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ARTICLE TYPE

## Where does the Water go? A Computational Study on the Reactivity of a Ruthenium(V) Oxo Complex (bpc)(bpy)Ru<sup>V</sup>O

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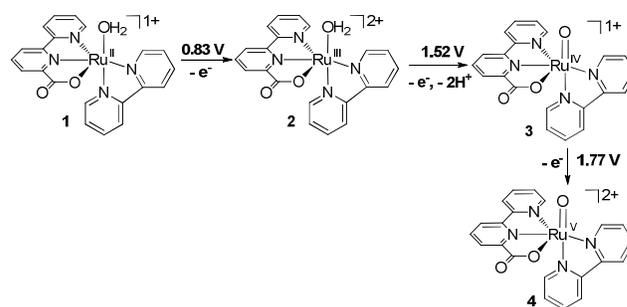
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Two possible reactive sites (the oxo site and the Ru site) for water on a high-valent ruthenium(V) oxo complex were examined. Our results suggest that the reaction on the ruthenium (via a seven coordinate intermediate) both has a lower barrier and a product with a lower free energy than the product of addition at the oxo.

Light-driven water splitting<sup>1</sup> has attracted much attention in recent years due to its potential to convert solar energy to chemical energy. This process includes two half-cell reactions: water oxidation to produce O<sub>2</sub> and proton reduction to generate H<sub>2</sub>. One of the challenges to make this process successful is the development of efficient and robust catalysts for water oxidation.<sup>2</sup>

A new family of mono-ruthenium complexes carrying anionic ligands<sup>3</sup> displays good performance for water oxidation, and some of them even show comparable performance (using Ce<sup>4+</sup> as a chemical oxidant) to the oxygen-evolving complex in photosystem II.<sup>4</sup> Creating new families of related Ru complexes by replacing or modifying the anionic ligands is a synthetically feasible way of making catalytic systems with enhanced properties. One new water oxidation catalyst **1** [(bpc)(bpy)Ru<sup>II</sup>OH<sub>2</sub>]<sup>1+</sup> that contains the tridentate mono-anionic ligand (bpc) was recently prepared by Sun and co-workers.<sup>5</sup> The incorporation of a mono-anionic ligand to the ruthenium complex gives a catalyst that was soluble in water and capable of oxidising water, which allowed for experimental studies of the mechanism. Here we list some of the findings from that study and will connect these observations to the calculated mechanism. 1) The complex was readily oxidised from Ru<sup>II</sup>-OH<sub>2</sub> to Ru<sup>IV</sup>=O by addition of two equivalents of Ce(IV). 2) Addition of another equivalent of Ce(IV) led relatively rapid oxidation to a complex that was likely Ru<sup>V</sup>=O. 3) The Ru<sup>V</sup>=O complex reacted to form another species in a reaction that had an activation free energy of 18.1 kcal/mol. The activation free energy had a large negative entropic contribution. 4) The rate of the catalytic reaction was similar to the rate for the reaction of the Ru<sup>V</sup>=O species, indicating that this reaction is rate limiting in the catalytic process. Based on previous proposals<sup>6</sup> it was proposed that the Ru<sup>V</sup>=O species reacted with water to form Ru<sup>III</sup>-OOH. However, there is no direct experimental evidence for such species in the literature and these complexes have not been fully characterised.<sup>7</sup> In theory the indirect evidence for its existence could also be consistent with other types of reaction paths. In this paper we will

investigate two different reactions at Ru<sup>V</sup>=O and we will discuss the connection with the experiments and explain why one reaction is favoured over the other.



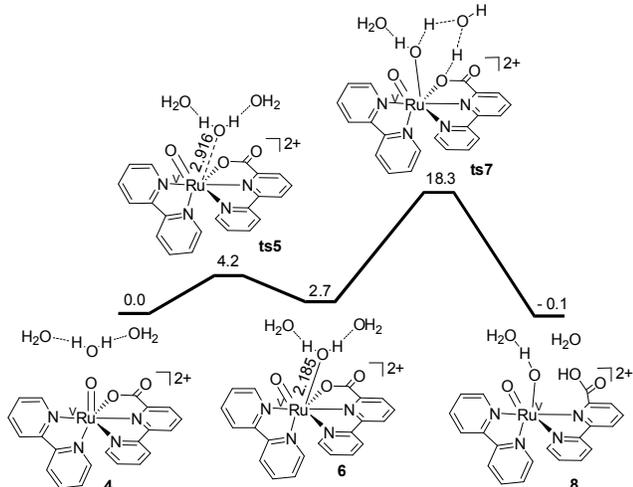
**Scheme 1.** Calculated redox potentials from **1** to **4**. All calculated potential values are referred to NHE.

Ru-aqua complexes can be oxidised to their high valent states by losing protons and electrons sequentially or simultaneously.<sup>8</sup> One electron oxidation of **1** gives **2** [(bpc)(bpy)Ru<sup>III</sup>OH<sub>2</sub>]<sup>2+</sup> at pH 0, and the reduction potential of the Ru<sup>III/II</sup> couple is calculated at 0.83 V (Scheme 1). The following oxidation from **2** to **3** [(bpc)(bpy)Ru<sup>IV</sup>=O]<sup>1+</sup> is a two-proton coupled one electron transfer process with a calculated potential of 1.52 V. The high valent **4** [(bpc)(bpy)Ru<sup>V</sup>=O]<sup>2+</sup> is generated after subsequent oxidation of **3** and the potential for this event is calculated at 1.77 V. The resulting higher oxidation state is stabilised by tridentate mono-anionic ligand.

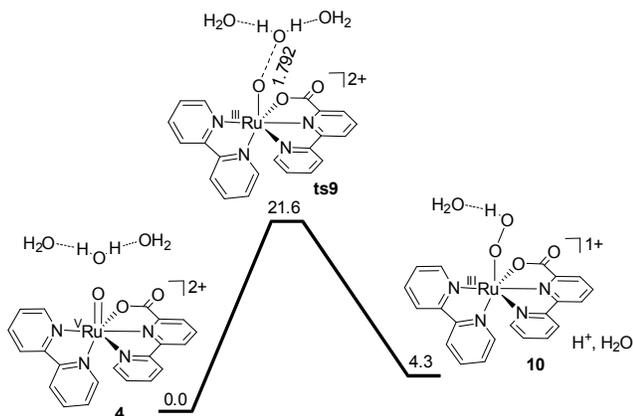
The generated active high-valent **4**, which is believed to be the reactive state of the catalyst,<sup>9</sup> can release O<sub>2</sub> by reacting with water nearby. We explored the possibilities of the different reaction between **4** and water. Since O<sub>2</sub> is observed most studies have investigated the reactions with water to give a hydroperoxide complex Ru-OOH via nucleophilic addition of water at the oxo group.<sup>10</sup> However, since seven coordinate species are known to form at oxidised ruthenium<sup>11</sup> we considered the possibility of reaction of water at the ruthenium centre rather than at the oxo ligand (Figure 1).

To investigate what occurs when a Ru<sup>V</sup>=O species such as **4** reacts as observed in experiments we looked at the reaction between **4** and water. To reproduce the solvation correctly we used three water molecules so that the reacting one is hydrogen bonded to two additional waters. Firstly we look at the reaction of water at the metal that gives the seven-coordinate complex **6**. Interestingly, this reaction is very facile with a free energy barrier

of only 4.2 kcal/mol via **ts5**. The following step is a proton transfer from the newly coordinated water to the oxygen site of the carboxylate ligand via a second water molecule along with simultaneous dissociation of the carboxylate ligand. This leads to formation of the six-coordinate **8** via **ts7** at 18.3 kcal/mol. The optimised geometries of **ts5** and **ts7** are shown in Figure 3a and 3b, respectively.

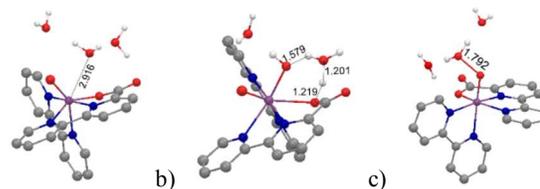


**Figure 1.** Profile of the calculated relative  $G$  for the reaction of water at the metal site of **4**. The relative Gibbs free energies are given in kcal/mol and the bond length is given in Å.

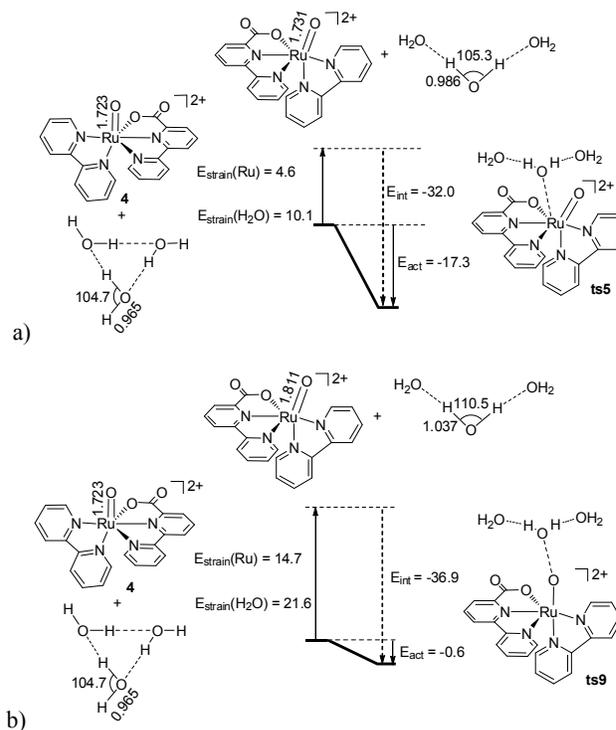


**Figure 2.** Profile of the calculated relative  $G$  for O-O bond forming reaction of water approaching at the oxo site of **4**. The relative Gibbs free energies are given in kcal/mol and the bond length is given in Å.

In most studies the disappearance of the  $\text{Ru}^{\text{V}}=\text{O}$  has been interpreted as a water nucleophilic addition on the oxo site, yielding a  $\text{Ru}^{\text{III}}-\text{OOH}$  intermediate. We therefore also studied the reaction of water attacking at the oxo group for comparison. The resulting hydroperoxo complex **10**, which contains the OO bond required for formation of  $\text{O}_2$ , is generated from the water attack at **4** accompanied with one proton transferred to the solvent. The activation free energy via **ts9** is calculated to be 21.6 kcal/mol (Figure 2). Simultaneous proton transfer avoids formation of the coordinated peroxide,  $\text{Ru}-\text{OOH}_2$ , which is usually a high-energy isomer. The optimised geometry of **ts9** is shown in Figure 3c. As for the reaction at the metal two explicit water molecules were added in the optimisation. One of the explicit water molecules acts both as a hydrogen-bond donor to the carboxylate O atom. We would also like to note that the reaction is calculated to be endergonic by 4.3 kcal/mol, indicating that it should not be observed unless an additional driving force is added to the reaction.



**Figure 3.** Optimised geometry of a) **ts5**; b) **ts7**; c) **ts9**. Hydrogen atoms except those bonding to the O atoms are omitted for clarity (Purple for Ru, blue for N, red for O, grey for C and white for H). The bond length is given in Å.



**Figure 4.** Activation strain analyses for a) The reaction of water approaching at the transition metal Ru site. b) The reaction of water approaching at O of the oxo site. All values are in kcal/mol, the bond lengths are given in Å and the bond angles are given in °.

To understand why nucleophilic addition to the  $\text{Ru}^{\text{V}}=\text{O}$  was much more favourable at the Ru site compared to the oxo site, we performed activation strain analyses<sup>12</sup> on the two transition states. The analyses of these two activation energy barriers were investigated in terms of the rigidity of the reactants and the geometrical deformation which is related to the transition state. The geometrical distortion is depicted as the destabilising strain energy  $E_{\text{strain}}$ , which means the energy associated with the difference between their equilibrium geometry of the reactants with the geometry they acquire in the transition state. The difference between the activation energy  $E_{\text{act}}$  and  $E_{\text{strain}}$  is defined as the interaction energy  $E_{\text{int}}$ , which is the actual interaction energy between the deformed reactants in the transition state. When water approaches the transition metal Ru site (Figure 4a), both the Ru-oxo  $E_{\text{strain}}(\text{Ru})$  and the water trimer  $E_{\text{strain}}(\text{H}_2\text{O})$

contribute to the total activation strain  $E_{\text{strain}}$  (14.7 kcal/mol). Merely 4.6 kcal/mol is associated with the rearrangement of the ruthenium complex indicating that bending the oxo ligand is relatively facile. The activation energy  $E_{\text{act}}$  is calculated to be -17.3 kcal/mol. The negative number may appear odd but it stems from the fact that the activation energy is related to the separated reactants in vacuum. The difference between  $E_{\text{strain}}$  and  $E_{\text{act}}$  is the interaction energy, calculated at -32.0 kcal/mol.

For the reaction of water approaching the oxo site (Figure 4b) the activation strain energy  $E_{\text{strain}}$  increased to 36.3 kcal/mol, with  $E_{\text{strain}}(\text{Ru})$  and  $E_{\text{strain}}(\text{H}_2\text{O})$  at 14.7 kcal/mol and 21.6 kcal/mol, respectively. This higher  $E_{\text{strain}}$  implies that the geometries of the reactants need to deform much more to meet the requirement of **ts9** than that of **ts5**.

In the experimental studies<sup>5</sup> a large negative entropy was measured in the activation free energy of the transition state. This finding is in agreement with a transition state such as **ts7** where one water molecule is fully bound to the Ru complex. Moreover, the free energy of activation was measured to 18.1 kcal/mol in the experiment, which is very close to the calculated free energy of activation in this report of 18.3 kcal/mol.

In conclusion, we found that the high oxidation state ruthenium oxo is a reactive intermediate, which is involved in the reaction with water. Our calculated results point towards a different reactivity to the previously proposed one. The favoured site of water nucleophilic attack is the Ru site which generates a seven-coordinate intermediate. The seven coordinate complex can then rearrange to a six-coordinate complex via proton transfer from the aqua ligand to the carboxylate ligand. Reaction at the oxo site is not only associated with a higher barrier but was also calculated to be endergonic indicating that it should not be an observable change, unless it is associated with an additional driving force. Activation strain analyses of the two water nucleophilic addition transition states showed that higher destabilising strain energy  $E_{\text{strain}}$  is required for reaction at the oxo site (**ts9**) compared to addition to the Ru site (**ts5**). Finally, we would like to point out that this finding does not exclude Ru-OOH species as intermediates. Instead we show that more possible reaction paths need to be considered when interpreting the experimental data.

## Notes and references

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<sup>†</sup> Electronic Supplementary Information (ESI) available: Figures S1 (optimised geometries), computational details, cartesian coordinates of all of the structures and all of the energy components. See DOI: 10.1039/b000000x/

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