

# Metalloporphyrins as acid catalysts in acetalization reaction

Charles Carvalho\*, Gabriel K. B. Ferreira, Shirley Nakagaki\*

Laboratório de Bioinorgânica, Universidade Federal do Paraná, Curitiba, PR - Brazil.

\* charlesscarvalho@gmail.com and shirleyn@ufpr.br

Acetalization of aldehydes and ketones is an important synthetic route widely used in organic synthesis to achieve the protection of carbonyl groups or starting materials that find practical application, as synthetic carbohydrates, steroids and pharmaceuticals<sup>1</sup>. For this purpose, the use of Brønsted or Lewis acid compounds are among the successful catalyst that have been used in this reaction<sup>2</sup>. In recent years, the development of catalysts based on metalloporphyrins (MP) has been investigated for different purposes<sup>3</sup>. Nevertheless, there have been few studies using this class of compounds as Lewis acid catalyst. These molecules are able to perform as Lewis acid catalyst due to the presence of metal ion at the ring cavity. Furthermore, the ring structure can be tailored aiming to improve the catalytic proprieties. In this work, we present some catalytic results of a set of catalysts based on metalloporphyrins complexes

[Zr(IV)Cl<sub>2</sub>(TPP)], [Fe(III)Cl(TPP)], [Zr(IV)Cl<sub>2</sub>(TPFPP)] and [Fe(III)Cl(TPFPP)],

where

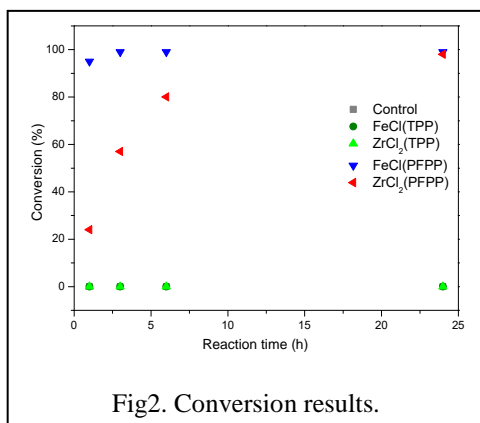
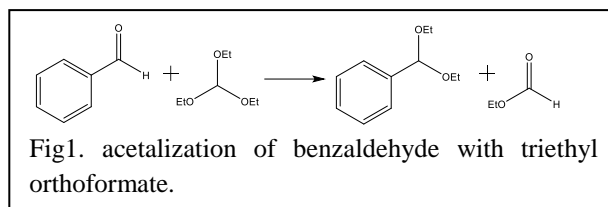


Fig2. Conversion results.

TPP = tetraphenylporphyrin and TPFPP = tetra-pentafluorophenylporphyrin that have distinct ring structure and different metal ions, performing the reaction of acetalization of benzaldehyde (Bz) with triethylorthoformate (TEOF) – molar ratio Bz/TEOF = 1:3, ethanol as solvent, 2% mol of catalyst at 70 °C and continuous stirring. The acetal product was analyzed by GC and yields were determined by area normalization. These metalloporphyrins were synthesized based on Lindsey<sup>4</sup> methodology and characterized by UVVIS, FTIR, RMN H<sup>1</sup> and F<sup>19</sup>, confirming the preparation of the desired compounds.

Preliminary catalytic results suggest the remarkable influence of the peripheral aryl substituents of the ligand on yields (95% FeCl(TPFPP) and 0% FeCl(TPP) after 1 hour of reaction). Therefore, the electron-withdrawing character of the pentafluorophenyl substituents of the ligand TPFPP raises strongly the electrophilic nature of the central ion throughout electron delocalization caused by fluoro presence on *orto*, *meta* and *para*, positions of aryl groups. In addition, these results suggest yet the influence of metal ion nature into ring cavity, which somehow affect the conversion rate (95% [FeCl(TPFPP)] and 24% ZrCl<sub>2</sub>(TPFPP) after 1 hour of reaction). The control reaction (without catalyst), and [FeCl(TPP)], [ZrCl<sub>2</sub>(TPP)] catalyst have not formed any desired compounds even after 25 hours in the same reaction conditions.

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