mixing [3,3] and [5,5] in equal amounts (two products, [3,4] and [4,5], would be expected if [4,5] was the intermediate), and Resonance Raman spectroscopy which indicates that only one species in solution contains a Ru=O bond (both [4,5] and [5,5] are expected to contain Ru=O bonds). Discrepancies between this second oxidation pathway and the original oxidation pathway obtained by cyclic voltammetry may result from differences in reaction conditions (1M HClO<sub>4</sub> vs. 0.5M CF<sub>3</sub>SO<sub>3</sub>H). Global analysis of the spectroscopic data obtained by Meyer points to a complex mechanism involving rapid conversion of [3,3] to [3,4], slow conversion of [3,4] to [4,5], rapid conversion of [4,5] to [5,5] and rapid decomposition of [5,5], but does not provide additional information regarding water oxidation.<sup>9</sup> Rate data taken by Hurst on the decay of [5,5] indicate it is an immediate precursor to water oxidation, but does not point to a specific mechanism. The immediate product of [5,5] decay is [4,4], suggesting that hydrogen peroxide may be formed in the reaction. The decay of [5,5] is first order with respect to [5,5].<sup>12</sup> Pseudo-zero-order kinetics observed for O<sub>2</sub> production in studies by Meyer may result from annation of the catalyst during catalytic turnover.<sup>9</sup>

<sup>18</sup>O-Labeling studies performed on [3,3] suggest that more than one mechanism is responsible for O<sub>2</sub> production. <sup>10-12</sup> In the studies, unlabeled [3,3] was incubated in H<sub>2</sub><sup>18</sup>O for extended periods to effect substitution of the unlabeled aquo ligands with labeled aquo ligands. Subsequent oxidation of the labeled [3,3] with one equivalent of Ce(IV) produced labeled [3,4] which was then treated with unlabeled H<sub>2</sub>O in the presence of a slight stoichiometric excess of oxidant to produce dioxygen. Product distributions obtained by Meyer indicate that roughly 13% of the O<sub>2</sub> produced received both oxygen atoms from the ruthenium dimer (<sup>36</sup>O<sub>2</sub>), whereas 64% of the O<sub>2</sub> received one oxygen atom from the ruthenium dimer and one oxygen atom from the solvent (<sup>34</sup>O<sub>2</sub>), and 23% of the O<sub>2</sub> received both oxygen atoms from the solvent (<sup>34</sup>O<sub>2</sub>).<sup>10</sup> In comparison the product distribution obtained by Hurst was roughly 50:50 <sup>34</sup>O<sub>2</sub>:<sup>32</sup>O<sub>2</sub> with little if any <sup>36</sup>O<sub>2</sub>.<sup>11,12</sup> General pathways for the production of O<sub>2</sub> from [5,5] are presented in Figure 4.



Figure 4: General Pathways for the production of O<sub>2</sub> from [5,5]

The small amount of  ${}^{36}O_2$  produced in the labeling studies implies that coupling of two terminal oxo groups is negligible (Pathways B-D). Other mechanisms are more difficult to exclude. Nucleophilic attack by water on a Ru=O group could account for the formation of  ${}^{34}O_2$  (Pathway A). Likewise nucleophilic attack by water on a bound peroxide or ozonide, formed by prior nucleophilic attack by water on a Ru=O group, could account for the formation of  ${}^{32}O_2$  (Pathway E). An alternative mechanism for the formation of  ${}^{32}O_2$  is nucleophilic attack by water on the bipyridine ring of the catalyst, followed by ligand-to-metal charge transfer and nucleophilic attack by a second water to form a bis-hydroxo species, which could eliminate hydrogen peroxide and eventually generate water (Figure 5). Evidence for nucleophilic attack by water on coordinated bipyridine rings is supplied by Dutta and co-workers who report water oxidation by zeolite-encaged Ru(bpy)<sub>3</sub><sup>3+,13</sup> EPR data taken for [5,5] is suggestive of a ligand-based radical. In the absence of a zeolite cage, Ru(bpy)<sub>3</sub><sup>3+</sup> oxidizes bipyridine to carbon dioxide and nitrogen gas.<sup>12</sup> Mechanisms involving the formation of free radicals are energetically prohibited.



Figure 5: Nucleophilic Attack on coordinated bipyridine and elimination of H<sub>2</sub>O<sub>2</sub>

Density Functional Theory (DFT) calculations on the addition of water to Ru=O support a mechanism in which initial ligand-to-metal charge transfer from the oxo ligands to the ruthenium atoms produces a pair of oxyl radicals, which then cleave the H-OH bond in water.<sup>14</sup> Proton transfer, metal-to-metal charge transfer, and ligand-to-metal charge transfer eventually lead to a bound superoxo intermediate which undergoes intersystem crossing and ligand-to-metal charge transfer to produce triplet  $O_2$  and triplet [3,3]. Intersystem crossing and oxidation of [3,3] to [5,5] complete the catalytic cycle. Redox potentials predicted by these calculations are in fairly good agreement with experimentally determined values and lend weight to these studies. Other mechanisms were not investigated. The ground state of [5,5] is predicted to be low-spin with weakly coupled antiferromagnetic state by rotation around Ru-O-Ru bonds is expected to be facile and to immediately precede ligand-to-metal charge transfer from the oxo ligands to the ruthenium atoms. Recent reports, however, have called into question the validity of these calculations.<sup>15</sup>

Other catalysts for the oxidation of water are shown in Figure 6.<sup>16-18,3</sup> Although these catalysts may follow mechanisms similar to [3,3], mechanistic studies on them have not been performed. Additional studies are required on these and on [3,3] before a clear picture of water oxidation by ruthenium-oxo complexes emerges.



Figure 6: Ruthenium-based catalysts for water oxdiation

## References

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