

Isotope-labeling Studies on Water Oxidation Reaction Catalyzed by a Monocobalt Polymolybdate

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The rate-determining step of water oxidation (WO) has been considered as either the inter/intramolecular O-O bond coupling of two metal-oxyl radicals (I2M) or intermolecular O-O coupling via the water nucleophilic attack (WNA) to the metal-oxo species.¹ Polyoxometalates (POMs) are known to be highly active and robust WO catalysts (WOCs) owing to their carbon-free framework. However, their detailed mechanism has not been clarified due to their relatively large size leading to afford various structures during the catalysis.

In this study, we investigated the mechanism of WO catalyzed by Anderson-type polyoxometalate (**Co-POM-Mo**, **Figure 1**)² by reacting it with $[\text{Ru}^{\text{III}}(\text{bpy})_3]^{3+}$ as an oxidant in an aqueous borate buffer solution. Kinetic traces for $[\text{Ru}^{\text{II}}(\text{bpy})_3]^{2+}$ generation were spectrophotometrically observed, and the rate constants of WO were determined. Interestingly, the analyses of Eyring plots show a positive activation entropy in any fitting models, suggesting that the rate-determining O-O bond formation takes place in an intramolecular fashion, which must

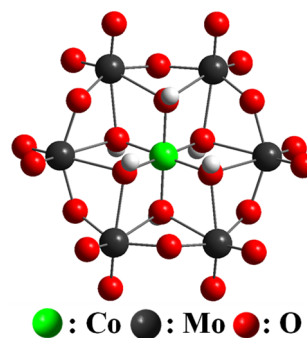
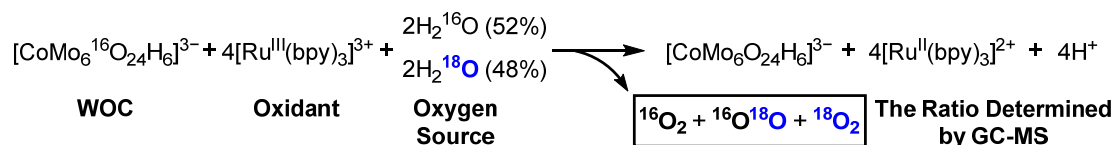


Figure 1. Structure of **Co-POM-Mo**.

be clearly distinguished from the intermolecular I2M and WNA pathways previously proposed for other WOCs. The isotope-labeling experiments using ^{17}O -NMR were performed to determine the rate for the oxygen exchange with bulk water in **Co-POM-Mo**. The rate constant obtained ($k_{\text{ex}} = 2.9 \times 10^{-5} [\text{s}^{-1}]$) clearly shows that its exchange is negligible during the analysis of WO. Then, O_2 evolved from 48% ^{18}O -enriched aqueous borate buffer solution was analyzed by the glovebox/GC-MS system developed in our group (see **Scheme 1**). The results obtained are in good agreement with the isotope distribution expected for the intramolecular O-O bond formation within the **Co-POM-Mo** core. Importantly, the DFT results also support the proposed mechanism.



Scheme 1. Isotope-labeling experiments conducted in this study.

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