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Hydrophilic and Hydrophobic Manganese Porphyrins: Synthesis and Catalytic Activity in the Oxidation of Ethylbenzene

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Acetophenone is a compound of interest to various industrial sectors, such as cosmetics, food, and pharmaceuticals[1]. The oxidation of ethylbenzene has been the main route for the production of acetophenone. In this context, this work refers to the synthesis of the porphyrin 5,10,15,20-tetrakis(3-carboxyphenyl)porphyrin, H_2T3CMPP, the coordination process with manganese to form chloride of 5,10,15,20-tetrakis(3-carbomethoxyphenyl)porphyrinmanganese(III), [Mn(T3CMPP)Cl] (**MnP1**), and its hydrolysis to obtain 5,10,15,20-tetrakis(3-carboxyphenyl)porphyrinmanganese(III), H_3[Mn(T3CPP)] (**MnP2**). Thus, the catalytic potential of the porphyrins **MnP1** and **MnP2** was compared in the oxidation of ethylbenzene to obtain acetophenone. Initially, the porphyrin H_2T3CMPP was obtained through the method described by Rebouças et al[1]., using methyl 3-formylbenzoate as the aldehyde. Subsequently, the metallation process was carried out using the chloroform: methanol method and manganese chloride to obtain **MnP1**. Following this, the process for obtaining the water-soluble porphyrin **MnP2** was undertaken. The obtained porphyrins were characterized by NMR ^{1}H (free base only), MALDI-TOF mass spectrometry analysis, and UV-vis spectroscopy. The Mn compounds were used as catalysts in the oxidation reactions of ethylbenzene, which were monitored by gas chromatography. Tert-butyl hydroperoxide was used as the oxidant, and dimethyl sulfoxide (DMSO) as the solvent. Reactions in the absence of solvent were also performed. Comparing the conditions (with and without solvent), an inversion in the performance of the porphyrins was observed, along with an increase in the conversion of ethylbenzene when DMSO was not added to the system. The main product in all systems was acetophenone. Additionally, three minor products were observed in the GC analyses, two of which were benzoic acid and benzaldehyde. Future experiments aim to identify the last minor product and achieve complete conversion of the substrate to acetophenone with even greater selectivity.

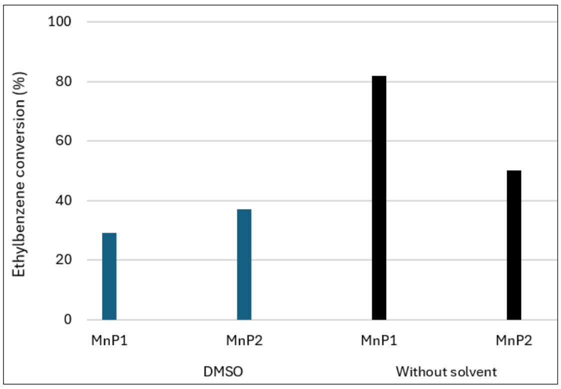

Figure 1. Oxidation of ethylbenzene catalyzed by manganese porphyrins derived from H_2T3CMPP.

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