

Computational study of the electrocatalytic CO₂ reduction reaction using a non-noble metal complex

Gabriela Garcia (PG),^{1*} Atualpa A. C. Braga (PQ)¹.

ggarcia@iq.usp.br; atualpa@iq.usp.br

¹Departamento de Química Fundamental, Instituto de Química da USP (IQ-USP).

Keywords: Computational Chemistry, Electrochemistry, Homogeneous Catalysis, Electrocatalysis, CO₂, Carbon-carbon bond.

Highlights

Theoretical calculations of CO₂ electroreduction's reaction path to form acetic acid, using a manganese complex with corrole ligand. A carbon-carbon bond is formed between two CO₂ molecules from the saturated atmosphere.

Abstract

The manganese complex with corrole ligand was used as the catalyst (Figure 1) for the CO₂ reduction reaction (CO₂RR). Based on this, a reaction mechanism was proposed, through computational methods, as a proof of concept to this type of reaction (Figure 2). The calculations were carried out with unrestricted B3LYP functional and Def2-SVP basis set. Since this is an open shell system, all structures were optimized with different multiplicities, resulting that they all are more stable as triplets or quartets, depending on how much electrons they gain. No spin contamination was found in any structure.

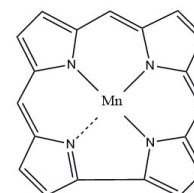


Figure 1: Mn-Corr Catalyst

It was verified that the species which activate the CO₂ comes from the electroreduction of the initial Mn (III) (R1) to Mn (II) (I1). As it follows, the intermediate I2 receives a proton from water (20% in acetonitrile solution). After receiving another electron, I3 becomes able to activate a second CO₂ molecule, forming the carbon-carbon bond, which is the most interesting step for this work, since its goal is to form C₂₊ products. On the following ones, the reaction undergoes successive proton coupled electron transfers, that in the end will release acetic acid and restore the initial catalyst.

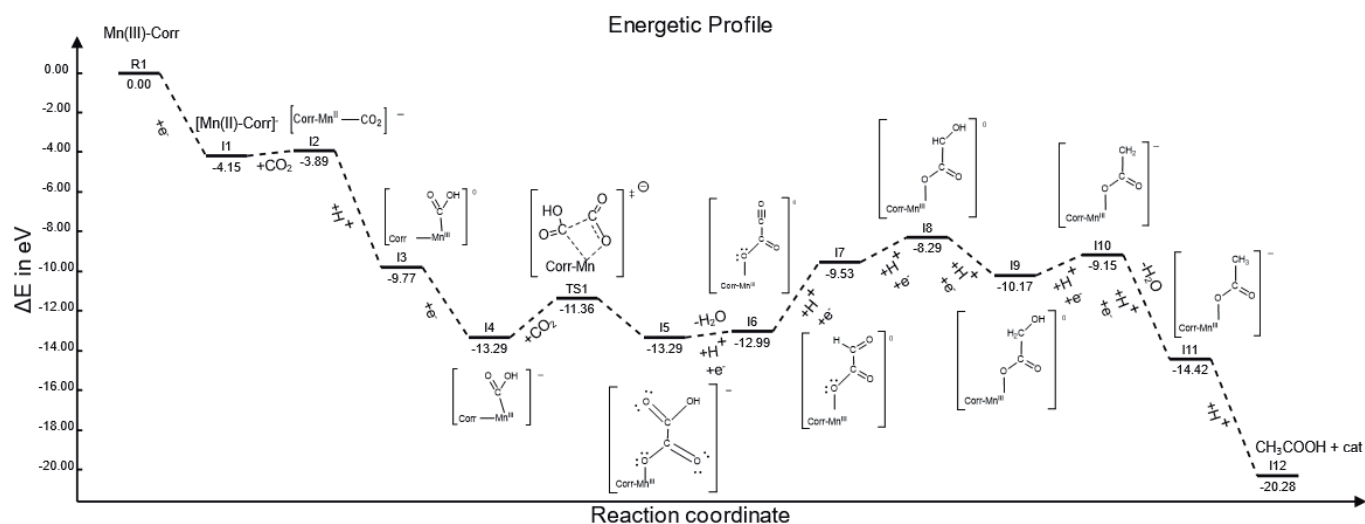


Figure 2: Energetic Profile

Acknowledgments

