Chapter- IV
Mechanisms Of Water Oxidation Catalyzed By
The Cis, Cis-[\textit{bpy}\textsubscript{2} \textit{Ru(OH)}_{2}]_{2} \textit{O}^{4+} \textit{Ion.}

Introduction

The splitting of water by visible light is of great importance for the photochemical conversion and storage of solar energy. Several studies\[1,2\] have been directed toward generation of \textit{H}\textsubscript{2} from aqueous solutions containing a photosensitizer to absorb light and generate a long lived excited state that can undergo electron transfer to a relay species. The oxidation of water to molecular oxygen involves the transfer of four electrons from water to an oxidant, coupled with the release of four protons.

\[2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-\]

The water oxidation to evolve dioxygen is catalyzed at the oxygen evolving center (OEC) in photosystem II (PSII) in photosynthesis\[3\]. Despite recent development on the structural information of OEC \[4\], the mechanism of water oxidation at molecular level still remains unresolved mystery \[5-9\]. Great efforts have been devoted to develop the OEC model complexes which can be applied to artificial photosynthetic systems for the splitting of water that could be utilized in fuel cells. Such systems would solve not only the energy but also environmental problems arising from combustion of fossil fuels. However, the catalytic systems capable of evolving \textit{O}_2 from water are rare, failing to provide any important mechanistic
insight. The discovery of a molecular catalyst, cis,cis-[(bpy)$_2$(H$_2$O)Ru$_{\text{III}}$(H$_2$O)(bpy)$_2$]$^{4+}$ (bpy=2,2'-bipyridine) and other catalysts of this type [10-21] has provided a platform from which to carry out mechanistic investigations into oxidation of water by ruthenium oxo complexes.

Similarly it was found that cis,cis-[(bpy)$_2$Ru(OH$_2$)$_2$] O$_{\text{IV}}$ was a remarkably effective catalyst for water oxidation by strong oxidants[22]. This report stimulated considerable interest in the underlying chemical reaction mechanisms, which have been viewed as relevant to biological reactions involving metal dinuclear and tetranuclear μ-oxo reaction centers[23] and potentially important to development of practical devices for large scale energy utilization. However, despite subsequent intensive investigation of reactions catalyzed by this ion and related complexes of the general formula cis,cis-[L$_2$Ru(OH$_2$)$_2$]$_2$O$_{\text{n}}^{n+}$,[24, 25] the reaction mechanisms remain obscure. (In the general formula, L represents a functionalized congener of 2,2'-bipyridine or a related diimine.)
Scheme –1. Detectable Redox States of the \( \mu \)-Oxo In Ion \(^{8a}\)

\[
\begin{align*}
\{3,3\} & \xrightarrow{-1e^-} \{3,4\} \xrightarrow{-1e^-} \{4,4\} \xrightarrow{-2e^-} \{5,5\} \\
& \quad \text{or} \quad \text{O}_2 \quad \text{H}_2\text{O}_2
\end{align*}
\]

\(^a\) The reduction potentials shown are for 0.5M CF\(_3\)SO\(_3\)H and are referenced against NHE. Decay of \(\{5,5\}\) may lead to either \(\text{H}_2\text{O}_2\) or \(\text{O}_2\) as the immediate product.

In the redox titrimetric and electrochemical studies, we established that, in dilute trifluoromethanesulfonic (triflic) acid, the \([(\text{bpy})_2\text{Ru(OH}_2\text{)}]_2\text{O}^{4+}\) ion undergoes progressive one-and two-electron oxidations with equivalent loss of protons to give ultimately the corresponding \(4e^-\) - oxidized product (designated \(\{5,5\}\) in Scheme 1) containing ruthenyl oxo atoms in place of the original water molecules. The \(\{5,5\}\) ion undergoes first order decay to the \(\{4,4\}\) ion with rate parameters that approximate those for \(\text{O}_2\) formation measured under steady-state conditions,[26] showing that the \(\{5,5\}\) ion is either the \(\text{O}_2\)-evolving species or its immediate precursor. In contrast, decay of the lower oxidation states (Scheme 1) is too slow for them directly involved in \(\text{O}_2\) formation. A variety of mechanisms have been examined for this reaction that focus almost universally upon the ruthenyl group, few of them are (Scheme 2) are include reductive elimination of ruthenyl oxo atoms derived from coordinated aqua ligands \(\text{H}_2\text{O}_2\) as a reaction intermediate [27,28].

100
In the present study, we describe mass spectrometric methods that allow once to follow in real time the course of evolution of O$_2$ in the $\{5, 5\}$ ion. Using $^{18}$O isotopically enriched catalyst, we show that the isotopic distribution of O$_2$ obtained is quantitatively accountable by invoking two reaction pathways, both of which involve incorporation of solvent oxygen atoms in the reaction product. These studies eliminate from further consideration pathways that involve either (1) internal rearrangement within a single complex ion with reductive elimination of O$_2$ or (2) bimolecular reactions between two complex ions with direct O-O bond formation between their co-ordinated oxygen-containing ligands.

**Scheme 2-**

Representative Pathways for O-O hand formation involving the Diruthenyl unit of the $\{5, 5\}$ ion.

**Intramolecular-**
Bimolecular:

\[
\begin{array}{c}
L_2 \text{Ru} \equiv \text{O} \equiv \text{RuL}_2 \\
\text{O} \quad \text{O} \\
+ H_2O \\
\text{(pathway C)}
\end{array} \rightarrow 
\begin{array}{c}
L_2 \text{Ru} \equiv \text{O} \equiv \text{RuL}_2 \\
\text{O} \\
\text{OH}
\end{array}
\]

or

\[
\begin{array}{c}
L_2 \text{Ru} \equiv \text{O} \equiv \text{RuL}_2 \\
\text{O} \quad \text{O} \\
\text{(pathway D)}
\end{array} 
\]

\[L_2 \text{Ru} \equiv \text{O} \equiv \text{RuL}_2 \\
\text{O} \quad \text{O}
\]

\[L_2 \text{Ru} \equiv \text{O} \equiv \text{RuL}_2
\]

\[a\] Only key intermediates are shown.

A novel reaction mechanism is proposed that features formation of a bipyridyl ligand B cation with reaction of solvent at the site, this mechanism may have precedents in water oxidation and other ligand reactions reported for a broader range of ruthenium bipyridyl complexes[29-33].

Experimental Section

Materials

The \(\mu\)-oxo-bridged dimeric ruthenium co-ordination complex \(\text{cis},\text{cis-}[(\text{bpy})_2\text{Ru(OH}_2)_2]_2\text{O}^{14}\) was prepared as the perchlorate salt following well established synthetic procedures\(^1\) and was recrystallized repeatedly to remove minor impurities[34]. The final product was
isolated as fine dark blue crystalline needles. Concentrations of reagent solutions of the \{3,3\} ion were determined spectrophotometrically using $\varepsilon_{636} = 2.2 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$. Purity was established by spectroscopically monitoring one e\textsuperscript{−} oxidative titrations of the \{3,3\} ion in 0.5-1.0 M trifluoromethane sulphonic(triflic)acid with Ce\textsuperscript{4+}. These reactions occurred with [Ce\textsuperscript{4+}]/[\{3,3\}] stoichiometries of 1.0. Five sharp isosbestic points (at 533, 404, 340, 294 and 261 nm) were observed in the optical spectra over the course of the titration, and changes in the absorption maxima of \{3,3\} at 636 nm and \{3,4\} at 448nm were proportional to the amount of added Ce\textsuperscript{4+}. The visible isosbestic points are particularly good criteria of purity because the impurities formed during preparation absorb strongly in these regions. Reagent solutions of the complex containing \textsuperscript{18}O-isotopically enriched aqua ligands were prepared by incubating the \{3,3\} ion in 97.2% [$^{18}$O]-H\textsubscript{2}O (ICON) to which has been added sufficient triflic anhydride to give 0.5M triflic acid. Under these conditions the reaction half times for water exchange at the cis-aqua position were $t_{1/2} \approx 2\text{min.}$ for the \{3,3\} ion and $t_{1/2} > 80 \text{d}$ for the \{3,4\} ion;\textsuperscript{[31]} exchange of the bridging $\mu$-oxo atom with solvent H\textsubscript{2}O did not occur in other oxidation state\textsuperscript{[34]}. The \textsuperscript{18}O-isotopically enriched \{3,4\} ions were kept in H\textsubscript{2}\textsuperscript{18}O until immediately before their use in isotope tracer experiments which was always with in a few hours of their preparation. The final enrichments were calculated by assuming that the $^{16}$O atoms
introduced upon adding of triflic anhydride equilibrated with solvent H$_2^{16}$O during the incubation period and that the isotopic composition at the cis-aqua positions were identical to the final solvent composition. As calculated, the enrichments for these preparations were 89-91%. Solutions of the analogous complex containing $^{18}$O in the bridging position, i.e.,[(pby)$_2$ Ru ($^{18}$OH$_2$)]$_2$ $^{18}$O$^{4+}$, were prepared from cis-Ru(bpy)$_2$ Cl$_2$ in $^{18}$O -enriched H$_2$O using the same procedures as normal {3,3} ion[35].

**Analytical Methods**

The kinetics of the decay of the {5,5} ion were monitored spectrophotometrically by using a computer interfaced HP 8452 diode array instrument. For most experiments, the {5,5} ion was prepared electrochemically by using a carbon fiber columnar flew electrolysis to a potentiostat. To conserve the dimeric co-ordination complex, the electrolysis cell was modified for experiments measuring the temperature dependence of {5,5} decay. In this case a thin 5.9mm i.d. porous Vycor tube (Bioanalytical systems) filled with carbon fibers is used in place of the larger standard 8.2mm. i.d electrode, allowing preparation of the {5,5} ion at a slower flow rate. The effluent from the cell was run directly into a 1mm or 2mm optical cell and the UV-vis spectra were repetitively recorded. Oxygen evolution experiments were conducted using reaction chambers composed of 6-10 ml reservoirs.
encased with in outer glass chamber through which thermostated fluids could be circulated from a constant temperature both. In a typical run, reaction was initiated by syringe addition of 0.25ml of 0.30M Ce$^{4+}$ through a septum to 6.75 ml of acidic solutions containing 0.10 mM of the $\{3,3\}$ ion, and the response of the electrode was recorded as a function of time using a strip chart recorder. The electrode was calibrated by measuring the amplitude of the pen deflection when air originally present in the chamber was replaced by Ar. For measuring the mass distributions of gaseous formed in the reaction chamber the O$_2$ electrode was replaced by a Lucite plug in which was mounted one end of a glass capillary column. In a typical run, 0.9ml of 0.25M Ce$^{4+}$ was added to 8.1ml of 0.5M triflic acid containing 0.4 –0.8 m M of the $^{18}$O isotopically enriched complex ion prepared as described in the preceding section.

Data Analysis

To avoid complications associated with the slow secondary conversion of $\{4,4\}$ to $\{3,4\}$, decay of the $\{5,5\}$ ion was analyzed from changes in optical absorption at wave lengths corresponding to the isosbestic points of the $\{4,4\}$ and $\{3,4\}$ ions (470nm in 0.5M triflicacid/H$_2$O and 468nm in 0.5 M triflic acid/D$_2$O). At these wave lengths, the reactions exhibited first order behavior over 3 to 4 half lives. Determination of O$_2$ evolution rates required knowledge of the
head space volume in the reaction cell, which was estimated from the
difference in weight of the cell when empty and filled with water.
Variations in the effective volume for a given run were estimated to
introduce a 10-15% uncertainty in the O\textsubscript{2} rates, which were calculated
in units of n mol O\textsubscript{2} forms. Prior studies has established that these rates
were linearly dependent upon \([5,5]\). The turn over number (K\textsubscript{cat}),
which is first order rate constant, was determined by dividing the O\textsubscript{2}
formation rate by the amount of catalyst present in the cell.

Isotopic distributions of $^{32}$O\textsubscript{2}, and $^{36}$O\textsubscript{2} formed in the catalyzed
reactions were corrected for background counts by substrating the
averaged intensities at these masses for 10-20 scans immediately prior
to adding Ce\textsuperscript{4+}. The background intensity for $^{32}$O\textsubscript{2} was relatively large
because of the presence of air in the spectrometer, whereas the amount
of $^{36}$O\textsubscript{2} produced in the catalyzed reaction was exceedingly small and
did not rise appreciably above the law background intensities recorded
at this mass. The relative yields of the three isotopes in individual
scans were calculated from the background–corrected mass intensities;
plots of these data vs time were made and extrapolated to $t = 0$ to
obtain the isotope distribution from the catalyzed reaction at the start of
the reaction. This procedure corrects for the small amount of isotopic
dilution that occurs by incorporation of coordinated $^{34}$O in to the O\textsubscript{2}
product and this subsequent replacement in the Ru-coordination sphere
by $^{32}$O from the solvent. The refined data were analyzed by
recognizing that there exist three possible types of reaction pathways, defined by whether the O\textsubscript{2} formed contains zero, one or two O atoms obtained from the ruthenyl O atoms. From the estimated isotopic composition of the $^{18}$O – enriched [(pby)$_2$-Ru(O)]\textsuperscript{4+} ions used in the reaction and the known composition of the reaction solution. One can calculate the O\textsubscript{2} isotopic distribution expected for each of the types of pathways.

In practice, this evaluation made use of the following equations.

$$\%(^{32}\text{O}_2) \text{ formed} = a_1x + b_1y + c_1z$$
$$\%(^{34}\text{O}_2) \text{ formed} = a_2x + b_2y + c_2z$$

Where $x$, $y$, $z$ represent the fractional contributions of each of the pathways, $a_1$ and $a_2$ are the percent formation of $^{32}$O\textsubscript{2} and $^{34}$O\textsubscript{2} predicted for pathway $x$ under the prevailing conditions, and the pairs $b_1$, $b_2$ and $c_1$, $c_2$ are analogously defined for pathways $y$ and $z$. The simultaneous solution of these equations subject to the constraint $x+y+z=1$, gives unique values for $x$, $y$, and $z$.

**Results**

$^{18}$O-Isotopic Labeling Studies

Use of closed reaction cells configured as described in the experimental section allowed rapid repetitive determination of the mass distribution of gaseous products evolved from triflic acid
solutions containing the catalyst and the strong oxidizing Ce\textsuperscript{4+} ion. In these experiments, \([(\text{bpy})_2 \text{Ru} \text{ (OH}_2\text{)}_2 \text{O}^{4+}\) ions were isotopically enriched in their cis-aqua positions were first oxidized to their \{3,4\} oxidation state while in 18\text{O}-enriched H\text{2O} to minimize any subsequent water exchange upon addition to isotopically dilute solvent[36]. Then, following brief bubbling with He to remove air, the reaction was initiated by syringe – addition of excess Ce\textsuperscript{4+}, causing near quantitative oxidation of the catalyst to its \{5,5\} oxidation state. Throughout this procedure and during the initial stages of the reaction, headspace gases were scanned every 2.0 to 2.5 S over the range of 10-50 amu. The recorded intensities at 32, 34 and 36 amu of a typical run are displayed in figure 1a. Prior to addition of the oxidant intensities at 34 \& 36 amu levels are negligible. The intensity of 32 amu is measurable, but unchanging; It represents the background level of O\text{2} in the instrument. Upon addition of Ce\textsuperscript{4+} gas formation was observed with in the reaction cell, which was reflected in a large immediate increase in the intensities at 32 and 34 amu with a much smaller increase occurring at 36 amu.
Fig 1. Mass spectrometric analysis of evolved gases from, $\mu$-oxo ioncatalyzed water oxidation. (a) Changes in peak intensities of $O_2$ isotopes at ambient temperature following addition of Ce$^{4+}$ to give a final solution composition of 0.86 mM 89.4% ISO-enriched cis,cis-[bpy]$_2$Ru(18O)$_2$O$^{4+}$, plus 25 mM Ce$^{4+}$ in 7.8% ISO-enriched $H_2$O (0.5 M $CF_3SO_3$H). As indicated, the upper and lower solid lines refer to intensities at 32 and 36 amu, and the dashed line refers to the intensity at 34 amu. (b) The 10-50 m/z spectrum for a scan at 75 s after initiation of the reaction. Peak assignments (relative intensities) are: m/z = 14, $N^+$ (0.6); m/z = 16, $O^+$ (6.6); m/z = 17, $^{16}OH^-$ (8.3); m/z = 18, $^{16}OH_2^+$ (35.7); m/z = 20, $^{18}OH_2^+$; m/z = 28, $N_2^+$ (26.2); m/z = 32, $^{32}O_2^+$ (99.6); m/z = 34, $^{34}O_2^+$ (100); m/z = 36, $^{36}O_2^+$ (8.0); m/z = 40, Ar$^+$ (0.5); m/z = 44, CO$_2^+$ (1.3).

Control experiments were performed in which Ce$^{4+}$ was injected into identical solutions that contained no catalyst, in these cases, no increase in intensities as 32, 34 and 36 amu were detected. The mass intensity at 28 amu also underwent no significant change during the course of injecting oxidant and subsequent $O_2$ formation in the catalyzed reaction.

Borely detectable increases were observed in the mass intensity at 44 amu, which appeared to become more pronounced with time of exposure to Ce$^{4+}$ is Known in figure 1b. Collectively, these results
indicate that the observed increase in O₂ mass intensities following oxidant addition arise solely from catalyzed water oxidation, that reagent manipulations introduce no detectable adventitious air, and that oxidative degradation of the catalyst is minimal despite being exposed to a large (30- fold to 250- fold) excess of Ce⁴⁺ ion.

Table-1

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<th>[Ru₂O] (mM)</th>
<th>conditions</th>
<th>⁵²O₂</th>
<th>⁵⁴O₂</th>
<th>⁵⁶O₂</th>
<th>class i</th>
<th>class ii</th>
<th>class iii</th>
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<td>0.01</td>
<td>0.44</td>
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<td>0.01</td>
<td>0.35</td>
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<td>0.05</td>
<td>0.48</td>
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* Calculated as indicated in the Experimental Section. a For all reactions, [Ce⁴⁺] = 25 mM, [CF₃SO₃H] = 0.5 M. c Fractional yields extrapolated to t = 0. d Both O atoms from {S,S} terminal ruthenyl (Ru=O) groups. e Both O atoms from solvent H₂O. f One O atom from Ru=O and one O atom from H₂O.

Solvent Deuterium Isotope Effects

We have previously estimated the kinetics of decay of electrochemically prepared {S, S} ion using both RR and optical spectrometric detection[34]. These methods are experimentally
The coordinated H$_2$O molecules in the {3,4} oxidation state of the μ-oxo ion are strongly acidic and undergo sequential one and two H$^+$ deprotonations, that is:

\[
\begin{align*}
(bpy)_2Ru-O-Ru(bpy)_2^{5+} & \overset{-H^+}{\underset{+H^+}{\longrightarrow}} (bpy)_2Ru-O-Ru(bpy) \quad (K_{1a}) \\
OH_2 & OH_2 \\
(bpy)_2Ru-O-Ru(bpy)_2^{3+} & \overset{-H^+}{\underset{+H^+}{\longrightarrow}} (bpy)_2Ru-O-Ru(bpy) \quad (K_{2a}) \\
OH & OH
\end{align*}
\]

Gilbert et al. reported ionization constants of $pK_{1a} \approx 0.4$ and $pK_{2a} \approx 3.2$ at room temperature[22]. In 99% D$_2$O the fully protonated {3,4} ion exhibits a symmetric visible absorption band at 442 nm; a corresponding symmetric band appears at 494 nm in the conjugate base. Spectrophotometric titration with 0.05–3.47M triflic acid in D$_2$O give a value for $pK_{1a}$ (D$_2$O) $\approx 0.69$. Thus, the equilibrium isotope ratio for the first ionization constant is $k_{1a}$ (H$_2$O)/$K_{1a}$(D$_2$O) = 1.9.

![Normalized resonance Raman spectra of 1 mM {3,3} in 0.5 M CF$_3$SO$_3$H, H$_2$O (solid line), and 99.7% D$_2$O (dashed line). Spectra are the average of 10 scans with 10 s accumulation times at 647 nm. The intense band at \( \approx 370 \text{ cm}^{-1} \) is attributable to the Ru-O-Ru symmetric stretching mode (\( \nu_s(\text{Ru-O-Ru}) \))][34]. The solvent isotope-dependent shift is evident in the H$_2$O-D$_2$O difference spectrum (inset).]
challenging because in the former case, the \{5,5\} ion undergoes photo reduction in the relatively intense laser beam use to obtain the RR spectra[34] and, in the latter case, the optical spectra of the \{5,5\} and \{4,4\} ions are very similar and decay of the \{4,4\} ion to \{3,4\} is sufficiently rapid to interfere with the \{5,5\} → \{4,4\} transformation (Scheme. 1). In re investigating the \{5,5\} decay kinetics, we have obtained reproducible data by monitoring the relatively small optical changes at the isobestic points for the \{3,4\} and \{4,4\} visible bonds, which were at 470nm in H₂O and 468 nm in D₂O under the prevailing medium conditions.

As described in the experimental section, the rates of O₂ evolution were measured by using a calibrated clark electrode suspended in the head space of a closed reaction cell. Reaction was initiated by addition of a 100 fold excess Ce⁴⁺ to a 0.5 M triflic acid solution containing the \{3,3\} ions; this amount of Ce⁴⁺ is sufficient to quantitatively oxidize the complex to its \{5,5\} oxidation state. Under these conditions, initial rates of O₂ formation are linearly dependent upon the catalyst concentration[25,34]. No O₂ was detected when the catalyst was omitted from the reaction medium. First order rate constants (Kcat) were determined by dividing the measured evolution rates by amount of catalyst in solution. In H₂O containing 0.5 M triflic acid, the value obtained 23°C was kcat (H₂O) = 5.2 (±1.0) x 10⁻³ s⁻¹, giving the apparent KIE for catalyst O₂ evolution of 1.7.
The coordinated H$_2$O molecules in the {3,4} oxidation state of the μ-oxo ion are strongly acidic and undergo sequential one and two H$^+$ deprotonations, that is:

\[
\begin{align*}
(bpy)_2\text{Ru-O-Ru(bpy)}_2^{5+} \xrightarrow{+H^+} (bpy)_2\text{Ru-O-Ru(bpy)}; \quad &\xrightarrow{+H^+} (bpy)_2\text{Ru-O-Ru(bpy)}_2^{3+} \\
\text{OH}_2 & \quad \text{OH} \\
\text{OH}_2 & \quad \text{OH}
\end{align*}
\]

(\text{K}_{1a}) \quad \text{(K}_{2a})

Gilbert et al. reported ionization constants of $pK_{1a} \approx 0.4$ and $pK_{2a} \approx 3.2$ at room temperature[22]. In 99% D$_2$O the fully protonated {3,4} ion exhibits a symmetric visible absorption band at 442 nm; a corresponding symmetric band appears at 494 nm in the conjugate base. Spectrophotometric titration with 0.05–3.47M triflic acid in D$_2$O give a value for $pK_{1a}$ (D$_2$O) $\approx 0.69$. Thus, the equilibrium isotope ratio for the first ionization constant is $K_{1a}$ (H$_2$O)/$K_{1a}$(D$_2$O) = 1.9.

![Normalized resonance Raman spectra of 1 mM {3,3} in 0.5 M CF$_3$SO$_2$H, H$_2$O (solid line), and 99.7% D$_2$O (dashed line). Spectra are the average of 10 scans with 10 s accumulation times at 647 nm. The intense band at \sim 370 cm$^{-1}$ is attributable to the Ru-O-Ru symmetric stretching mode ($\nu_2$ (Ru-O-Ru)) [34]. The solvent isotope-dependent shift is evident in the H$_2$O-D$_2$O difference spectrum (inset).](image)
The symmetric stretching frequency (vs) of the bridging Ru–O–Ru unit in the {3,3} and {3,4} ions appeared at slightly lower energies ($\nu = 2-5 \text{ cm}^{-1}$) in room temperature RR spectra of acidic D$_2$O solutions than in the corresponding spectra in H$_2$O. Representative spectra are given in figure 2. These results are very similar to data reported earlier on frozen solutions at 90K[35].

**Temperature Dependence of O$_2$ Evolution and {5,5} Decay**

The values for $k_{cat}$ increased progressively with temperature from 3.7x10$^{-3}$ s$^{-1}$ to 4.5 x 10$^{-2}$ s$^{-1}$ over the temperature range of 10-60°C. A plot of ln($k_{cat}/T$) vs $T^{-1}$ (Figure 3) was nearly linear and gave $\rho H^\pm = 7.6 \pm 1.2 \text{ k cal/mol}$ and $\rho S^\pm = -43(\pm 4) \text{ cal/mol}$ (23°C) as apparent activation parameters. Direct optical spectrophotometric measurement of the decay of electrochemically prepared {5,5} to {4,4} over the temperature range of 13 - 41°C gave similar value’s of $\rho H^\pm=7.9 \pm 1.1$ k cal/mol and $\rho S^\pm = -44 \pm 4 \text{ cal/mol}$. 

![Fig 3. Temperature dependence of first-order rate constants for O$_2$ evolution (■) and {5,5} decay (□). Conditions: 100 μM {3,3} plus 11 mM Ce$^{4+}$(O$_2$ evolution) or 0.25 mM {5,5} (decay) in 0.5M CF$_3$SO$_3$H: Solid lines are linear least-squares fits to the data.](image)
Fig 4. Normalized resonance Raman spectra of 0.18 mM \{3,4\} in 0.5 M CF$_3$SO$_2$H. Spectra re averages of 10 6-s accumulations taken with 40 mW excitation at 488 nm. Solid lines: spectra of \{3,4\} containing $^{18}$O in the $\mu$-oxo bridge before and after complete reaction with 7.2 mM Ce$^{4+}$; dashed line: spectra of \{3,4\} containing $^{16}$O in the $\mu$-oxo bridge. The intense $^{18}$O-isotope dependent band at \~390 cm$^{-1}$ is attributable to ($v_3$(Ru-O-Ru)), and the weaker band at \~780 cm$^{-1}$ is attributable to its first overtone (2$v_3$(Ru-O-Ru)). The inset shows the $^{18}$O-$^{16}$O difference spectrum (solid line) and the difference spectrum obtained for the $^{18}$O-substituted ion before and after 10 cycles of the catalyst (dashed line).

Discussion

Relative Contributions of the Path Ways

The mechanistic model used here to analyse the measured isotopic distributions of O$_2$ is predicted upon the assumption that exchange does not occur in the $\mu$-oxo bridge during catalytic turnover. We have established this point in previous studies by examining the position of the prominent Ru-O–Ru symmetric stretching mode ($v_3$(Ru–O–Ru)) in the RR spectrum of the \{3,4\} ion [25,34].

As shown in figure-4, this band appears at 389 cm$^{-1}$ in the solution spectra when the bridge contains $^{16}$O and at 382 cm$^{-1}$ when the
bridge contains $^{18}$O the large $^{18}$O-$^{16}$O difference spectrum provides a sensitive measure of isotopic substitution at that position. However, no difference peaks appear in the spectra of the \{3,4\} ion recorded before and after $>$10 catalytic cycles of water oxidation using either Ce$^{3+}$ or Ce$^{4+}$ as oxidants (figure-4) [25,34]. This clearly demonstrates the absence of O substitution with in the bridge following repetitive cycling of the catalyst, not only justifying the analytical model but also allowing one to eliminate from consideration path ways such as those shown in scheme 2, pathway B, that involve formation of symmetric di-\(\mu\)-oxo bridge intermediates with in a single complex ion[37]. Specifically, if this were the mechanism, one would predict substantial substitution with in the bridge after only a single turn over. These experiments do not exclude similar di-\(\mu\)-oxo-bridged intermediates that might be formed by bridging between terminal cis-oxo ligands of two complex ions.

Listed in Table 1 are the result of calculations that allow one to distinguish between three classes of reaction pathway based upon the molecular origins of O atoms in the O$_2$ products, namely; (i) both atoms derived from the ruthenyl oxo atoms, (ii) both atoms derived from solvent H$_2$O, or (iii) one atom from each source. The results of these calculations (Table-1). Clearly indicate that contribution of pathways of class I are negligible under all reaction conditions investigated. The small amount of $^{36}$O$_2$ that is formed is attributable
almost entirely to reaction between [(bpy)$_2$ Ru ($^{18}$O)]$_2$O$^{+4}$ and H$_2$$^{18}$O by class iii pathways. Consequently, it can be concluded that all unimolecular and bimolecular reactions that involve direct O-O bond formation between cis-ruthenyl oxygen are negligible and can be excluded from further consideration. This includes pathways A,B and D shown in scheme 2. Further more, relative contributions of the other two pathways are large and demonstrably temperature dependent in O$_2$ formation that acts by at least two distinct mechanisms[38]. These results are totally consistent with earlier data reported for reactions of the same complex ion with Ce$^{+3}$ in ambient temperature[25].

**Temperature Dependence and Reaction Models**

The existence of at least two reaction pathways is suggested from the temperature dependence of the O$_2$ isotopic distributions (Table-1). In contrast, Eyring plots for catalyzed rates of O$_2$ evolutions and {5,5} decay are linear with in experimental uncertainty (Figure–3). This temperature dependence is consistent with two simple reaction models, in which either a common intermediate is formed in the rate limiting step or there are two independent concurrent pathways for reaction between {5,5} and solvent whose activation enthalpies (pH$^+$) are fortuitously similar (Scheme-3). For the former model, the relative yields of isotopic products are governed by the rates of decomposition of the intermediate by the two pathways, but the overall rates of O$_2$
formation and \{5,5\} decay are independent of the intermediate partitions. For the latter model, the observed temperature dependence of the isotopic yields should also appear in the overall rate of \(O_2\) formation, which is equal to the sum of the decay rates by the various pathways.

**Scheme- 3.**

Kinetic Models for First-Order Decay of the \{5,5\} ion.

\[
\begin{align*}
\{5,5\} & \xrightarrow{\text{slow}} [\text{int}] \\
& \quad \xrightarrow{k_{\text{cat}}} 3^2O_2 \\
& \quad \xrightarrow{k_{\text{ii}}} 2H_2O \\
& \quad \xrightarrow{k_{\text{iii}}} H_2O \\
& \quad \xrightarrow{k_{\text{iii}}} ^34O_2
\end{align*}
\]

**Scheme- 4.**

Hypothetical Intermediates for O-O Bond Formation by the \(K_{\text{iii}}\) Pathway

**Reaction Mechanisms Class iii Pathway**

We have previously suggested that the pathway involves nucleophilic attack of \(H_2O\) upon an electrophilic ruthenyl \(O\) atom, as illustrated by the structure in scheme 4. Hydrogen bonding to the
adjacent bridging O atom may facilitate O-O bond formation both by properly orienting and increasing the nucleophilicity of the water molecule. The solvent dependence of ν$_s$(Ru-O-Ru) in the {3,3} and {3,4} ions (Figure –3) provides indirect evidence for this type of interaction. Although the D$_2$O induced shifts are small. They are comparable to shifts measured in biological M-O-M centers, where H-bonding to the μ-oxo bridge has been confirmed by X-ray crystallography [39].

Experimental data obtained for oxidations of O-H and C-H bonds in peroxides,[40] hydroquinones[41], alcohols,[42,43] and arenes [44,45] by monomeric ruthenyl polypyridyl compounds (e.g., [(bpy)$_2$(py)Ru$^{IV}$O]$^{2+}$) strongly suggest that these reactions proceed by hydride[43] or hydrogen atom abstraction mechanisms. The unusually strong O-H bond in H$_2$O poses severe energetic constraints of these types of mechanisms for water oxidation by the {5,5} ion. If a similar mechanism is operative, then H-atom abstraction also be coupled to formation of a peroxo O-O bond because intermediary formation of a discrete hydroxyl radical, even if H bonded to the μ-oxo atom, is energetically prohibitive. Direct formation of a peroxo bound {4,4} ion by a concerted mechanism such as that shown in scheme-4 may also be slightly endergonic, From the relevant two electron potentials, one calculates E$^o$=−0.19V for the reaction, {5,5} +2H$_2$O$^\gamma$({4,4}) + H$_2$O$_2$; the analogous reaction to form a peroxo anion to stabilized by co-
ordination to a highly charged ruthenium center in the \{4, 4\} ion should have similar thermodynamic values. The thermodynamic driving force for the overall reaction, \(2\{5,5\} + 2H_2O \rightarrow 2\{4,4\} + O_2\), is large, with \(\rho E^\circ = 0.71\text{V}\); For this mechanism, the overall reaction would therefore be driven to completion by the highly exergonic reaction between the intermediate or \(H_2O_2\) and an additional \{5,5\} ion.

A more serious mechanistic issue arises from the absence of an appreciable KIE when the reactions were run in D_2O. On basis of the nature of the postulated reaction intermediate, one would expect relatively large KIEs resulting from substantial stretching of the O-H bond in the transition state if the reaction involved rate limiting bimolecular interaction between \(H_2O\) and the \{5,5\} ion. Indeed, one characteristic feature of the oxidation reactions of the monomeric ruthenyl analogous. The very small change in the \(^{32}O_2 / ^{34}O_2\) distribution measured in D_2O under these conditions (Table -1) indicates that the pathways leading to formation of each of these products have similar KIE’s. If the reaction between solvent and \{5,5\} is direct (Scheme-3) it follows from the fact that the overall rate of \(O_2\) formation is the sum of the concurrent pathways that neither pathway can have a large KIE. For this reaction model, one calculates from the data (Table-1) that KIE \(\approx 2.0\) for the class iii pathway and KIE \(\approx 1.1\) for the class ii pathway. If the reaction proceeds by rate limiting formation of a common intermediate, one can calculate from the
solvent isotopic dependence on the $^{32}\text{O}_2^{34}\text{O}_2$ distribution only that the two pathways for $\text{O}_2$ formation have very similar KIE's.

The intensity of this cryogenic signal is proportional to the \{5,5\} concentration. Although the signal is as yet unidentified, its spectroscopic features are consistent with those expected for a ligand radical cation \[^{[47]}\], suggesting the possible existence of an intramolecular redox equilibrium of the type.

$$
\text{H}^+ + \{5,5\} \Delta [(\text{bpy})(\text{bpy} \text{B}^{2+})\text{Ru}^\text{IV}(\text{OH})-\text{O-Ru}^\text{V}(\text{O})(\text{bpy})_2]^{5+}
$$

in which the \{5,5\} ion is predominant species. The B cation radical is presumably stabilized by protonation of the proximal terminal ruthenium oxygen and by the $-\text{O-Ru}^\text{V}(\text{O})(\text{bpy})_2$ unit which, at least in lower oxidation states, appears by several criteria\[^{[48,49]}\] to be strongly $\sigma$ donating relative to simple monomeric $(\text{bpy})_2\text{RuX}_2$ analogues and might thereby significantly lower the HOMO of Coordinated bipyridine. The "pushpull" asymmetry generated by electronic redistribution with in this complex could enhance reactivity by strengthening the H-bond between the $\mu$-oxo atom and the reacting solvent molecule (Scheme-3), thereby increasing its nucleophilicity without proportionately decreasing the electrophilicity of an adjacent Ru\textsuperscript{V} terminal oxo atom.
Class ii Pathway

The existence of a pathway by which O₂ is formed catalytically by two solvent molecules was already evident from earlier ¹⁸O-labeling experiments [35]. Devising a plausible mechanism to account for this reaction, however, has been challenging. This task is not diminished by the recognition from this (Figure-1) and other recent studies [36] that the catalyst does not undergo aqua ligand exchange with solvent during catalysis.

It has been previously suggested[35] that reactive intermediate with hydroperoxide anions bound to each of the Ru atoms might form, for example, by addition of a second H₂O molecule to the covalent hydrate in Scheme-3 to give a {3,3}-dihydroperoxy complex, as in, for example

\[
[(\text{bpy})_2\text{Ru(\text{OOH})O Ru(OH)(pby)}_2]^{4+} + \text{H}_2\text{O}
\]

\[
\text{[(bpy)}_2\text{Ru(\text{OOH})}_2\text{]}^{2+} + 2\text{H}^+
\]

Subsequent intramolecular rearrangement to yield O₂ or H₂O₂ might proceed via a bridging tetroxide intermediate.

These intermediates are plausible in the sense that H₂O₃ is well established chemical entity[50,51] and the experiment evidence also exists for the formation of hydrogen tetroxide (H₂O₄);[50] the hypothetical oxo-polyoxo dibridged intermediates represent ruthenium coordinated analogues of the hydrogen polyoxides. Both polyoxides are unstable; unimolecular decomposition of H₂O₃ given O₂ (¹p) as a
product and oxidized water species are also produced upon decomposition of the less well characterized H₂O₄. Examination of structural models suggests that there are no large stearic restrictions to formation of mixed dibridged complexes of the catalyst containing the analogous dianions. However, reactions involving formation of either intermediate may be untenable on energetic grounds [34]. Specifically, the reaction \( \{4,4\} + H₂O₂ + H₂O \gamma \{3,3\} + H₂O₃ \) can be used as a rough guide for the energetics of the reaction.

\[
\frac{[(bpy)_2Ru(OOH)ORu(OH)(bpy)_2]^4}{\text{4}} \rightarrow \frac{[((bpy)_2Ru_2)(\mu-O) (\mu-1,3-O_3)]^{1+2} + 2H^+}{\text{12}}
\]

On the basis of a recent estimate for the enthalpy of formation for H₂O₃ of \( \rho H^\circ = -23 \text{ kcal/mol} [51] \), with the assumption that entropy contributions approximately cancel, one calculates \( \rho E^\circ \sim -0.7 \text{ V} \) for the former reaction. Similarly, one obtains \( \rho E^\circ \sim -0.5 \text{ V} \) as an estimate of the energetics of reaction 1 using previously determined redox potentials[34] for the reaction \( \{4,4\} + 2H₂O\gamma \{3,3\} + H₂O₂ \). Formation of both dibridged intermediates should be considerably less favorable than these estimates because in both cases they require release of protons to the highly acidic medium and are accompanied by reduction of the over all electrostatic charge on the complex from +4 to +2. there by decreasing coordinate bond stabilization.

In these studies, no low energy pathways involving nucleophilic attack of the O atom of a water molecule on the central O atom of
H$_2$O$_3$ have been identified. If analogous mechanisms are applied to
decomposition of the hypothetical \(((\text{bpy})_2\text{Ru})(\mu-\text{O})(\mu-1,3-\text{O}_3))^{2+}\)
intermediate, $^{34}$O$_2$, rather than $^{32}$O$_2$, would be the isotopic product of
the $^{18}$O-labeled ruthenium complexes. Thus, these putative law energy
pathways cannot account for the appearance of $^{32}$O$_2$ in the product
gases (Figure-1). The activation barrier for reaction 1 must also be
relatively high because the reactant ruthenium complex contains no
ruthenyl group to initiates H-atom abstraction from H$_2$O. Furthermore,
it Is difficult to rationalize by this type of mechanism why monomeric
analogues of the type, cis-L$_2$ Ru (OH)$_2^{2+}$, and dinuclear ions not
containing the (H$_2$O)RuORu(OH)$_2$ core, for example, [(bpy)$_2$(py)
RuORu (H$_2$O(bpy)$_2$)$_{4+}$, appear incapable of catalyzing water oxidation.

A bipyridine ligand based mechanism for class (ii) water
oxidation by \{5,5\} that incorporates key features of the Ru (bpy)$_3^{3+}$
reactions is given in scheme 1. The reaction is initiated by additions of
the elements of water to form a covalent hydrate in which OH$^-$ is added
to a bipyridine ligand and H$^+$ protonates a terminal ruthenyl O atom.
This reaction would also be considerably facilitated by internal
electronic rearrangement that generated a \{4,5\}-pby$^{0+}$ radical cation.
Alternatively, covalent hydrate formation might be promoted by H-
atom abstraction at a Ru=O center in a concerted reaction similar to
that proposed for the class iii reaction (scheme-4) In this case, the OH
segment is positioned to add to the ring six-position to form a\{4,5\}
intermediate containing a neutral ligand radical (Scheme 5). In this manner, the reaction could avoid intermediary formation of the \{4,5\}bpy$^{0+}$ radical cation. The neutral radical also represents an alternative candidate for the cryogenic EPR signal detected in frozen solutions of the \{5,5\} ion.[25,35]

**Scheme-5.**

Hypothetical Intermediate for O-O Bond Formation by the $k_{ii}$ Pathway

![Scheme diagram](image)

Specifically, internal ligand ligand-to-metal electron transfer could be fairly slow, as has been demonstrated for the [(NH$_3$)$_3$Copy-OH$^{+}$]$^{3+}$ radical adduct,[52, 53] allowing accumulation of the ligand radical to EPR detectable level during catalyst turn over. Subsequent addition of a second H$_2$O molecule to a modified bipyridine ring to form a \{4,4\}-coordinated bipyridine diol (Scheme-5) is suggested by
analogy to similar reactions proposed in the overall reactions between Ru (pby)$_3$$^{3+}$ and OH$^-$ that lead to ligand decomposition [30].

This reaction would be facilitated in the dinuclear μ-oxo ion by the pendant [(bpy)$_2$Ru(=O)O]$^+$ moiety, which can function as an electron sink for the unpaired electron. Unlike monomeric Ru$^{11}$[bpy)$_2$-(bpy(OH)$_2$)$_2$$^{+2}$ analogues, the bipyridine dial in the dinuclear ion is coordinated to a two-electron oxidizing center which is nearly as strongly oxidizing as the original {5,5} ion.

**Additional Comments**

The mechanism presented here is a minimal scheme that best accommodates the existing data and is subject to refinement as detectable intermediates become better characterized. For example, the rate constants for first order decay of {5,5} measured by optical spectroscopy vary by as much as 4-fold under different experimental conditions[34], which might ultimately be attributable to the appearance of strongly absorbing intermediate. Furthermore, the mass spectral kinetic profiles obtained immediately following addition of Ce$^{+4}$ suggest that there is a very short induction period prior to formation of $^{32}$O$_2$ that is not observed for $^{34}$O$_2$. This behavior is consistent with accumulation of a reactive intermediate in the class ii pathway that is not required for the class iii pathway, a circumstance that would require expansion of the simple mechanisms given in
Scheme-4. Similarly, the increase in $^{34}\text{O}_2 / ^{32}\text{O}_2$ ratio observed at the highest \{5,5\} concentration (Table-1, data for 28°C) might be indicative of minor contribution from a bimolecular pathway involving, For instance, reaction between an intermediate species and \{5,5\}. Identification of the anomalous signal in the low temperature EPR spectra of the complexes, currently in progress, is expected to elucidate many of these mechanistic issues.
References


38. It is perhaps useful to note that these conclusions were already evident from the raw data, that is, before the analyses described in the Experimental Section were performed. Since the complex was~90% enriched in cis-[¹⁸O]H₂O and the solvent typically contained <3% [¹⁸O]H₂O, the measured relative yields of ³⁶O₂ and ³⁴O₂ must reflect fairly closely the relative contributions of pathways I-iii, respectively.


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