

# Water Oxidation by Ruthenium Dimers

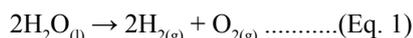
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## Introduction

Hydrogen is generally considered the best fuel for the future due to its ease of application in fuel cells and clean burning properties. This fuel could be used to replace oil as the source of electricity, heat and transportation to give us a *hydrogen economy*. This future has many issues to be overcome before it can be realized, but the most pressing is the production of this most desired gas. Currently most hydrogen is produced from fossil fuels, and offers little advantage over oil.<sup>1</sup>

Transformation of water into hydrogen and oxygen (Eq. 1) requires an energy input of about 120 kJ/mol which is equivalent to that of four 1008 nm photons. This implies that most of the energy which is incident on the earth from the sun could be capable of contributing to the production of hydrogen. Calculations that take into account energy losses from higher energy photons, and quantum efficiencies less than unity, give a theoretical efficiency of about 30% for light of wavelength 770 nm or longer, presupposing a system involving only one light absorbing unit; a system involving two light absorbing units of different energies can have a theoretical efficiency of *ca.* 41%.<sup>2</sup> Thus, an attractive system would use catalysts to produce H<sub>2</sub> and O<sub>2</sub> from H<sub>2</sub>O with sunlight driving the process. Although there are acceptable methods of catalyzing H<sub>2</sub> production, O<sub>2</sub> has received much less attention and for the process to be catalytic, it must be produced at the same time as hydrogen. In nature, the process is accomplished though the O<sub>2</sub>-evolving centre (OEC) in Photosystem II which, while not fully understood, is known to comprise of four manganese atoms driven by light absorption from a series of porphyrin arrays.<sup>3</sup> Attempts have been made to use Mn-containing complexes to mimic this system but this approach is yet to yield a complex capable of producing O<sub>2</sub> from water.<sup>4</sup> On the other hand, in 1982 one ruthenium complex, a relatively simple dimer, was found to produce O<sub>2</sub> in the presence of a strong sacrificial electron acceptor.<sup>5</sup>

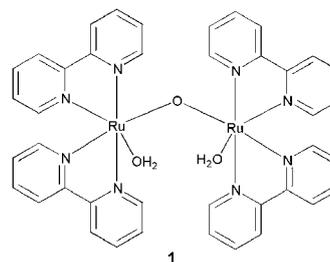


An overview of the catalyst used to decompose water and the mechanisms that could apply follows, although the work has yet to evolve to the stage of providing O<sub>2</sub> using only light energy. It focuses on the advances of the past five years and the nature of O<sub>2</sub>-producing complexes. These compounds act as the catalyst for the oxygen-producing half cell of redox equation (1), freeing protons to be used for the desired hydrogen production; the energy for the catalytic process comes from an oxidant. The oxidation state of Ru is referred to using the notation: 3.3 for Ru(III)-O-Ru(III), 4.5 for Ru(IV)-O-Ru(V), *etc.*; the mixed valance state 3.4 mostly likely is delocalised exten-

sively over the two metal atoms.



Ruthenium dimer (1) catalyses H<sub>2</sub>O decomposition when supplied with an excess of oxidising agent, typically cerium(IV) ammonium nitrate. It is isolated from the synthesis in the 3.3 state and can be oxidized with the loss of four electrons to the 5.5 complex. The final step releases O<sub>2</sub> and regenerates the starting 3.3 complex from addition of two water (solvent) molecules.<sup>6</sup> The X-ray structure of the 3.3 complex shows the coordinated H<sub>2</sub>O molecules at 90° to each other but free to rotate about the Ru-O-Ru bond.<sup>7</sup> The H<sub>2</sub>O molecules can protonate/deprotonate depending on the solvent pH in processes that are influenced by the redox states of the Ru atoms which, in turn, have a redox potential influenced by the pH of the solution. This means that for those processes in which the redox potential is pH dependent, a change in protonation must accompany the change in the redox state.



Electrochemically, the 3.3 state is oxidized to the 3.4 state by one electron.<sup>8</sup> Then follows a complex process with three possible interpretations: i) 3 x one-electron processes occurring at similar potentials, ii) a two-electron process to the 4.5 state followed closely by one-electron oxidation,<sup>7</sup> and iii) a one electron process to a 4.4 state followed by a two electron process directly to the 5.5 state.<sup>9</sup> Mixing equimolar samples of the catalyst in the 3.3 and 5.5 states produces only one compound presumed to be 4.4. Path (i) would provide a complex mixture of all three states (3.4, 4.4 and 4.5). The two electron process of path (ii) implies the intermediate 4.4 state to be unstable and to disproportionate to an equimolar mix of 3.4 and 4.5. The distinct electronic spectrum of the 3.4 compound was not detected during the experiment making path (iii) the most likely. Moreover, calculations indicate any redox process involving a 4.5 state would have to be proton-linked to give the necessary potential in the region of 1.4 V.<sup>9</sup> This is in conflict with the experimental evidence which shows the process at this voltage to be pH independent. The work is further complicated by the precipitation of a highly oxidized species as its perchlorate salt.<sup>7</sup> Stoichiometric addition of the oxidising agent has led to isolation of the reactive 3.4 state that, over the 10-30 min of the O<sub>2</sub>-producing experiment, did not undergo water ex-

change; its half-life exceeds 80 days. The key experiment used to elucidate the mechanism of the reaction employs  $^{18}\text{O}$ -enriched water. The early experiment<sup>10</sup> has now been repeated<sup>8</sup> with continuous sampling and  $\text{O}_2$ -monitoring by mass spectroscopy. The amount of  $^{18}\text{O}$ - $^{18}\text{O}$  produced solely from the  $\text{H}_2^{18}\text{O}$ -containing catalyst is negligible. In the initial stages, an approximate 1:1 ratio of  $^{16}\text{O}$ - $^{18}\text{O}$  and  $^{16}\text{O}$ - $^{16}\text{O}$  is formed.

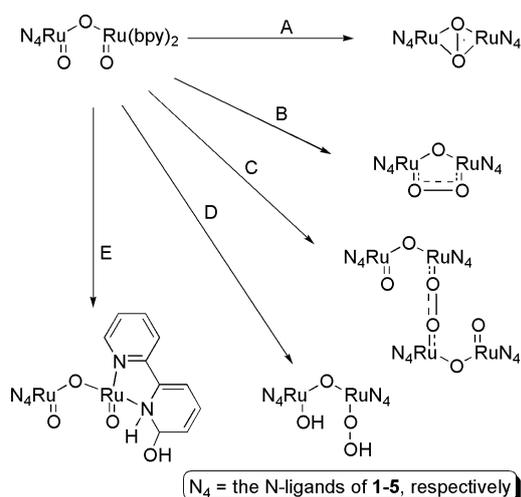
When the bipyridyl ligands of **1** are 6, 6'-disubstituted dimerization becomes impossible and the complexes fail to evolve  $\text{O}_2$  under the reaction conditions.<sup>11</sup> Thus, there is a requirement for a second ruthenium atom, or at least some motif which can reproduce its hydrogen bonding ability.

### Other catalysts

For nearly 15 years **1** was the only ruthenium complex known to catalyze *water to oxygen* although one group working in this area used the simpler  $(\text{NH}_3)_5\text{RuORu}(\text{NH}_4)\text{ORu}(\text{NH}_4)_5$ . This compound does provide  $\text{O}_2$  but it also gives  $\text{N}_2$  from the decomposition of the amine ligands. Encapsulation of the complex in plastic membranes helps to control this,<sup>12,13</sup> but the newer complexes **2-5** (Chart 1), developed over the past few years, show more promise (see below). The most important factors that relate to the catalyst are the Turnover Number (TN) (which describes catalyst stability in terms of the number of cycles the molecule can survive) and the rate of  $\text{O}_2$  production ( $k_{\text{O-O}}$ ). For bipyridyl dimer **1** the TN  $\sim 7$ -10 and the  $k_{\text{O-O}} = 2.3 \times 10^{-3} \text{ s}^{-1}$  at 25°C in 0.5 M acid with a 100 fold excess of oxidant.

The literature has recorded five pathways by which oxygen production from the fully oxidized Ru 5.5 state could occur. The final step of each is shown in Scheme 1. These are broadly classified as intra- or bi-molecular<sup>14</sup> and are shown in Scheme 1 where the stylized  $N_4$  represents each of the ligand types in **1-5**. Path A requires the bridging oxygen to bond to one of the pendant  $\text{Ru}=\text{O}$  oxygens to form a symmetrically bridged species and then expel water. Raman studies<sup>15</sup> have shown only small changes to the  $\text{Ru}-\text{O}-\text{Ru}$  stretching vibration occur during the course of the reaction and these are ascribed to oxidation state changes of the ruthenium atoms. The lack of major change in the frequency implies the moiety not to be altered during  $\text{O}_2$  production, and recent evidence from exchange of water and formation of mononuclear by-products make this pathway even less likely; isotopic labelling shows no substitution at the bridging oxygen.<sup>8</sup> Path B received much support until recently. Here, the pendant oxygens bond to give a peroxy bridge prior to rapid  $\text{O}_2$  expulsion and replacement by water. Initial isotopic labelling experiments supported this mechanism but recent more accurate results discussed below argue against it.

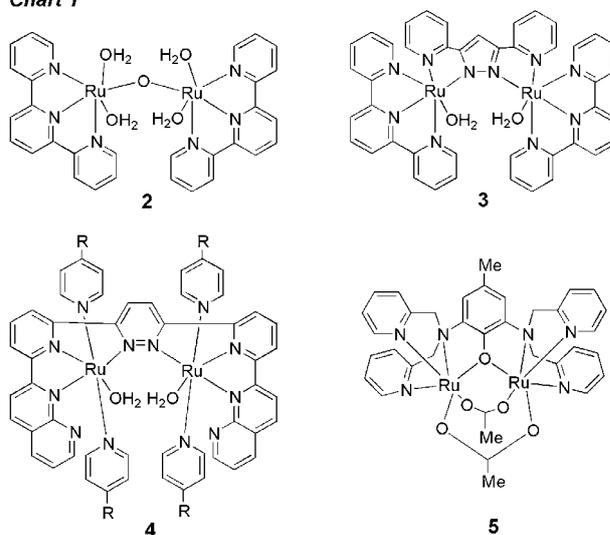
Like path B, bimolecular path C is discounted by the labelling experiments as both the oxygen atoms necessarily come from the catalyst and require the interaction of two catalyst molecules—but it does have relevance for  $\text{O}_2$  production from a mononuclear complex. Paths D and E involve radicals and have gained support in recent times. Path D equates to the original explanation for  $\text{O}_2$  formation, with  $\text{O}-\text{O}$  bond formation on one ruthenium



Scheme 1

atom by the attack of a radical  $\text{Ru}-\text{O}$  on a (solvent) water molecule. It gains strong support from DFT calculations<sup>9</sup> that provide a low energy pathway for  $\text{O}_2$  formation and a simple explanation for  $^{18}\text{O}$ - $^{16}\text{O}$  production. However, it fails to account for the  $^{16}\text{O}$ - $^{16}\text{O}$  oxygen.<sup>16</sup> Path E offers an explanation<sup>14</sup> for  $^{16}\text{O}$ - $^{16}\text{O}$  formation. Reportedly, it is possible for water to add to bipyridine coordinated to ruthenium as well as other metal complexes.<sup>17,18</sup> More than one water may be attached to the complex at any time thereby allowing for the formation of unlabelled oxygen. However, the details of this route have been called into question repeatedly, and it must be viewed with suspicion.<sup>19,20</sup>

Chart 1



Of the new catalysts **2-5**, Meyer produced analogue **2** of **1** that carries a terpyridine ligand on each Ru atom leaving two of each six coordination sites for water ligands.<sup>21</sup> Oxidation of this complex is facile but oxygen production is quantitative per mole of complex, not catalytic. This stems the formation of mononuclear complexes and the incorporation of perchlorate ions, both of which terminate the catalytic cycle. In the work of Llobet, *et al.*<sup>22,23</sup> the bridging oxygen of **2** is replaced by a bridging 3,5-dipyridylpyrazole moiety as **3**. Here the pyridines co-ordinated to provide for two water ligands as in **1**, but the stability of the complex is improved. The removal of  $\text{H}^+$  provides for favourable  $-\text{O}\cdots\text{H}-\text{O}-$  bridging. However, the stability of the complex is only modestly improved even though TN increases to 20 with  $k_{\text{O-O}}$  rising by a factor of six to  $1.4 \times 10^{-2} \text{ s}^{-1}$ .<sup>24</sup>

A more substantial structural change has come from the laboratory of Thummel<sup>25,26</sup> with the synthesis of **4**. Here the bridging unit is a pyridazine ring bonded through positions 3 and 6 to separate 2-(2-pyridyl)-1,8-naphthyridines as the critical ligands. These latter bidentate ligands are held such that they point into the cavity that holds the coordinated water and each can, through the available N atom, H-bond to water such that the latter is held in an appropriate orientation for oxygen formation. The co-ordination sphere is completed with two 4-substituted pyridines per Ru. Substituent (R) has been varied from weakly donating (-Me) to strongly withdrawing (-CF<sub>3</sub>) to elicit the effect on catalysis whereby an increased stability in **4** is reflected by TN which increases to 100 (CF<sub>3</sub>) and 3200 (CH<sub>3</sub>); the rate increases to  $k_{O-O} = 7.7 \times 10^{-2} \text{ s}^{-1}$  (**4**; R = Me). This is seen more clearly in the case of the similar mononuclear complexes. Here, the bulky ligands prevent dimer formation as demonstrated by Sauvage<sup>11</sup> for 6,6'-disubstituted derivatives of **1**. Thus there can be no requirement for one water on each of the two ruthenium atoms because pre-organization is controlled by the naphthyridine rings. Interestingly,  $k_{O-O}$  is much lower for mononuclear complexes thereby implying that there is only one pathway for O<sub>2</sub> formation rather than the two for a binuclear complex.<sup>26</sup>

The binuclear complex **5** has been prepared by Sun.<sup>27</sup> Its design follows extensive study of corresponding Mn complexes that, unfortunately, fail to produce O<sub>2</sub>. This complex again uses bridging oxygen but here it is phenolic in nature.<sup>4</sup> The ligands also differ through use of the nitrogen of an aryldialkylamino moiety that acts both as ligand and structural motif for two picoline units. The remaining two Ru vacancies are occupied by acetate as bridging ligands incorporated during synthesis. No data on O<sub>2</sub> production from **5** have been reported, but a further important step has seen incorporation of the light absorbing Ru(bipy)<sub>3</sub> unit. Preliminary electron transfer experiments indicate that this addition provides for extraction of an electron from the catalytic unit upon excitation with visible light.

## Conclusions

This brief overview indicates directions being taken in this blossoming field of research. To date, this has relied on chemical oxidants driving O<sub>2</sub>-production but it is now ready to move to the next step and use light as the energy source. When coupled with a similar hydrogen producing unit an excellent source of cheap, clean energy can be expected. As energy becomes more expensive from the demands of a higher quality of life by more people, the traditional energy sources are becoming depleted; there is a clear demand for new and more economic options. Recent resurgence in technologies for storage and usage of hydrogen suggests that H<sub>2</sub> production from water using light will revolutionize the world's energy market.

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