

A mixture of electron deficient β -brominated Mn-porphyrins as a highly efficient catalyst for cyclohexane oxidation by PhIO

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Keywords: Manganese porphyrins, Cyclohexane oxidation, Iodosylbenzene, β -octabromination.

Abstract

A mixture of third generation Mn-porphyrins is an efficient catalyst for cyclohexane oxidation under mild conditions.

Introduction

Synthetic manganese porphyrins (MnP) are extensively studied as biomimetic models for cytochrome P-450, acting as catalysts for the oxidation of organic substrates¹. The oxidation of cyclic alkanes, such as the cyclohexane, is of industrial relevance because the products are precursors of nylon-6 and nylon-66. In this context, sterically and electronically protected metalloporphyrins oxidize organic substrates more efficiently and selectively. Thus, this work describes the synthesis, characterization and use of a second- (MnP2) and an unprecedented third-generation (MnP3) manganese porphyrin (Fig. 1) as catalysts in cyclohexane oxidation, using iodosylbenzene (PhIO) as the oxidant. It also compares the catalytic activity of the synthesized porphyrins with [Mn^{III}TPPCl] (MnP1), which is a classic first-generation MnP².

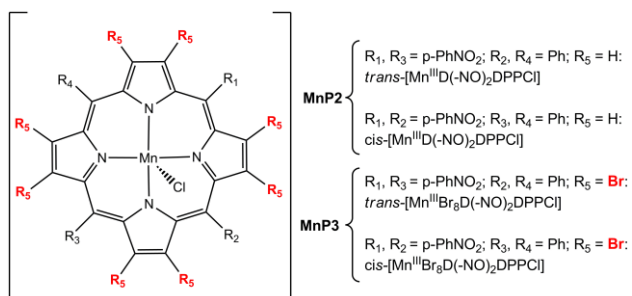


Figure 1. Structure of the manganese porphyrins.

Results and discussion

Cis and *trans* mixtures (5:1) of the second- and third-generation catalysts were synthesized according to the methods described by Silva et al². The attempt to separate such porphyrins (*cis* and *trans*) was not successful. The compounds were characterized by UV-vis and IR spectroscopies. For the third-generation porphyrin, the results of UV-vis absorption spectroscopy showed the bathochromic shift of the Soret band and a decreased intensity of this absorption band, characteristic of octabromination of the β -pyrrole positions. In addition, ¹H NMR was performed after demetallation, and it was possible to

verify the β -octabromination. The cyclohexane oxidation reaction was analyzed by capillary gas chromatography, using the internal standard method².

Cyclohexanol (Cy-ol) and cyclohexanone (Cy-one) were the main reaction products. Table 1 summarizes the catalytic results. The second-generation MnP (MnP2) affords higher Cy-ol yield and selectivity than the first-generation one (MnP1). This result is associated with the presence of the electron-withdrawing nitro group in *para*-mesoaryl positions of the porphyrin macrocycle, which enhances the reactivity of the high-valent active species Mn^V(O)P and facilitates oxygen atom transfer from this species to the substrate³. Similarly, the third-generation MnP affords higher yield and selectivity than the first- and second- generation ones. The introduction of eight bromine atoms in the β -pyrrole positions withdraws electron density from the macrocycle and also destabilizes the high-valent active species³.

Table 1. Yields of the oxidation of cyclohexane by PhIO, catalyzed by MnP in CH₂Cl₂.

Systems	Yields (%) ¹		Selectivity (%) ²
	Cy-ol	Cy-one	
MnP1	14	11	56
MnP2	27	10	73
MnP3	61	15	80

1. Yield based on the oxidant; 2. Selectivity = (100 x Cy-ol)/(Cy-ol + Cy-one)

Conclusion

The MnP2 and MnP3 synthesized gave larger product yields and improved selectivity compared with MnP1. The introduction of the nitro group and bulky bromine atoms increased catalytic activity, making the new third-generation porphyrin (MnP3) a more efficient catalyst than the second-generation one (MnP2).

Acknowledgements

CNPq, FAPEMIG and UFMG.

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²Silva, V. S., et al. *Appl. Catal. A: Gen.* **2014**, 469, 124.

³Latifi, R. et al. *Arch. Biochem. Biophys.* **2011**, 507, 4.