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Effect of coordination ability of axial ligands on the stability and catalytic activity of chloro(tetramesitylporphyrinato)manganese(III) and lifetime of Mn-oxo intermediate

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ABSTRACT

Some nitrogen donors, acetate and bromide ions were used as co-catalyst in the epoxidation reaction of *cis*-stilbene by *meta*-chloroperbenzoic acid catalyzed by chloro(tetramesitylporphyrinato)manganese(III). Cyclic voltammetry was used for comparison of coordination ability of these axial ligands. Stability of manganese porphyrin complex and lifetime of Mn-oxo intermediate species were compared using UV–vis spectroscopy in the presence of these axial ligands. It was shown that increasing coordination ability of these axial ligands has positive effects on the stability of the catalyst and also on the stability of Mn-oxo intermediate species but has a negative effect on the catalytic activity of the manganese porphyrin complex.

1. Introduction

Synthetic manganese porphyrin complexes as models for cytochrome P-450 have been used as catalysts for epoxidation of alkenes by oxygen atom donors such as iodosylbenzene [1], sodium hypochlorite [2], molecular oxygen [3], hydrogen peroxide [4,5], *m*-chloroperbenzoic acid (*m*-CPBA) [6,7], urea-hydrogen peroxide [8], potassium and tetra-*n*-butylammonium monopersulfate [9,10]. Stabilization of these complexes and improving their catalytic activities are of great interest. The presence of axial ligands such as pyridines and imidazoles appeared to enhance the conversion and selectivity of the epoxidation reaction [11–15]. Much effort has been made to characterize intermediate active oxidants involved in the possible reaction pathways and to demonstrate reaction mechanisms [16–18].

It has been shown that axial ligands have different effects on the reduction potential of heme due to their different effects on the equilibrium between the oxidized and reduced states of heme. A negative shift in potential indicates that the oxidized state is more stabilized than the reduced state, while a positive shift indicates that binding stabilizes the reduced state [19].

In this work, we obtained the reduction potentials of chloro (tetramesitylporphyrinato)-manganese(III) complex, MnTMP(Cl), in the presence of various axial ligands using cyclic voltammetry. We studied the effects of axial ligands on the catalytic activity and extent of oxidative degradation of MnTMP(Cl) and the lifetime of Mn-oxo intermediate species using these reduction potentials as a measure of metal–axial ligand bond strength.

2. Experimental

2.1. Materials

The free base porphyrin $TMPH_2$ was prepared and purified as reported previously. MnTMP(Cl) was obtained using $MnCl_2{\cdot}4H_2O$ according to the procedure of Adler et al. [20,21]. Nitrogenous bases and tetra-*n*-butylammonium bromide were purchased from Merck or Fluka. *n*-Bu_4NOAc was prepared by adding sodium acetate (30 mmol) to a solution of tetra-*n*-butylammonium hydrogen sulfate (2.0 g, 5.9 mmol) in water (20 mL). The solution was extracted with CH_2Cl_2 (40 mL) and the organic phase was dried over sodium sulfate and filtered. After evaporation of the solvent, the remaining paste was washed with hexane (10 mL) and dried under vacuum.

2.2. General oxidation procedure

Stock solutions of MnPor catalysts (0.003 M) and axial ligands (0.5 M) were prepared in CH_2Cl_2. In a 10 mL round-bottom flask, MnPor (0.001 mmol, 0.3 mL), nitrogen donor (0.1 mmol), *cis*-stilbene (0.1 mmol) were added in 0.5 mL CH_2Cl_2. *m*-CPBA (0.2 mmol) was then added to the reaction solutions at room temperature. The solvent was removed *in vacuo*, the products and

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unreacted alkene were extracted with *n*-hexane. The isomer ratios were determined by ^{1}H NMR spectroscopy.

2.3. UV–vis studies

The electronic absorption spectra were recorded in CH_2Cl_2 solutions by a Perkin Elmer Lambda 25 UV–vis spectrophotometer.

2.4. Cyclic voltammetry

All measurements were performed using a Metrohm electroanalyzer Model 797 VA at room temperature in a conventional three-compartment electrochemical cell consisting of Pt-button working electrode, platinum rod auxiliary electrode and *Ag*/*Ag+* (in CH_3CN solution) electrode as the reference. Cyclic voltammetry measurements were carried out in dry 1,2-dichloroethane using 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte at a scan rate of 0.1 V s^{-1}. However, due to little solubility of 2-MeIm in 1,2-dichloroethane, the cyclic voltammetry measurements in the presence of 2-MeIm were done in dry dichloromethane.

3. Results and discussion

3.1. Effect of coordination ability of axial ligand on the reduction potential of MnTMP(Cl)

Various axial ligands have different effects on the stability and reactivity of MnTMP(Cl) complex. For interpreting these differences, we obtained the reduction potential shifts of Mn(III)/Mn(II) for MnTMP(Cl) (0.001 M) in the presence of some of these axial ligands (0.1 M; 100 times to MnTMP(Cl) complex) (Table 1). For MnTMP(Cl) itself, the Mn(III)/Mn(II) reduction occurs at about −0.45 V in $C_2H_4Cl_2$. ΔE(Mn(III)/Mn(II)) is the difference between the reduction potential of Mn(III)/Mn(II) in the presence of these axial ligands and in the absence of them. The shifts in the reduction potential of MnTMP(Cl) complex (ΔE) are positive for pyridine axial ligand, while these shifts for imidazole axial ligand and OAc^- are negative (Fig. 1). The molar ratio of axial ligand/MnTMP(Cl) has also a significant effect on the reduction potential of MnTMP(Cl). Pyridines causes smaller shift in the reduction potential of MnTMP(Cl) complex in contrast to what observed for imidazoles and specially for OAc^- (Fig. 2). The reduction potentials are nearly constant after molar ratio of 100, thus we used this molar ratio for comparing the results in Table 1 and Fig. 1.

Table 1
Reduction potential shifts of Mn(III)/Mn(II) for MnTMP(Cl) in the presence of various axial ligands (100 times to MnTMP(Cl) complex).

Entry	Axial ligand	pK_a[a]	ΔE(Mn(III)/Mn(II))[b]
1	Py	5.25	0.079
2	4-MePy	6.02	0.025
3	ImH	6.95	−0.076
4	2-MeIm	7.86	−0.27
5	OAc^-	4.76	−0.74
6	Br^-	−8.7	−0.11

[a] For conjugated acid.
[b] $\Delta E = E' - E$, E' and E are the reduction potentials of Mn(III)/Mn(II) in the presence and absence of axial ligands respectively.

ΔE could be related to coordination ability of these axial ligands to Mn center [19,22–24]. But the coordination ability of these axial ligands could not be illustrated merely by pK_a values of their conjugate acid (Table 1). π-bond effects should also be considered. A ligand with a greater σ-donation or greater π-donation ability could stabilize the higher oxidation states of the metal and reduction potential should be more negative. 4-MePy is a better σ-donor than Py (as their pK_a values show), so its reduction potential is less positive. Imidazole ligands are better σ donors and better π donors than pyridine ligands, so their reduction potentials are more negative. Although OAc^- is a weaker σ-donor, but it is very strong π-donor, its most negative reduction potential could be related to its great π-donation. Br^- is a very weak σ-donor, but it is a good π-donor, so its reduction potential is negative, but not as negative as OAc^-.

3.2. Effect of coordination ability of axial ligand on the stability of MnTMP(Cl) and on the life time of intermediate oxo species

The reaction of MnTMP(Cl) complex with *m*-CPBA oxidant was studied in the presence of different concentrations of some selected nitrogen donors and two anionic axial ligands, under MnTMP(Cl)/axial ligand/*m*-CPBA molar ratio of 1/*x*/200 in CH_2Cl_2 at room temperature. The Soret band of Mn-oxo in the presence

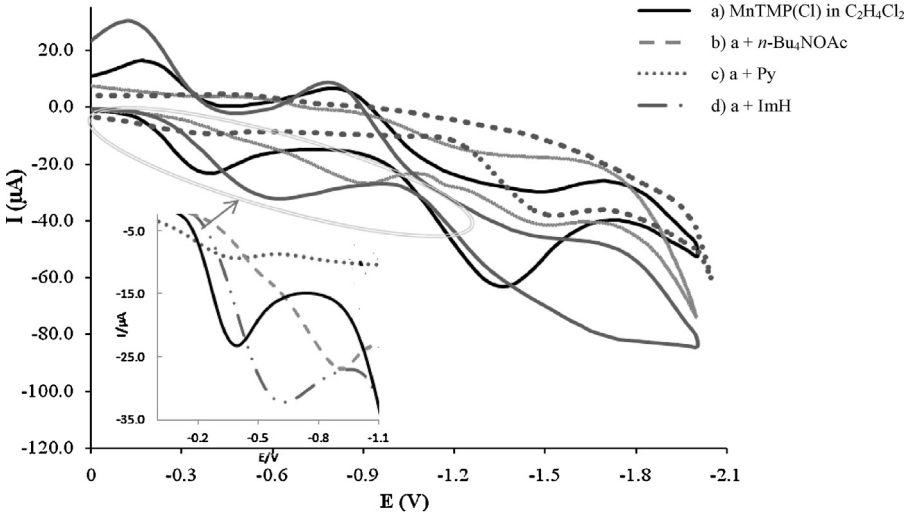

Fig. 1. Cyclic voltammogram of MnTMP(Cl) (0.001 M): (a) in the absence of axial ligand, (b) in the presence of acetate, (c) in the presence of pyridine, (d) in the presence of imidazole (axial ligand/MnTMP(Cl) molar ratio equal to 100/1). The inset shows the peak position of the reduction potential of Mn(III)/Mn(II) in the absence of axial ligand (solid line) and in the presence of acetate (dashed line), pyridine (dotted line), and imidazole (dash-dotted line). Cyclic voltammetry measurements were carried out in dry dichloroethane using 0.1 M tetrabutylammonium perchlorate (TBAP) as supporting electrolyte at a scan rate of 0.1 V s^{-1}.