



**48<sup>a</sup>**  
**Reunião Anual da**  
**Sociedade**  
**Brasileira de**  
**Química**

**Emergências Climáticas?  
A Química Age e Reage!**

**ANAIS**

**08 a 11 de junho de 2025, Campinas, Expo Dom Pedro**

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**Revisão textual e gramatical:** Responsabilidade dos respectivos autores.

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**Dados Internacionais de Catalogação na Publicação (CIP)  
(Câmara Brasileira do Livro, SP, Brasil)**

Reunião Anual da SBQ (48. : 2025 : Campinas, SP)  
Anais da 48<sup>a</sup> Reunião Anual da SBQ [livro  
eletrônico] / Sociedade Brasileira de Química. --  
1. ed. -- Campinas, SP : Aptor Software, 2025.  
PDF

Vários autores.  
Vários colaboradores.  
Bibliografia.  
ISBN 978-85-63273-70-3

1. Química I. Sociedade Brasileira de Química.  
II. Título.

25-282696

CDD-540

**Índices para catálogo sistemático:**

1. Química 540

Eliete Marques da Silva - Bibliotecária - CRB-8/9380

## Computational study of the Copper-catalyzed water oxidation catalytic cycle using macrocyclic ligands: unraveling the role of $\text{HPO}_4^{2-}$

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Palavras Chave: *water oxidation, catalysis, computational chemistry, density functional theory*

### Highlights

- The catalytic cycle of copper-catalyzed water oxidation with a macrocyclic N-donor ligand was computationally investigated based on previous experimental studies
- The reaction intermediates and transition states were computed using quantum chemical calculations, in which the energy profile of the catalytic cycle reproduces well the experimental turnover overall frequency (TOF).
- Computational analysis reveals that  $\text{HPO}_4^{2-}$  facilitates O–O bond formation.

### Resumo/Abstract

The oxidation of water is a key reaction in both natural and artificial photosynthesis mechanisms. This process is thermodynamically challenging, and therefore, the development of efficient water oxidation catalysts (WOCs) is crucial for achieving industrial-scale applications [1]. Specifically, Yu *et al.* [2] reported an efficient electrocatalytic water oxidation using a Cu-based catalyst with the 1,4,8,11-Tetramethylcyclam (TMC) ligand. A TOF of 30  $\text{s}^{-1}$  was achieved under neutral pH conditions (0.1 M phosphate buffer), demonstrating excellent electrocatalytic water oxidation activity. However, the catalytic cycle remains poorly understood. We computationally investigated the electrochemical transformations, including the role of  $\text{HPO}_4^{2-}$ , possible intermediates and transition states of the water oxidation mechanism with Cu-TMC complexes. Specifically, when the O–O bond formation transition state by a single water molecule was calculated (Fig. 1a), the barrier was found to be 40 kcal/mol. However, in the presence of  $\text{HPO}_4^{2-}$  as a proton acceptor with  $\text{H}_2\text{O}$  (Fig. 1b) lowered this barrier to 17 kcal/mol, highlighting the important role of phosphate in enhancing the catalytic efficiency of water oxidation.

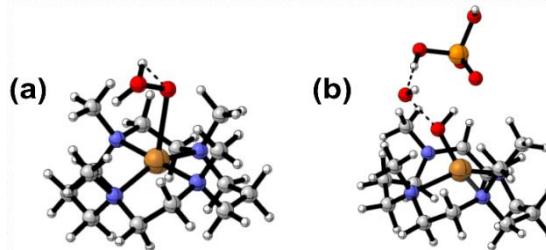


Figura 1: O–O bond formation transition states of the catalyst with: (a) a single water molecule; (b) a phosphate and a water molecule

All calculations were carried out using the B3LYP-D3 density functional, associated with the LANL2TZ(f) and def2-SVP basis sets for copper and lighter atoms, respectively. The solvent effects were considered implicitly using the SMD model.

[1] Marenich *et al.* *Angewandte Communications*, 51, 12810–12814. 2012; [2] Yu *et al.* *Chemical Communications*. 52, 10377–10380. 2016.

### Agradecimentos/Acknowledgments

