



ELSEVIER

Journal of Molecular Catalysis A: Chemical 111 (1996) 7–9

JOURNAL OF
MOLECULAR
CATALYSIS
A: CHEMICAL

Reactivity of polyhalogenated metalloporphyrins in epoxidation of propene with magnesium monoperoxyphthalate

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Received 24 August 1995; accepted 6 May 1996

Abstract

Epoxidation of propene with magnesium monoperoxyphthalate used as oxidant and manganese as well as iron polyhalogenated porphyrins as catalysts has been investigated under mild conditions. The systems with manganese tetra-*ortho*-dichlorophenyl- and tetrapentafluorophenylporphyrin appeared very effective and high turnover numbers and selectivities were observed. Porphyrin complexes in which halogen atoms were present in both the phenyl and pyrrole rings showed lower catalytic activity than the complexes with ligands carrying halogen substituents only on the phenyl rings.

Keywords: Metalloporphyrins; Propene; Oxidation

1. Introduction

The oxidants most commonly used in the catalytic metalloporphyrin-based systems for epoxidation of olefins were iodosylarenes, sodium hypochlorite, molecular oxygen, alkyl hydroperoxides, hydrogen peroxide, amine N-oxides, potassium monopersulphate and peroxy acids [1]. Only a few papers deal with the systems employing magnesium monoperoxyph-

thalate which appeared a very efficient and selective oxidant carrying out epoxidation of such olefins as styrene, cyclohexene, cyclooctene, 1-dodecene, 1-octene and propene [2–6]. In this paper we are reporting the results of our further investigations on epoxidation of propene, which is a gaseous and rather inert olefin, with magnesium monoperoxyphthalate (MMPP) and iron as well as manganese halogenated and perhalogenated porphyrins as the catalysts of the reaction.

2. Experimental

Reactions were carried out in a thermostated glass reactor of 150 ml volume, equipped with a magnetic stirrer and branched to an electronic system of valves controlling the supply of

Abbreviations: TTP = 5,10,15,20-tetrakis(*p*-tolyl)porphyrin; TMP = 5,10,15,20-tetrakis(mesityl)porphyrin; TDCPP = 5,10,15,20-tetrakis(*ortho*-dichlorophenyl)porphyrin; TPFPP = 5,10,15,20-tetrakis(pentafluorophenyl)porphyrin; TDCPβCl₈P = 2,3,7,8,12,13,17,18-octachlorotetrakis(*ortho*-dichlorophenyl)porphyrin; TPFβ-Br₈P = 2,3,7,8,12,13,17,18-octabromotetrakis(pentafluorophenyl)porphyrin

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propene and maintaining its constant pressure over the reagent solution. The system was automatically supplying new doses of propene when its pressure dropped in the course of the reaction. Temperature was kept at 25°C.

In a standard experiment the reactor was filled with propene and its contents was checked by GC analysis. The reactions were carried out when the propene concentration was higher than 95%. First 5 ml of ethyl acetate solution of the catalyst were introduced to the reactor and then 10 ml of aqueous solution containing 5×10^{-5} mol of tetrabutylammonium chloride, used as the phase transfer agent, 3.5×10^{-3} mol of magnesium monoperoxyphthalate and 3.125×10^{-4} mol of 4-*tert*-butylpyridine were added. Before each measurement the contents of the active oxygen was checked by iodometric titration.

Metalloporphyrins were synthesized according to the procedure described in [7–10] and their purity was checked by taking UV–vis and NMR spectra. Magnesium monoperoxyphthalate produced by Aldrich contained 80% of the pure complex. 4-*tert*-butylpyridine produced by Aldrich, *tert*-butylammonium chloride purchased from Fluka and ethyl acetate from POCH Gliwice were of purity grade.

The reaction product was identified by MS analysis using GC MS LKB 9000 and more precise measurements were carried out on a Finnigan Incos 500 equipped with NIST Library. The only product found was propene oxide. The amounts of propene oxide were determined by GC analysis using a Chrom 5 apparatus equipped with columns filled with Carbowax 20 M.

3. Results and discussion

All three generations of Mn(III) and Fe(III) porphyrins have been employed as catalysts of epoxidation of propene: simple porphyrins (TTP), sterically hindered porphyrins with methyl or halogen substituents (TMP, TDCPP,

Table 1
Epoxidation of propene with magnesium monoperoxyphthalate and manganese and iron porphyrins as catalysts

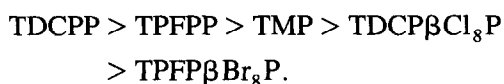
Catalyst	N-base	Turnover ^a	
		[epoxide]/ [catalyst]	[epoxide]/ [propene] × 100
Mn(TMP)Cl	–	0	0
	+	47	95
Mn(TDCPP)Cl	–	200	80
	+	230	80
Mn(TPFPP)Cl	–	224	87
	+	211	91
Mn(TDCPβCl ₈ P)Cl	–	99 ^b	100
	+	132 ^b	72
Mn(TPFPPβBr ₈ P)Cl	–	22	49
	+	26	40
Fe(TDCPP)Cl	–	10 ^b	2
	+	23 ^b	35
Fe(TPFPP)Cl	–	23	59
	+	38	59
Fe(TPFβBr ₈ P)Cl	–	34	47
	+	28	36

[catalyst] = 8×10^{-4} M, [4-*t*-BuPy]:[catalyst] = 25:1, [MMPP] = 2.3×10^{-1} M, [Bu₄NCl] = 3.3×10^{-3} M, $p_{\text{propene}} = 1013$ hPa, $T = 25^\circ\text{C}$.

^a Turnover after 1 min.

^b Turnover after 90 min.

TPFPP) at *ortho* positions of the phenyl rings and perhalogenated porphyrins with halogen substituents present in both the phenyl and the pyrrole rings. Mn(TTP)Cl and Fe(TTP)Cl were found inactive in the investigated reaction and total destruction of the porphyrin ligand was taking place in the course of the reaction. A similar effect was observed for Fe(TMP)Cl while the manganese complex yielded satisfactory results. The experimental results are displayed in Table 1 and Fig. 1, where the propene uptake curves registered during the first two minutes of the reactions catalyzed by the manganese porphyrins are shown. The order of activity found for the manganese porphyrins is the following:



Generally, manganese porphyrins appeared much more active catalysts than the correspond-

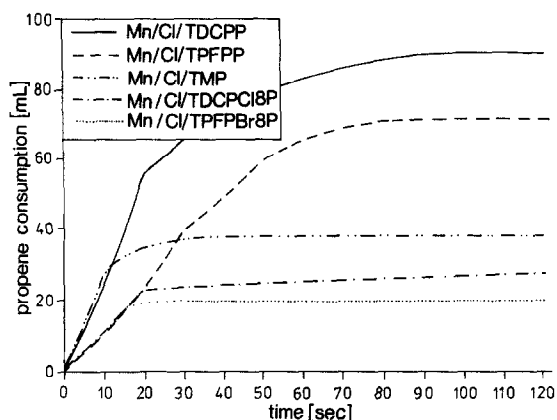


Fig. 1. Propene consumption in the course of epoxidation catalyzed by manganese porphyrins in the presence of 4-*t*-BuPy.

ing iron porphyrins. Contrary to what could have been expected on the basis of the literature data [8,11–14], the activity of the perhalogenated porphyrins appeared lower than that of the halogenated porphyrins. A similar effect was observed in the reactions carried out with hydrogen peroxide and was ascribed to the attack of the oxidant on the β -pyrrolic position of the porphyrin macrocycle [15–17]. The UV–vis measurements proved that the halogenated and perhalogenated manganese porphyrins were still present at the end of the investigated reactions, however at lower concentrations, and the reactions catalyzed by Mn(TDCPP)Cl and Mn(TFPFP)Cl could have been continued with new doses of the oxidant. Lower activity of the latter was observed despite higher electronegativity of the fluorine substituents. This is justified by the small size of the fluorine atoms, which cannot effectively prevent dimerization [18]. The spectrum of the reagent solutions containing the perhalogenated manganese and iron porphyrins taken at the end of the reaction showed the Soret band displaced about 10–20 nm towards shorter wavelengths. Such a shift of the Soret band may be produced by the loss of one or more of the peripheral substituents due to the attack of the oxidant on the β -pyrrolic positions [19,20]. The effect of the N-base on the activity of the system is much less important

than that observed in the reactions with hydrogen peroxide.

When compared with the results obtained by other authors investigating epoxidation of terminal olefins such as 1-dodecene [2] and 1-octene [3,4] with magnesium monoperoxyphthalate and catalyzed correspondingly by Mn(TDCPP) or Mn(TMP), propene is epoxidized with even higher yields and turnovers.

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