

Theoretical Study of H₂O Oxidation by a Half-Sandwich Iridium Complex

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A half-sandwich iridium complex $[(\text{Ir}^{\text{III}}(\eta^5\text{-C}_5\text{Me}_5)\{\text{bpy}(\text{COOH})_2\}(\text{H}_2\text{O}))]^{2+}$, where $\text{bpy}(\text{COOH})_2$ is 2,2'-bipyridine-4,4'-dicarboxylic acid, has an ability to oxidize both H₂ and H₂O molecules.¹ In this study, the detailed reaction mechanism of the H₂O oxidation is investigated using density functional theory (DFT) calculation.² All reaction intermediates were calculated by using the B3LYP-D3 functional, as implemented in Gaussian 16 program package. We used TZVP basis set for the H, C, N, and O atoms and SDD basis set for the Ir atom. Here, O–O bond formation is especially focused.

DFT calculation shows that an iridium-oxo complex, which is the reactant complex of O–O bond formation, has three possible spin states (triplet, open-shell singlet, and closed-shell singlet states) caused by the two-degenerate π^* orbitals between the Ir-5d and O-2p. In the O–O bond formation, we consider two possible paths: using one or two H₂O molecules as shown in **Fig. 1**. In the path using one H₂O molecule, a hydrogen of the H₂O is abstracted by oxo ligand to form two radical species, which occurs radical-radical coupling to lead to an O–O bond in the open-shell singlet state. On the other hand, two H₂O molecules react with oxo ligand as a substrate and a catalyst to form an O–O bond through the water nucleophilic attack (WNA) mechanisms.³ Compared with both paths, the path using two H₂O molecules is energetically favored so that an O–O bond formation proceeds as the WNA mechanisms.

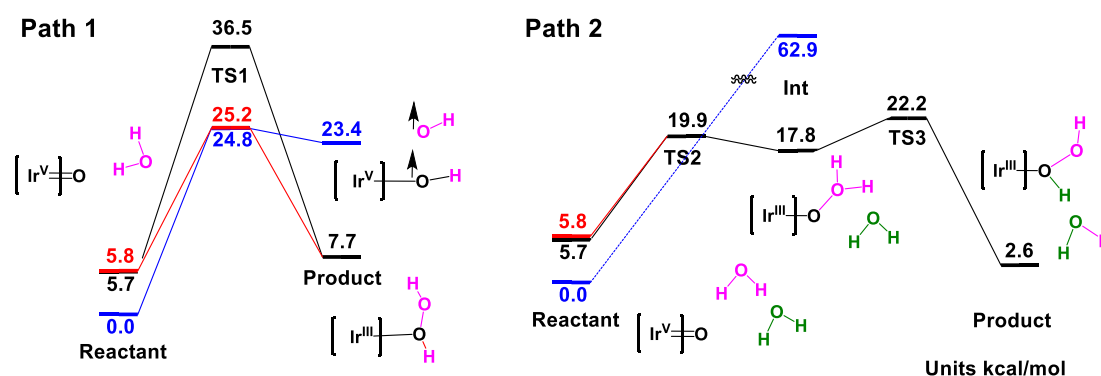


Fig. 1. Computed reaction diagrams for H₂O oxidation by a half-sandwich iridium complex. Black, red, and blue lines correspond to closed-shell singlet, open-shell singlet, and triplet states, respectively.

References

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