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Formic Acid Acting as an Efficient Oxygen Scavenger in Four-Electron Reduction of Oxygen Catalyzed by a Heterodinuclear Iridium−Ruthenium Complex in Water

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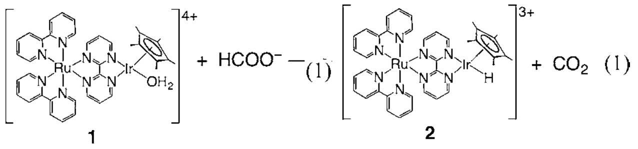
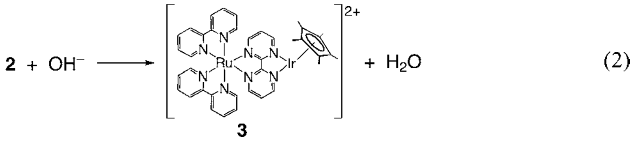
Abstract: A heterodinuclear iridium−ruthenium complex $[Ir^{III}(Cp^*)(H_2O)(bpm)Ru^{II}(bpy)_2](SO_4)_2$ ($Cp^* = \eta^5$-pentamethylcyclopentadienyl, bpm = 2,2′-bipyrimidine, bpy = 2,2′-bipyridine) acts as an effective catalyst for removal of dissolved O_2 by the four-electron reduction of O_2 with formic acid in water at an ambient temperature.

Oxygen (O_2) dissolved in water is known to cause the corrosion of components in a large variety of systems.[1] Thus, extensive efforts have been devoted to develop methods to substantially reduce the oxygen content in water.[2−5] Although the principles of vacuum degasification and thermal deaeration are simple, these methods require a lot of energy for operation. Alternatively, dissolved O_2 can be removed by reduction with hydrazine and hydrogen.[2−5] However, the reductive removal of oxygen requires a highly active catalyst to obtain a sufficient reduction rate for the removal of dissolved O_2 in water at an ambient temperature, because it is practically impossible to enhance the reduction rate by heating the vast amount of water.[2−5] There has so far been no report on an efficient water-soluble catalyst to remove dissolved O_2 in water by an appropriate reductant at an ambient temperature.

We report herein a heterodinuclear iridium−ruthenium complex $[Ir^{III}(Cp^*)(H_2O)(bpm)Ru^{II}(bpy)_2](SO_4)_2$ (**1**, $Cp^* = \eta^5$-pentamethylcyclopentadienyl, bpm = 2,2′-bipyrimidine, bpy = 2,2′-bipyridine) acting as an effective catalyst for removal of dissolved O_2 by the four-electron reduction of O_2 with formic acid in water at an ambient temperature. This is followed by the catalytic decomposition of formic acid to hydrogen and CO_2.[6] The catalytic mechanism of the four-electron reduction of oxygen with formic acid is examined by monitoring the reaction intermediates. The present method provides a convenient way to remove dissolved O_2 in water completely at an ambient temperature.

The catalyst **1** was synthesized by a reaction of $[Ru^{II}(bpy)_2(bpm)](SO_4)$ with $[Ir^{III}(Cp^*)(H_2O)_3](SO_4)$ in H_2O at 298 K as reported previously.[6] When 1 equiv of **1** was added to a deaerated aqueous solution of HCOOH at pH 5.2, where HCOOH is deprotonated to form $HCOO^-$ ($pK_a = 3.8$), **1** reacts with $HCOO^-$ to afford the hydride complex $[Ir^{III}(Cp^*)(H)(bpm)Ru^{II}(bpy)_2]^{3+}$ (**2**) and CO_2 (eq 1).[6] The hydride complex **2** is deprotonated at pH 5.2 to afford the Ir^I complex $[Ir^I(Cp^*)(bpm)Ru^{II}(bpy)_2]^{2+}$ (**3**) (eq 2), because the pK_a value (3.9) is much lower than pH 5.2.[6] Both **2** and **3** were well characterized by the ^1H NMR spectra.[6]





The Ir^I complex (**3**) reacts efficiently with O_2 as shown by the spectral titration in Figure 1, where the absorption spectra due to **3** are changed to those of **1**. The titration curve in the inset of Figure 1 indicates that **3** reacts with 0.5 equiv of O_2 to produce **1**. Thus, the four-electron reduction of O_2 by **2** occurs efficiently to produce **1** (eq 3).

$$\mathbf{3} + 1/2\ O_2 + 2H^+ \rightarrow \mathbf{1} \tag{3}$$

The time profile of the reaction of **3** with O_2 was monitored by a stopped flow technique. During the conversion from **3** to **1**, two reaction intermediates were observed as transient absorption spectra as shown in Figure 2. First, **3** (red: $\lambda_{max} = 512$ nm) is converted to an intermediate **A** (blue: $\lambda_{max} = 420$ and 540 nm) at 0.05 s, and then **A** is changed to another intermediate **B** (green: $\lambda_{min} = 410$ and 590 nm) at 2.3 s. **B** is slowly changed to **1**, which corresponds to the black line that is the difference spectrum obtained by subtracting the final spectrum (red line in Figure 1) from the spectrum observed at 10 s. In such a case, **B** is observed as a negative absorption spectrum (green) in Figure 2.

The rate of the first step to produce **A** is too fast to determine the accurate rate of the reaction of **3** with O_2 even at low temperature (e.g., 275 K). The rate of the second step to produce **B** remains unchanged irrespective of pH (> 4.2) (see Supporting Information Figure S1). The rate of the final step to produce **1** increases with increasing concentration of $HCOO^-$ (Figure S2).

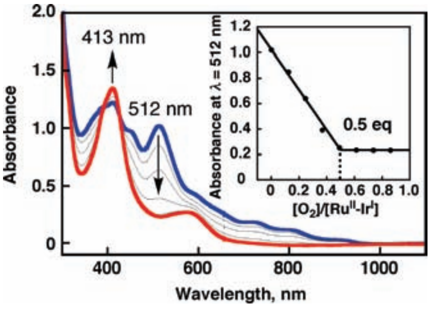


Figure 1. UV−vis−NIR absorption spectral changes in the reaction of **3** with various concentrations of O_2 in H_2O (pH 5.2) at 298 K. **3** is produced by the reaction of **1** (1.0 mM) with HCOOH/HCOONa (1.0 mM). Inset: Plot of absorbance at $\lambda = 512$ nm due to **3** vs the ratio of $[O_2]/[\mathbf{3}]$.

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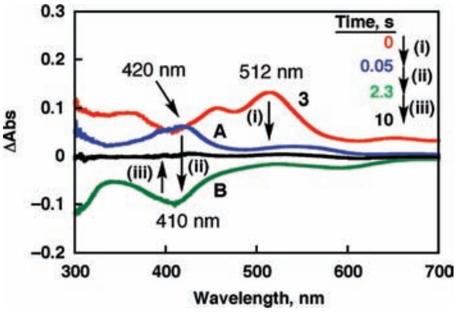
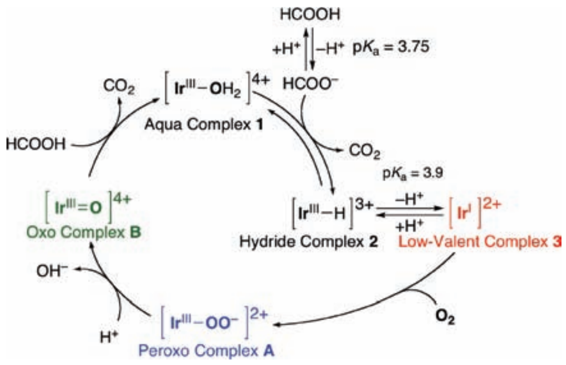


Figure 2. UV−vis difference absorption spectral changes observed in the reduction of O_2 (0.13 mM) by **3** (red line, 0.10 mM) in the presence of HCOOH/HCOONa (0.10 M) in H_2O at pH 5.2 at 298 K.

Scheme 1



Judging from such kinetic behaviors of the intermediates, three well-resolved steps for the reaction of **3** with O_2 are proposed as given by eqs 4−6. First, **3** reacts with O_2 to give the peroxo complex (**A**) (eq 4). The O−O bond of the peroxo complex (**A**) is heterolytically cleaved to produce the Ir(V)-oxo complex (**B**) irrespective of the concentration of H^+ at a pH higher than 4.2 (eq 5). **B** reacts with $HCOO^-$ to yield **1** and CO_2 (eq 6). The formation of an iridium-peroxo complex by the reaction of a low-valent iridium complex with O_2 has previously been reported.[7] The formation of an iridium(V)-oxo complex with cleavage of the O−O bond of an iridium(III)-peroxo complex has also been reported.[8] In addition, the observed spectrum (green line in Figure 2) agrees with the authentic spectrum of an iridium(V)-oxo complex (**B**) (λ_{min} = 410 nm, 590 nm) generated by the addition of peracetic acid ($CH_3C(O)OOH$) to a water solution of complex **1** (Figure S3).

$$[\mathbf{Ir}^{I}]^{2+}(\mathbf{3}) + O_2 \rightarrow [\mathbf{Ir}^{III}{-}OO^-]^{2+}(\mathbf{A}) \tag{4}$$

$$[\mathbf{Ir}^{III}{-}OO^-]^{2+} + H^+ \rightarrow [\mathbf{Ir}^{V}{=}O_2]^{4+}(\mathbf{B}) + OH^- \tag{5}$$

$$[\mathbf{Ir}^{V}{=}O]^{4+} + HCOOH \rightarrow [\mathbf{Ir}^{III}{-}OH_2]^{4+}(\mathbf{1}) + \mathbf{CO_2} \tag{6}$$

Based on the above results, the overall catalytic cycle of the four-electron reduction of O_2 by $HCOO^-$ with **1** is shown in Scheme 1. The hydride complex **2**, which is produced by the reaction of **1** with $HCOO^-$ (eq 1), deprotonates to generate the low-valent complex **3**. The Ir^I complex **3** reacts with O_2 to produce the iridium(V)-oxo complex (**B**) and water via formation of the iridium(III)-peroxo complex (**A**). The oxo complex (**B**) reacts with HCOOH to reproduce **1**.

The catalytic four-electron reduction of O_2 with formic acid proceeds during an induction period observed for the hydrogen evolution reaction in the decomposition of formic acid catalyzed by **1** in aerated water as shown in Figure 3 (●). When O_2 in water was completely removed by freeze−pump−thaw cycles (5 times), no induction period was observed as shown in Figure 3 (○). O_2 dissolved in the reaction solution and in the head space (total 6.0 μmol) was completely eliminated (TON = 5.0, $[O_2] < 1$ ppb in solution below the detection limit of an oxygen electrode: YSI Model 5300A) after 150 min in the decomposition of formic acid in aerated H_2O. Essentially the same slope of the plots in Figure 3 after O_2 removal implies the robustness of the complex **1** in the catalytic O_2 reduction.

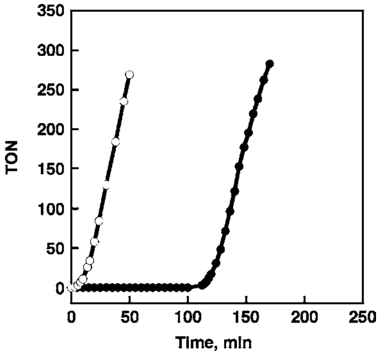


Figure 3. Time course of the turnover number (TON) of the H_2 evolution in the decomposition of HCOOH/HCOONa (0.83 M) catalyzed by **1** (0.5 mM) in deaerated (freeze−pump−thaw cycles, 5 times) H_2O (○) and in aerated H_2O (●) at pH 3.6 at 298 K.

In summary, we have achieved the efficient four-electron reduction of O_2 with formic acid in water at ambient temperature by using complex **1**, which is the most effective catalyst for hydrogen generation in the decomposition of formic acid in water at room temperature.[6] The complete deoxygenation of water ($[O_2] < 1$ ppb) has been achieved successfully. The four-electron reduction of O_2 is suggested to proceed via an iridium(III)-peroxo complex and an iridium(V)-oxo complex, both of which are regarded as the key intermediates in Ir catalyzed water oxidation.[9]

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Supporting Information Available: Experimental procedures, figures (S1−S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) The more definitive assignment of the intermediates is now in progress.

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