XXI Brazilian Meeting on Inorganic Chemistry
X Brazilian Meeting on Rare Earths
III Workshop on Theoretical Bioinorganic Chemistry
Belo Horizonte, September 12 - 15th 2024

Investigation of the parameters of the oxidation reaction of 4-nitrophenyl-beta-D-Glucopyranoside catalyzed by [Cu(bmimapy)Cl]ClO4

Camilla Maria, Roberto B. Faria, Marciela Scarpellini

Departmento de Química Inorgânica, Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil

E-mail: marciela@iq.ufrj.br,camillamaria@gradu.iq.ubrj.br

Thematic Area: Biological Inorganic Chemistry

Keywords: Catalyst, Oxidative Process, Bioinorganic Chemistry

The processes of cleaving polysaccharides are central to the global carbon cycle for both: obtaining energy from living organisms and producing chemical inputs and biofuels. In nature, these processes are carried out by enzymes that work collaboratively. One class of enzymes that acts in these cleavages is the lytic polysaccharide monoxygenases (LPMOs), which assist hydrolases by oxidizing terminal sites on polysaccharide chains. In most LPMOs, the active site contains Cu(II) ions coordinated equatorially by histidine residues, exposed to the solvent, which are reduced to Cu(I) species by external reductants, generating the active species for catalysis. In view of the active site found in LPMO, biomimetic complexes seek to emulate the so-called “histidine bracers” through the use of nitrogen ligands coordinated equatorially to Cu(II) ions.(1)In this work, the catalytic activity of the complex [Cu(L)(Cl)](ClO4)], where the ligand L = N,N-bis((1-methyl-1H-imidazol-2-yl)methyl)-2-(pyridin-2-yl)ethanamine, (2) was evaluated in the oxidation of the model substrate p-nitrophenyl-β-D-glucopyranoside (PNPG). The reaction was monitored spectrophotometrically by the formation of the product p-nitrophenolate (λmax = 400 nm / ε = 18,500 L mol-1 cm-1)(3). The kinetic data were obtained in carbonate buffer (pH 10), H2O2 (0.6 mM), triethylamine (0.6 mM), in the presence of the complex (1.5 × 10-3 mM) and varying the substrate (1.5 × 10-1 to 6.0 × 10-1 mM). The data obtained in analogous experiments in the absence of the complex were used to discount any effect of substrate non-catalyzed degradation. Employing the initial rates method, the Michaelis-Menten curve and the Lineweaver-Burk plot, the Vmax and the KM values obtained were 5.0 ×10-10 mmol L-1s-1 and 0.14 mmolL-1, respectively. At this point, it is possible to conclude that this complex presents low ability to oxidize the substrate PNPG, when compared to the analogous complexes(3) with tridentate ligands also bearing the “histidine bracer”.

Acknowledgments: CAPES, CNPq, FAPERJ, PIBIC-UFRJ.

References

1. TOVAR, et al.Chem. Sci., 2024, Advance Article, DOI: 10.1039/d4sc01762e
2. SCARPELLINI *et al. Polyhedron, 2004, v. 23, 511.*
3. CONCIA, A. L. *et al. Inorg. Chem., 2017, v. 56, n.3, 1023.*