Journal of Porphyrins and Phthalocyanines
J. Porphyrins Phthalocyanines 2001; **5**: 428–430
DOI: 10.1002/jpp.332

SHORT COMMUNICATION

The manganese complex of 2,3,7,8,12,13,17,18-octaphenylporphyrin as epoxidation catalyst

ABÍLIO J. F. N. SOBRAL and ANTÓNIO M. D'A. ROCHA GONSALVES*

Departamento de Química, FCTUC, Universidade de Coimbra, P-3049 Coimbra, Portugal

Received 16 July 1999; Revised 27 May 2000
Accepted 19 June 2000

ABSTRACT: The 2,3,7,8,12,13,17,18-octaphenylporphyrinato manganese(III) chloride was prepared and its behaviour as epoxidation catalyst was studied. The role of the phenyl substituents in the ß-pyrrolic positions concerning the stability of the catalyst to the reaction conditions and the efficiency and selectivity of the oxidations was accessed in a comparative study with MnTPP and MnEtio II. Copyright © 2001 John Wiley & Sons, Ltd.

KEYWORDS: 2,3,7,8,12,13,17,18-octaphenylporphyrin; epoxidation catalysts

INTRODUCTION

Significant efforts have been devoted in the last few decades to the development of biomimetic oxidation. Metalloporphyrin-catalysed oxidations, either in natural or synthetic processes, have been reckoned to occur through high-valence oxygenated species, formed by transfer of an oxygen atom to the metalloporphyrin from a suitable oxygen donor. Reasonably stable active complexes were found, allowing the use of various oxygen donors [1–4]. Studies and attempted rationalisations for the role of substituents at the porphyrin periphery on the catalytic activity can also be found in the literature, involving the introduction of halogens or bulky groups in the *meso*-phenyls [5, 6] or halogenation of the pyrrolic positions [7, 8] of the basic *meso*-tetraphenylporphyrin skeleton. In specific cases elaborate porphyrin structures for the catalyst were also used [9, 10].

In this paper we present a first study of the 2,3,7,8,12,13,17,18-octaphenylporphyrinato manganese (III) chloride as epoxidation catalyst, designed to understand the influence of phenyl substituents in the ß-pyrrolic positions on the overall performance of the manganese metalloporphyrin based epoxidation catalysts.

EXPERIMENTAL

All reagents were synthesis grade (Aldrich) and all solvents were purified by the usual methods before use. The GLC analyses during the epoxidation reactions were carried out on a Hewlett-Packard HP5890 with a HP-1 column (silica, OV-1, 5 m × 580 μm) using nitrogen as carrier gas at a flow rate of 5 ml min^{-1}. The injector and the FID detector were at 250 °C and the oven temperature started at 50 °C for 2 min and then increased to 200 °C at a rate of 15 °C min^{-1}.

In a typical epoxidation experiment, 1 mmol of metalloporphyrin is added to 10 ml of CH_2Cl_2 with 100 mmol of 1-methyl-cyclohexene, 20 mmol of pyridine and 2 mmol of tetrabutylamonium bromide as phase transfer agent. To that, 10 ml of NaOCl 0.6M are added and the reaction kept with controlled stirring at room temperature.

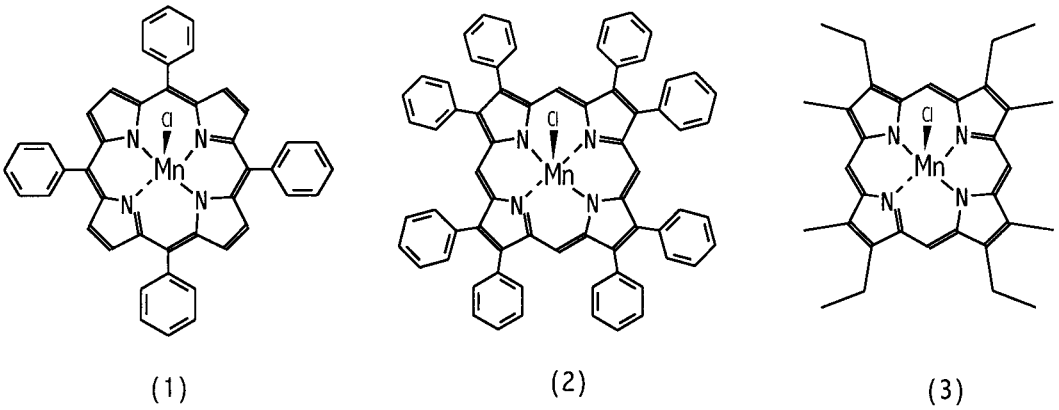
The porphyrin free bases and the manganese complexes were synthesised using literature methods, purified by chromatography, crystallised and characterised by mass spectrometry (FAB^+), visible spectroscopy and ^1H NMR, giving spectroscopic data in full agreement with that expected. *Meso*-tetraphenylporphyrin (**1**) was prepared by the Rothemund–Adler method [12] and purified following an established procedure [13]. The 1,2,3,4,5,6,7,8-octaphenylporphyrin (**2**) was synthesised by the method of Friedman [14] and the 1,4,5,8-tetramethyl-2,3,6,7-tetraethylporphyrin (**3**) was synthesised by the procedure described by Rose *et al.* [15]. The manganese complexes used as catalysts in the epoxidation reactions were synthesised and purified by the procedure of Adler *et al.* [16] starting from the porphyrin free base and manganese(II) chloride in dimethylformamide.

RESULTS AND DISCUSSION

It has been reported that a relationship exists between the structure of a metalloporphyrin and its catalytic activity, but this complex relation is not fully clarified. Further studies using simple porphyrins and their metallocomplexes as catalysts can still bring new important information to clarify the effect of the substituents on the activity of this type of catalysts, and contribute to achieve more efficient catalysts.

Our approach to this problem was based on the

*Correspondence to: A. M. d'A. Rocha Gonsalves, Departamento de Química, FCTUC, Universidade de Coimbra, P-3049 Coimbra, Portugal.



Scheme 1.

preparation of a selected group of manganese porphyrins bearing different substituents, either in the pyrrolic or *meso* positions (Scheme 1) and in monitoring the stability of the catalyst during the oxygenation reaction, by visible spectroscopy, and the conversion of the substrate into the products, by GC/MS. The epoxidation of 1-methyl-cyclohexene by aqueous sodium hypochlorite in a two-phase system with a phase transfer agent, following previously described experimental conditions [11], was studied using our selected catalysts. In all cases epoxide was the main product but 3-methyl-2-ene-cyclohexanol and 3-methyl-2-ene-cyclohexanone were also identified as secondary oxidation products.

The presence of bulky groups like phenyl or appropriately substituted phenyls in the *meso* positions of metalloporphyrins originates stable oxygenation catalysts, and these phenyl groups have been considered to play the role of preventing the formation of the less active μ-oxo-dimers and to have a deactivating effect on radical processes at the *meso* positions, thereby decreasing the rate of oxidative macrocycle degradation. This is usually used to explain the success of the MnTPP (**1**) family of catalysts and justify our choice of MnTPP as a comparative catalyst in this study of 2,3,7,8,12,13,17,18-octaphenylporphyrinato manganese-(III) chloride, MnOPP (**2**). However, since natural oxidation catalysts are based on *meso*-free metalloporphyrins, we extended our study using as a comparative reference the manganese complex of etioporphyrin II, MnEtio II (**3**).

The course of each experiment was checked by visible spectroscopy to evaluate the stability of the catalyst through the intensity of the Soret band. In all cases a gradual loss of intensity of that band was observed simultaneously with the progress of the epoxidation. The epoxide production stops at the moment that the Soret band vanishes and the solution becomes colourless. The disappearance of the Soret band was not followed by the appearance of any new bands in the visible region, showing that the catalyst was indeed destroyed by degradation of the porphyrin macrocycle and not inactivated by any non-destructive process or by poisoning of the catalyst.

As shown in Fig. 1, the *meso*-free MnEtio II is quickly destroyed. However, the catalyst shows an extremely high efficiency to oxygenate the substrate, originating 18% conversion in 5 min, which competes with a very rapid degradation of the macrocycle, therefore giving very poor catalytic turnovers. Comparing the data in Fig. 2 it is clear that MnTPP promotes oxidations at a much slower rate than MnEtioII. MnTPP only gives 10% conversion after 5 min, but it gives higher overall yields of oxidation products because this complex withstands the reaction conditions for 4 h.

The results with MnOPP were unique. Being a *meso*-free porphyrin, the MnOPP, with its 4-h lifetime in these conditions, has a stability and activity more similar to the *meso*-substituted MnTPP, than to that of MnEtio II which withstands the reaction conditions for only 30 min.

The 55% selectivity in epoxide production presented by MnOPP is also more similar to that shown by MnTPP, 60%, than that presented by MnEtio II. With this catalyst the yield of epoxide, among other products, is only 45%.

The role of the phenyl groups on the porphyrin periphery as been considered to be more of a steric than electronic nature for the catalysts based on *meso*-phenyl substituted porphyrins such as TPP. The results presented in this study

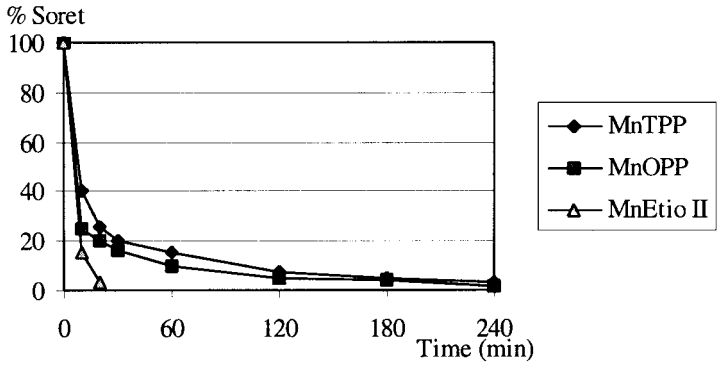


Fig. 1. Time variation of the Soret band of the catalysts.

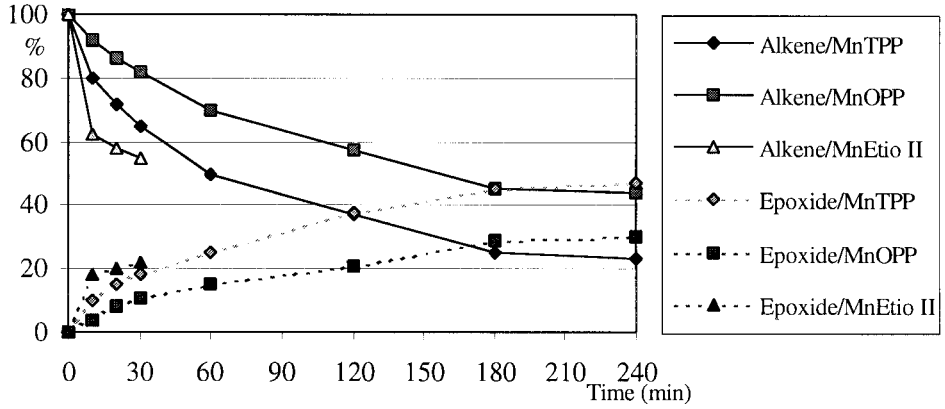


Fig. 2. Alkene and epoxide evolution in the epoxidation reaction with catalysts **1**, **2** and **3**, until exhaustion of the catalyst.

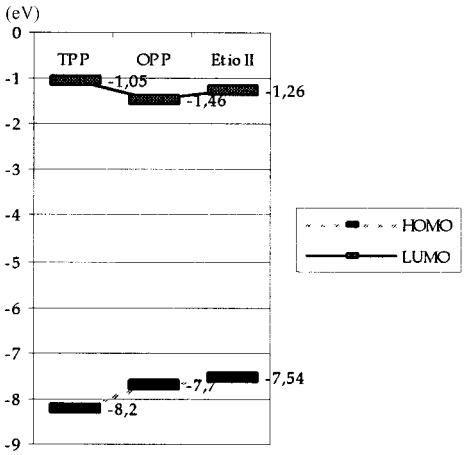


Fig. 3. HOMO and LUMO values for the porphyrins involved in this study. Values from Hyperchem v.3 using the semi-empirical AM1 with a Polak–Ribiere alogorithm and a final gradient of 0.01 kcal Å mol^{-1}.

point to a similar situation in the *meso*-free porphyrin OPP. The HOMO–LUMO values (Fig. 3) for OPP are closer to those of the other *meso*-free porphyrin Etio II than to those of TPP. This may suggest a small electronic effect of the ß-phenyl groups at the porphyrin periphery, pointing more to a steric effect similar to that observed with TPP, and justifying the TPP like behaviour of the *meso*-free OPP.

CONCLUSION

Taking into account the overall results of the present study we may conclude that the nature of the side chains is worth exploiting, both in the *meso* and ß-positions of the macrocycle periphery, in order to control the catalytic performance of the metalloporphyrins as oxidation catalysts and thus extending the general attempts which so far concentrate on the study of *meso*-phenylporphyrins.

The results of this work will be used to guide the design of new metalloporphyrins to be tried as oxidation catalysts in order to protect the catalyst from oxidative degradation while increasing its activity and selectivity.

Acknowledgements

We would like to thank Chymiotechnon, Portugal, for financial support and Dr R. A. W. Johnstone from the Chemistry Department of the University of Liverpool (UK) for the FAB spectra.

REFERENCES

1. Battioni P, Renaud JP, Bartoli JF, Reina-Artiles M, Fort M, Mansuy D. *J. Am. Chem. Soc.* 1988; **110**: 8462.
2. Bortolini O, Meunier B. *J. Chem. Soc., Chem. Commun.* 1983, 1364.
3. Mansuy D, Fontecave M, Bartoli J-F. *J. Chem. Soc., Chem. Commun.* 1983; 253.
4. Campestrini S, Robert A, Meunier B. *J. Org. Chem.* 1991; **56**: 3725.
5. Renaud J-P, Battioni P, Bartoli J-F, Mansuy D. *J. Chem. Soc., Chem. Commun.* 1985; 888.
6. Ellis PE Jr., Lyons JE. *J. Chem. Soc., Chem. Commun.* 1989; 1315.
7. Gonsalves AMd'AR, Johnstone RAW, Pereira MM, Shaw J, Sobral AJFN. *Tetrahedron Lett.* 1991; **32**: 1355.
8. Bartoli J-F, Brigaud O, Battioni P, Mansuy D. *J. Chem. Soc., Chem. Commun.* 1991; 440.
9. Bortolini O, Momenteau M, Meunier B. *Tetrahedron Lett.* 1984; **25**: 5773.
10. Manka JS, Lawrence DS. *J. Am. Chem. Soc.* 1990; **112**: 2440.
11. De Carvalho M-E, Meunier B. *Tetrahedron Lett.* 1983; **24**: 3621.
12. Adler AD, Longo FR, Finarelli JD, Goldmacher J, Assour J, Korsakoff L. *J. Org. Chem.* 1967; **32**: 476.
13. Barnett GH, Hudson MF, Smith KM. *J. Chem. Soc., Perkin Trans. 1* 1975; 1401.
14. Friedman M. *J. Org. Chem.* 1965; **30**: 859.
15. Lecas A, Levisalles J, Renko Z, Rose E. *Tetrahedron Lett.* 1984; **25**: 1563.
16. Adler AD, Longo FR, Kampas F, Kim J. *J. Inorg. Nucl. Chem.* 1970; **32**: 2443.