

INVESTIGATING REACTIVE INTERMEDIATES FORMED IN THE $[\text{Ru}(\text{BPY})(\text{TPY})(\text{OH}_2)]^{2+}$ CATALYZED WATER OXIDATION REACTION

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In an effort to find alternative energy sources to fossil fuels, there is much interest in coupling water oxidation and CO_2 reduction reactions to create “solar fuels”. Through water oxidation, the following reaction occurs: $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 4\text{e}^- + \text{O}_2$. The de facto representative of homogenous mononuclear water oxidation catalysts is $[\text{Ru}^{II}(\text{bpy})(\text{tpy})(\text{H}_2\text{O})]^{2+}$, or more simply $[\text{Ru}^{II}\text{H}_2\text{O}]^{2+}$. For this catalyst, the rate limiting step and reaction bottleneck is the O-O bond formation step, which proceeds through a water nucleophilic attack of the electrophilic Ru=O bond. The two intermediates that can potentially undergo this water nucleophilic attack to form the O-O bond are $[\text{Ru}^{IV}=\text{O}]^{2+}$ and $[\text{Ru}^V=\text{O}]^{3+}$. Kinetic evidence and our calculations suggest that the $[\text{Ru}^{IV}=\text{O}]^{2+}$ intermediate is significantly less reactive with H_2O than the $[\text{Ru}^V=\text{O}]^{3+}$ species, which may be due to the Ru=O bond being less electrophilic in the $[\text{Ru}^{IV}=\text{O}]^{2+}$ species than the $[\text{Ru}^V=\text{O}]^{3+}$ species. Experimentally, we form these highly reactive intermediates in an octopole ion trap by introducing a buffer gas mix of O_3/O_2 to $[\text{Ru}^{II}]^{2+}$ or $[\text{Ru}^{III}]^{3+}$, and then capture them by evaporative quenching of collision complexes. This has allowed us to isolate the $[\text{Ru}^{IV}=\text{O}]^{2+}$ species and will allow us to later focus on isolating and probing $[\text{Ru}^V=\text{O}]^{3+}$ using cryogenic ion IR predissociation spectroscopy. These predissociation spectra allow us to determine the Ru=O stretching frequencies of these two intermediates, which can be confirmed through isotopically labeled ^{18}O substitution. In particular, the frequency of the Ru=O stretching mode is likely sensitive to the electronic structure of the Ru=O bond. Also, with the addition of our dual reaction traps, we will cluster water on $[\text{Ru}^{IV}=\text{O}]^{2+}$ and $[\text{Ru}^V=\text{O}]^{3+}$ in order to elucidate the water bonding orientation and arrangement, which will reveal if the water acts as a nucleophile, or if it is the Ru=O that is the electrophile in the water addition step.