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Impact of the Ligand Flexibility and Solvent on the O–O Bond Formation Step in a Highly Active Ruthenium Water Oxidation Catalyst

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S Supporting Information

ABSTRACT: By advanced molecular dynamics simulations, we show that for a highly active ruthenium-based water oxidation catalyst the dangling carboxylate group of the catalyst plays an important role in the crucial O–O bond formation step. The interplay of the flexible group and solvent molecules facilitates two possible pathways: a direct pathway with a single solvent water molecule or a mediated pathway involving two solvent water molecules, which have similar activation barriers. Our results provide an example for which a realistic molecular dynamics approach, incorporating an explicit description of the solvent, is required to reveal the full complexity of an important catalytic reaction in aqueous solvent.

With a substantial growth in worldwide energy demand, there is a strong urgency in identifying affordable, renewable, and clean energy sources. Sunlight-driven water splitting to produce molecular hydrogen holds promise as an alternative for fossil fuels. The overall water splitting process consists of two subreactions: the oxygen evolution reaction (OER; $2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + 4\text{e}^- + \text{O}_2$) and a proton reduction reaction ($4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$). The OER is considered to be the current bottleneck of this process because of a high overpotential, thereby hindering economically viable applications. Therefore, an important step to help artificial photosynthesis compete with fossil fuels lies in the development of highly efficient, abundant, and stable water oxidation catalysts (WOCs).

Among homogeneous catalysts, a number of highly effective ruthenium-based molecular catalysts have been synthesized^{1,2} since their discovery by Gersten et al.³ While most of these catalysts contain multiple metal centers,^{4,5} a number of mononuclear catalysts have also been reported.^{6–8} Two general types of mechanisms have been proposed for formation of the O–O bond during the OER by these catalysts. In one mechanism, this key step involves an O–O radical coupling of two ruthenium–oxo radicals (I2M).⁹ The other mechanism involves water nucleophilic attack (WNA) by a water molecule on a high-valent ruthenium–oxo species. In the context of the WNA mechanism, a new family of $[\text{Ru}(\text{tda})(\text{py})_2]^{m+}$ ($m = 0–2$) type catalysts, recently reported by Matheu and co-workers,¹⁰ is of particular interest. One such catalyst, $[\text{Ru}^{\text{IV}}(\text{OH})(\text{tda}-\kappa\text{-N}^3\text{O})(\text{py})_2]^+$ (**1+**), exhibits a remarkably high turnover frequency of 8000 s^{-1} at pH 7.0 (Figure 1). They attribute this high efficiency to easy access of high oxidation states provided by

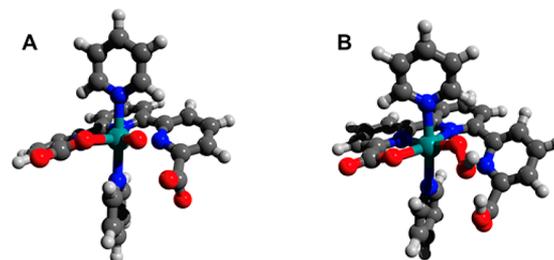


Figure 1. Reactant **1+** (A) $[\text{Ru}^{\text{V}}(\text{tda}-\kappa\text{-N}^3\text{O})(\text{py})_2\text{O}]^+$ (doublet) and product (B) $[\text{Ru}^{\text{III}}(\text{OOH})(\text{Htda}-\kappa\text{-N}^3\text{O})(\text{py})_2]^+$ (doublet) structures of the WNA step.

the tda^{2-} ligand and the presence of a dangling carboxylate group, which facilitates an intramolecular proton transfer during the crucial WNA step. Such an enhancement of the catalytic activity by the presence of a pendant base to abstract the proton during WNA has also been observed in a number of previous studies.^{11,12}

An accurate molecular understanding of the key WNA step is essential in identifying crucial structure–activity relationships that can help in the rational catalyst design of such highly efficient WOCs. In this context, molecular modeling can provide important novel insights that are complementary to experimental studies. Previous work on similar systems has emphasized the importance of an explicit solvent description for accurate predictions of the reaction mechanisms and activation barriers.^{13–15} Additionally, some recent modeling studies of cobalt- and iron-based molecular catalysts for water oxidation have incorporated an explicit solvent for a detailed understanding of the reaction mechanism.^{16–18}

Here, we report a density functional theory (DFT)-based molecular dynamics (MD) study of the WNA step of complex **1+**, incorporating a realistic explicit solvent description in full molecular detail. This allows us to gain quantitative insight on the intramolecular proton-transfer mechanism during the O–O bond formation. We used constrained dynamics^{19,20} to sample, in a controlled manner, the O–O bond formation and proton-transfer steps. This allowed us to determine the reaction mechanism and associated free-energy profiles. Calculations were performed with the CP2K package.²¹ The model consisted of the ruthenium catalyst with 93 explicit water molecules in a

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cubic periodic system ($L = 15 \text{ \AA}$), ensuring at least two solvation shells around the reactive region. The temperature is controlled by a thermostat set to 350 K.²² The electronic structure was determined using the BLYP functional,^{23,24} supplemented with a dispersion correction.²⁵ We use the method of constraints to control the O–O bond formation and determine the associated free-energy profile along the reaction pathways.

An important first observation in a 60 ps (ps) production run of the reactant (A) in aqueous solution is that the dangling carboxylate group shows a large extent of flexibility, as quantified in Figure 2. An important consequence is that, for smaller $O_{\text{Ru}}-C_{\text{COO}}$

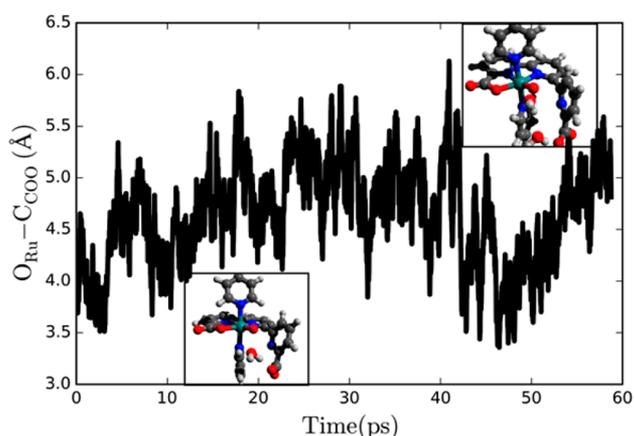


Figure 2. Calculated distances between the Ru–O moiety (O_{Ru}) and the carbon of the carboxylate group (C_{COO}) during the production run. The flexibility of the dangling carboxylate group allows for the bridging by one and two water molecules.

O_{COO} distances (up to 4.0 Å), there is typically one water molecule that could attack the Ru–O moiety, while transferring a proton directly to the carboxylate oxygen. For larger distances, a significant part of the trajectory shows two water molecules near the Ru–O moiety, which allows for the possibility of a O–O bond formation accompanied by a water-mediated proton transfer to the carboxylate oxygen. We have not observed configurations with three intermediate water molecules. From a quantitative analysis of the 60 ps trajectory of the solvated reactant, in combination with additional constrained dynamics calculations (see the Supporting Information), we estimate that the range of $O_{\text{Ru}}-O_{\text{COO}}$ distances up to 4.0 Å (mostly configurations with one intermediate water molecule) is 10–20 times less probable than the range of longer $O_{\text{Ru}}-O_{\text{COO}}$ distances (mostly configurations with two intermediate water molecules). This corresponds to a free-energy difference of 1–2 kcal mol⁻¹.

Although the simulations of the solvated compound suggest that configurations with two intermediate water molecules are more frequent than those with one water molecule, the associated free-energy difference is relatively small. We therefore consider it useful to estimate the competition between these different mechanisms, also because the latter had already been proposed by Matheu and co-workers.¹⁰ We performed constrained dynamics with the O–O bond distance as the reaction coordinate (Q), to estimate their respective activation barriers. For both mechanisms, we observed the proton transfer to occur spontaneously and reversibly when the O–O distance is reduced to 1.8 Å. This suggests that, with the chosen imposed reaction coordinate, the relevant configurations along the entire reaction pathway are properly sampled. Additionally, this reaction

coordinate has been successfully used in previous studies on the WNA step.^{17,26}

The activation barriers for both of these mechanisms are similar, 11.7 and 11.6 kcal mol⁻¹, respectively, as shown in Figure 3. The relative stabilities of the two states are also of the same

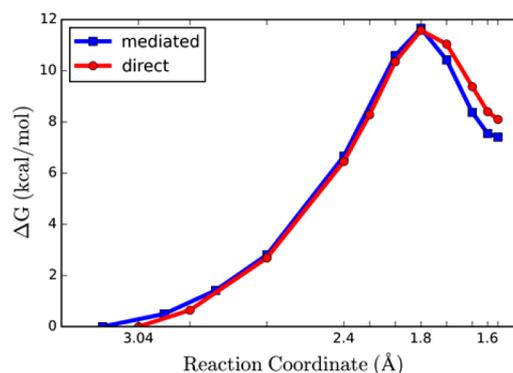


Figure 3. Free-energy profiles for the direct (Mech-1) and mediated (Mech-2) mechanisms in solution.

magnitude (7.4 and 8 kcal mol⁻¹). This indicates that both of these mechanisms could occur. A comparable barrier makes sense for both mechanisms because they are similar: the mediating water molecule acts as a proton relay to assist in proton transfer to the acceptor base, which is the dangling carboxylate group in this case. Such water-mediated mechanisms have been observed earlier in modeling studies^{27–29} and are a manifestation of the Grotthuss mechanism.³⁰ The observation that, in the MD trajectory of the reactant, most of the configurations favored the possibility of a mediated mechanism (Figure 2) is an indication that this mechanism is more likely in an aqueous solvent. Further study and analysis of dynamical reaction pathways, using, e.g., transition path sampling,³¹ are required to quantify the kinetic aspects of the O–O bond formation WNA step.

Llobet and co-workers report the activation barrier to be 16.8 kcal mol⁻¹ using a (different) meta-GGA functional in the gas phase, with corrections using the implicit solvation model.¹⁰ Here we should note that a substantial part of the discrepancy may have its origin in the use of different functionals (see the Supporting Information).

Representative snapshots of configurations from the constrained dynamics simulations for the investigated mechanisms are shown in Figure 4. At an O–O distance of 1.80 Å, in the case of the mediated mechanism, we see that the proton is transferred back and forth between the attacking water and the carboxylate group. Figure 4A shows an example configuration where the mediating water molecule exists as a hydronium ion (H_3O^+) stabilized by hydrogen bonds with surrounding water molecules for a few femtoseconds, before transferring the proton to the carboxylate group. At an O–O distance of 1.80 Å for the direct mechanism (Figure 4B), the proton is also transferred back and forth. It appears that the transition states occur at the same reaction coordinate distance for both mechanisms and, unlike the study by Hynes and co-workers,³² the mediating water molecule does not seem to lower the activation barrier, but acts as a relay to facilitate proton transfer to the dangling carboxylate ligand.

To conclude, we have studied the WNA step of a highly active ruthenium-based catalyst in explicit solvent using DFT-based MD. We find the dangling carboxylate group of the catalyst to show a high degree of flexibility in solution, allowing for two

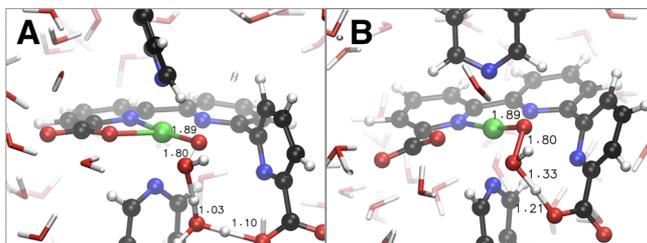


Figure 4. Representative snapshots selected from the MD trajectories (distances shown in angstroms). (A) Transition-state structure for the mediated mechanism, just before O–O bond formation. Here, the attacking water molecule has transferred a proton to the second water molecule, which exists as a hydronium ion (H_3O^+) for a few femtoseconds (fs), before transferring a proton to the carboxylate group. (B) Transition-state structure for the direct mechanism, just before the O–O bond formation. Here, with the attacking water approaching the oxo moiety, the proton is simultaneously transferred to the carboxylate group.

possible mechanisms during the WNA step. Using advanced biased sampling techniques, we provide a strong indication that these are competing mechanisms because they have the same activation barriers. As the simulations show that configurations with two intermediate water molecules are more likely by a factor in the range of 10–20, the water-mediated mechanism might be the dominant process in an aqueous solution.

The flexibility has been recognized as a potential important characteristic of WOCs.^{33,34} For example, it has been suggested as the main factor to switch from a WNA-type mechanism to the radical coupling mechanism.³⁴ The present work provides an important novel result and insight into another aspect of flexibility: we show in explicit molecular detail, on a quantitative level of accuracy, how the thermal motion of a flexible ligand leads to multiple distinct reaction pathways that are mediated by different solvent structures. In a broader context, our results demonstrate that a realistic modeling approach, incorporating a molecular description of solvent- and temperature-induced fluctuations, can be essential to reveal the full complexity of catalytic reactions in an aqueous solvent. We anticipate that using this approach will be of significant importance in the rational design and synthesis of efficient WOCs.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.inorgchem.8b00619](https://doi.org/10.1021/acs.inorgchem.8b00619).

Video 1. A movie of the transition state trajectory from the constrained MD simulations for the direct mechanism (Mech-1) at the O–O distance of 1.8 Å ([AVI](#))

Video 2. A movie of the transition state trajectory from the constrained MD simulations for the mediated mechanism (Mech-2) at the O–O distance of 1.8 Å ([AVI](#))

Details on electronic structure and MD calculations ([PDF](#))

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Notes

The authors declare no competing financial interest.

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