

# Catalytic activity of iron and cobalt phthalocyanine complexes towards the oxidation of cyclohexene using *tert*-butylhydroperoxide and chloroperoxybenzoic acid

Nthapo Sehlotho, Tebello Nyokong\*

Department of Chemistry, Rhodes University, P.O. Box 94, Grahamstown 6140, South Africa

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## Abstract

Cyclohexene oxidation using *tert*-butylhydroperoxide (TBHP) or chloroperoxybenzoic acid (CPBA) in the presence of iron(II) polychlorophthalocyanine ( $\text{Cl}_{16}\text{PcFe}$ ), iron(II) phthalocyanine ( $\text{PcFe}$ ) and cobalt(II) phthalocyanine ( $\text{PcCo}$ ), results in the formation of the following products: cyclohexene oxide, 2-cyclohexene-1-ol and 2-cyclohexene-1-one. Adipic acid was also formed after long reaction times. The selectivity for 2-cyclohexene-1-one is favoured when  $\text{Cl}_{16}\text{PcFe}$  or  $\text{PcCo}$  catalysts are employed, while  $\text{PcFe}$  is selective towards the formation of 2-cyclohexene-1-ol. The  $\text{Cl}_{16}\text{PcFe}$  catalyst is transformed into a  $\mu$ -oxo dimer ( $\text{Cl}_{16}\text{PcFe}^{\text{III}}\text{--O--}^{\text{III}}\text{FePcCl}_{16}$ ) during the oxidation process. The catalytic process using the unsubstituted  $\text{PcCo}^{\text{II}}$  and  $\text{PcFe}^{\text{II}}$  catalysts involved  $\text{PcM}^{\text{III}}$  species as an intermediate. The active form of the  $\text{Cl}_{16}\text{PcFe}$  catalyst was stable to degradation in that it was still active even after 4 weeks of continued catalysis.

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## 1. Introduction

Metalloporphyrin complexes can catalyse the oxidation of the relatively inert carbon–hydrogen bond under mild conditions, thus mimicking the action of cytochrome P-450 dependent monooxygenases. Transformation of alkenes to high value chemicals such as alcohols and ketones is of importance to industry.

Synthetic iron porphyrin complexes have been extensively investigated as models for the catalytic action of cytochrome P-450 [1–4]. However, porphyrins often degrade during the catalytic process. One way of circumventing this problem has been to create a more resistant porphyrin ring through ring substitution using electron withdrawing axial ligands [5–11]. Metallophthalocyanine ( $\text{PcM}$ ) complexes have a similar structure to the porphyrins, but are more stable to degradation. Both  $\text{PcM}$  and porphyrin complexes have been shown to exhibit good biomimetic catalytic activity [12,13]. As with porphyrin complexes, ring substitution in phthalocyanines with electronegative substituents was

found to enhance their catalytic activity [14]. The use of halogenated metallophthalocyanines as heterogeneous catalysts for the oxidation of cyclohexane has been reported in a patent application [15]. Perfluorinated iron phthalocyanine was found to have less catalytic activity than  $\text{PcFe}$  towards the formation of cyclohexanol from cyclohexane, this was attributed to the low solubility of the perfluorinated catalyst in dichloromethane [1]. Supported  $\text{PcM}$  complexes show better catalytic activity than the corresponding unsupported derivatives towards oxidation of cyclohexane [16].

Even though there has been several reports on the use of  $\text{PcM}$  complexes as biomimetic catalysts for the oxidation of alkanes [1,13,15–17], there has been less attention on the use of these molecules for the epoxidation of alkenes [14,18]. The oxidation of cyclohexene in the presence of  $\text{Mn(III)}$ ,  $\text{Co(II)}$  and  $\text{Fe(II)}$  tetra-*tert*-butylphthalocyanines resulted in the formation of cyclohexene oxide and 2-cyclohexene-1-one [18]. The catalytic oxidation was performed in the presence of a reducing agent, isobutylaldehyde. The main products of the epoxidation of styrene using  $\text{CuPc}$  were styrene epoxide and benzaldehyde [14]. It has been reported that  $\text{PcMn}$  and  $\text{PcFe}$  are among the effective phthalocyanine complexes for epoxidation of alkenes when iodosylbenzene was employed as an oxidant [19].

\* Corresponding author. Tel.: +27-46-6038260; fax: +27-46-622-5109.  
E-mail address: [t.nyokong@ru.ac.za](mailto:t.nyokong@ru.ac.za) (T. Nyokong).

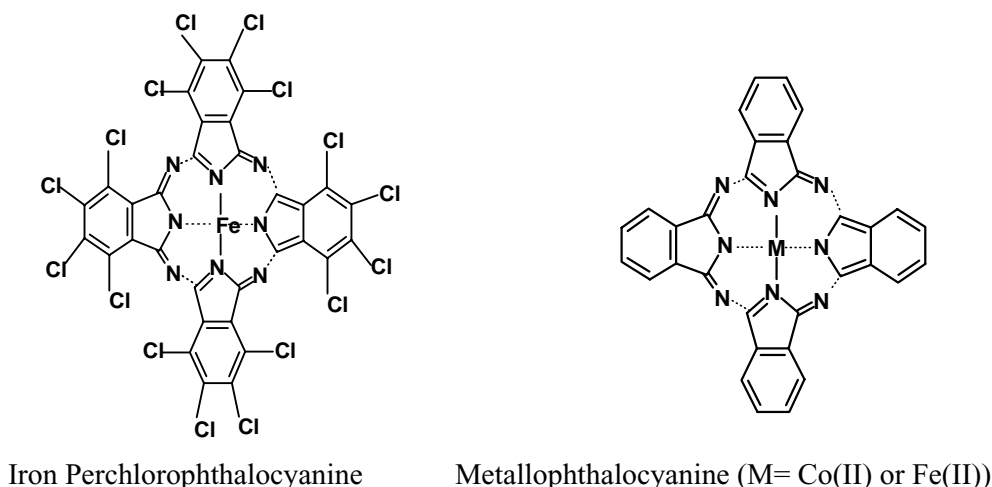


Fig. 1. Molecular structure of Fe(II) perchlorinated phthalocyanine ((Cl)<sub>16</sub>PcFe) and unsubstituted Fe(II) and Co(II) phthalocyanines.

When porphyrins were employed as catalysts for catalytic oxidation of cyclohexene, cyclohexene epoxide has been reported to be the main product, with cyclohex-2-en-1-ol and cyclohex-2-en-1-one as the minor products [6,20]. Total yields greater than 100% have been reported for porphyrin catalysed oxidation of cyclohexene and have been attributed to autooxidation involving dioxygen trapping of cyclohexenyl radicals [20]. Deactivation of the active form of the catalyst by the oxidant has also been reported in Fe porphyrins [10]. Relative yields of the oxidation products as well as the stability of the catalyst, depend on the nature of the substituents attached to the porphyrin and phthalocyanine ring. In this work, we report on the use of iron polychlorophthalocyanine (Cl<sub>16</sub>PcFe), Fig. 1, as a catalyst for the oxidation of cyclohexene, with the aim of improving product selectivity and increasing the range of products. Since degradation is still a problem for porphyrin catalysts, the search for more stable catalysts is of interest. Pcs are generally more stable to degradation than porphyrins, hence the interest in their study as catalysts for the transformation of alkenes. The catalytic activity of this species is compared to that of unsubstituted PcFe and PcCo. The study of the fate of the Pc catalyst during catalysis is of importance for the development of new catalysts. The fate of the Pc catalyst has not been fully investigated following catalysis of cyclohexene transformation using these compounds in previous studies. The changes in the nature of the Cl<sub>16</sub>PcFe catalyst was monitored using UV-Vis spectroscopy.

## 2. Experimental

### 2.1. Materials

Iron(II) hexadecachlorophthalocyanine (Cl<sub>16</sub>PcFe) was synthesized, purified and characterized according to literature methods [21]. *Tert*-butylhydroperoxide (TBHP, 70%

in water), chloroperoxybenzoic acid (CPBA), diazabicyclooctane (DABCO), cyclohexene, cyclohexene oxide, 2-cyclohexene-1-ol and 2-cyclohexene-1-one were purchased from Aldrich and used as received. Dimethylformamide (DMF), dichloromethane and methanol were of gas chromatography (GC) or high pressure liquid chromatography (HPLC) grade.

### 2.2. Oxidation reactions

The solvent mixture containing DMF and dichloromethane (3:7) was employed for the catalysis, since all the reagents dissolved and this ratio gave the highest yields of the products. The reaction mixture was as follows: known amounts of the Cl<sub>16</sub>PcFe, PcCo or PcFe catalyst and cyclohexene were dissolved in the solvent mixture, the GC trace was recorded, then the oxidant (TBHP or CPBA) was added and the reaction monitored with time using GC. The UV-Vis absorption spectra of the catalyst was monitored with time during the catalysis. Reported yields are based on the substrate. Reactions were run at least in triplicates and not always using the same batches of the catalysts, oxidant or substrate. The molar extinction coefficient of Cl<sub>16</sub>PcFe catalyst has been reported [17] to be  $7.4 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$  in the DMF/dichloromethane solvent mixture. This value was employed for the determination of concentration of this species in solution.

The oxidation products were identified by spiking using standards and by measurements of retention times in gas chromatography. The nature of the products were also determined by a gas chromatograph connected to a mass spectrometer (GCMS).

### 2.3. Physical measurements

The GC traces were recorded with an Hewlett-Packard HP 5890 Gas Chromatograph fitted with an FID detector, using a cross-linked methyl siloxane capillary column

(30 m length, 0.32 mm internal diameter and 0.25  $\mu\text{m}$  film thickness). The parameters for analysis were: carrier gas  $\text{N}_2$  at  $30.7 \text{ cm s}^{-1}$ , injector temperature =  $200^\circ\text{C}$ , detector temperature =  $250^\circ\text{C}$ . Mass spectra was recorded with Finnigan LCQ-MS coupled with J&W Scientific column of 30 m length, 0.32 mm internal diameter and 0.25  $\mu\text{m}$  film thickness. UV-Vis spectra was recorded with the Cary 500 UV-Vis/NIR Spectrophotometer.

### 3. Results and discussion

#### 3.1. Catalytic oxidation products

The use of TBHP as an oxidant was based on the earlier studies on the oxidation of cyclohexane [17], this oxidant was found to cause minimal destruction of the phthalocyanine catalyst, and to give better selectivity of the products. For comparative purposes, CPBA was also employed as an oxidant. Three products were clearly identified using gas chromatography by both spiking and comparison with standards. These products are cyclohexene oxide, 2-cyclohexene-1-ol and 2-cyclohexene-1-one, Table 1. Product identification was confirmed by mass spectra, which showed M-1 peak at 97  $m/z$  for cyclohexene oxide and cyclohexene-ol, and  $\text{M}^+$  peak at 96  $m/z$  for cyclohexene-1-one. Reported [18] products for the oxidation of cyclohexene in the presence of metallo tetra-*tert*-butylphthalocyanine complexes are cyclohexene oxide and 2-cyclohexene-1-one, with the former being the major product. This work shows the formation of 2-cyclohexene-1-ol in addition to cyclohexene oxide and 2-cyclohexene-1-one when phthalocyanine complexes are employed as catalysts. After prolonged reaction time, a new peak was formed which was identified by GC and GC-MS as being due to adipic acid. It was also confirmed (using GC) that TBHP is converted to tert butanol during the catalytic process.

The nature and the relative yields of the products formed by catalytic oxidation of cyclohexene using porphyrins vary considerably depending on the catalyst and oxidant. When iron porphyrin containing nitrate or perchlorate as axial ligands was employed for the oxidation of cyclohexene using chloroperoxybenzoic acid, large yields of cyclohexene oxide were obtained (68–78%), but when chloride axial ligands

were employed using the same oxidants, the yields of cyclohexene oxide were less than 2% [22]. Higher yields of cyclohexene oxide relative to the other products were observed for most porphyrins using oxidants such as chloroperoxybenzoic acid or iodosylbenzene [6,20]. However, photooxygenation of cyclohexene using titanium porphyrins resulted in the formation of cyclohexene hydroperoxide as a major product, with cyclohexene oxide being one of the side products [23]. Table 1 shows that the catalyst,  $\text{Cl}_{16}\text{PcFe}$  favoured the formation of 2-cyclohexene-1-one to the rest of the products. The yields for the formation of cyclohexene oxide shown in Table 1 are comparable in some cases to those reported for oxidation of cyclohexene using porphyrins and iodozobenzene as an oxidant [6,20], and are higher than the yield of cyclohexene oxide using iron porphyrin derivatives axially ligated with chloro or hydroxo [22] and using hydrogen peroxide as oxidant. The yields of products using the  $\text{Cl}_{16}\text{PcFe}$  catalyst reported in Table 1 are after 8 h and again after 4 weeks of catalysis. Thus, the yields increased steadily with time and improved to total values greater than 100% after 4 weeks. Yields consistently higher than 100% have been reported for porphyrins catalysts and attributed to autooxidation as has been proposed before [20]. Thus, after prolonged catalysis, the yields obtained for Pc catalysts are comparable to porphyrins with added stability for the former.

The yields observed for the formation of cyclohexene oxide from the oxidation of cyclohexene in the presence of  $\text{Mn(III)}$ ,  $\text{Co(II)}$  and  $\text{Fe(II)}$  tetra-*tert*-butylphthalocyanines (MTTBPC) and in the presence of a reducing agent, isobutyraldehyde [18] are higher than those reported in this work. However, the yields obtained using the MTTBPC as catalysts stabilized after about 10 h, while as will be discussed below, the yields for the cyclohexene-one, cyclohexene oxide and cyclohexene-ol increased even after 4 weeks of the reactions. The fact that the  $\text{Cl}_{16}\text{PcFe}$  catalyst is selective to the formation of 2-cyclohexene-1-one over that of cyclohexene oxide and maintained stability (of the active form of the catalyst) even after prolonged use, are useful observations. Relatively high turn-over values were obtained for the catalytic process employing  $(\text{Cl})_{16}\text{PcFe}$ , Table 1.

Unsubstituted PcFe showed selectivity towards cyclohexene-ol not cyclohexene-one observed for perchlorinated  $\text{Cl}_{16}\text{PcFe}$ , Table 2. Unsubstituted PcCo, however showed selectivity towards the cyclohexene-one, Table 2. Catalytic reactions of PcM complexes may be assumed to be accompanied by coordination of the oxidant to the central metal

Table 1

Product yields (based on the substrate), selectivities and turnover numbers for the oxidation of  $1.6 \text{ mol dm}^{-3}$  cyclohexene using TBHP ( $0.5 \text{ mol dm}^{-3}$ ) as an oxidant and  $\text{Cl}_{16}\text{FePc}$  ( $1.7 \text{ mg/ml}$  as the catalyst)

Product	Yield (%) <sup>a</sup>	Yield (%) <sup>b</sup>	Selectivity (5)	Turnover number
Cyclohexene oxide	3.5	8.5	7.8	39.8
2-Cyclohexen-1-ol	9.1	78.6	20.0	209
2-Cyclohexen-1-one	32.7	98.9	72.2	494

<sup>a</sup> After 8 h.

<sup>b</sup> After 4 weeks.

Table 2

Product selectivities when using different catalysts, namely  $\text{Cl}_{16}\text{FePc}$ ,  $\text{FePc}$  and  $\text{CoPc}$  ( $1.7 \text{ mg/ml}$ ) and TBHP ( $0.5 \text{ mol dm}^{-3}$ ) as an oxidant

Product	$\text{FeCl}_{16}\text{Pc}$	$\text{FePc}$	$\text{CoPc}$
Cyclohexene oxide	7.8	3.8	5.5
2-Cyclohexen-1-ol	20.0	71.2	33.7
2-Cyclohexen-1-one	72.2	25.0	60.8

Cyclohexene =  $1.6 \text{ mol dm}^{-3}$ .

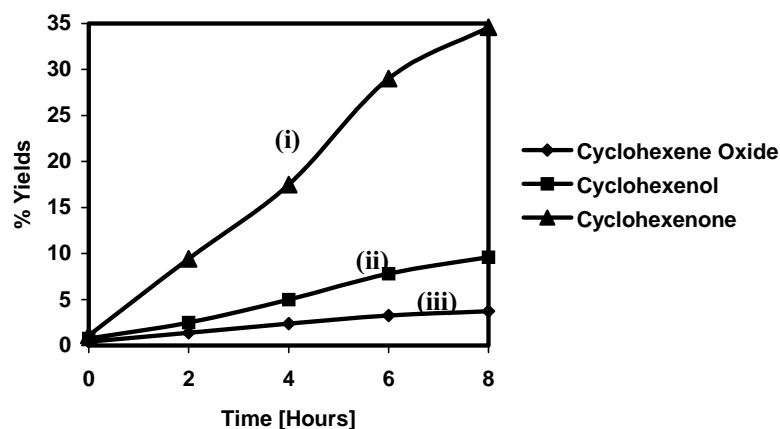


Fig. 2. Variation of product yield with time. (i) 2-cyclohexene-1-one, (ii) 2-cyclohexene-1-ol and (iii) cyclohexene oxide. Starting concentrations: cyclohexene =  $1.6 \text{ mol dm}^{-3}$  and TBHP =  $0.5 \text{ mol dm}^{-3}$ ; Catalyst =  $(\text{Cl})_{16}\text{PcFe}$  ( $1.7 \text{ mg/ml}$ ). Dimethylformamide/dichloromethane (3:7) solvent mixture.

of the catalyst, in a similar manner to porphyrins [24]. PcM complexes containing different central metal ions will have varying coordination abilities and this may result in varying modes and rates of cleavage of the PcM-oxidant bonds hence resulting in different product selectivities.

It has been shown [25] that CPBA oxidant coordinates to the Fe porphyrin complex during catalysis, followed by heterolytic O–O bond cleavage to afford the active O–Fe species. The rate of O–O bond cleavage was found to be lower for Fe porphyrin complexes containing electron withdrawing ring substituents. Since it has been proposed [26] that the mechanism of alkene epoxidation using phthalocyanine catalysts may be similar to that of porphyrins, the presence of electron withdrawing groups could affect the rate of formation of active intermediates in PcFe derivatives, resulting in different selectivities of products for the PcFe and  $(\text{Cl})_{16}\text{PcFe}$  complexes.

Experiments were carried out with varying amounts of the  $\text{Cl}_{16}\text{PcFe}$  catalyst, oxidant or substrate and using fixed amounts of the other two reagents. Fig. 2 shows that for fixed oxidant and substrate molar ratio, the yield for all the prod-

ucts increased with time, and showed slowing down after 8 h. However, the yields of the products: cyclohexene-one, cyclohexene oxide and cyclohexene-ol showed slow increase even after 4 weeks of the reaction. With the substrate larger than the oxidant (and fixed amount of catalyst), the product yield showed no significant dependence on the substrate:oxidant ratio, Fig. 3. The yield generally increased with catalyst concentration as shown in Fig. 4.

When unsubstituted PcFe or PcCo were employed as catalysts, the products were formed within a very short time, and the product yield did not increase significantly with time after about 4 h, Fig. 5.

### 3.2. The fate of the catalysts

The spectra of iron phthalocyanines has been a subject of several reports [27,28] and much controversy. In the absence of oxygen, the spectra of  $\text{Cl}_{16}\text{PcFe}$  in DMF consists of a sharp Q band due to the monomeric species [27]. In the presence of oxygen, the spectra broadens and shifts to the blue due to the formation of  $\mu$ -oxo dimeric species of

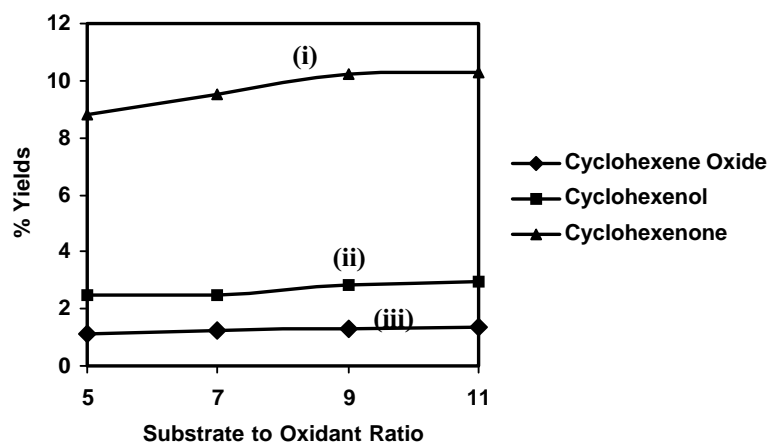


Fig. 3. Variation of product yield with substrate to oxidant molar ratios (substrate in excess). (i) 2-cyclohexene-1-one, (ii) 2-cyclohexene-1-ol and (iii) cyclohexene oxide. Catalyst =  $(\text{Cl})_{16}\text{PcFe}$  ( $1.7 \text{ mg/ml}$  of solvent mixture). Dimethylformamide/dichloromethane (3:7) solvent mixture. Reaction time 8 h.

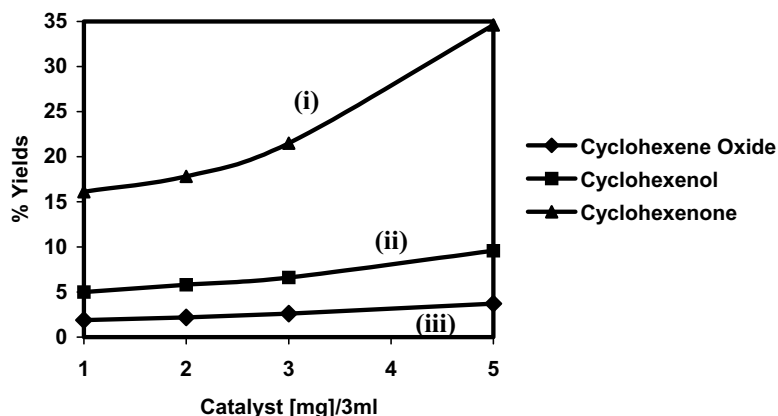


Fig. 4. Variation of product yield with the amount of catalyst. (i) 2-cyclohexene-1-one, (ii) 2-cyclohexene-1-ol and (iii) cyclohexene oxide. Starting concentrations: cyclohexene =  $1.6 \text{ mol dm}^{-3}$ , TBHP =  $0.5 \text{ mol dm}^{-3}$ . Dimethylformamide/dichloromethane (3:7) solvent mixture. Reaction time 8 h. Catalyst =  $(\text{Cl})_{16}\text{PcFe}$ .

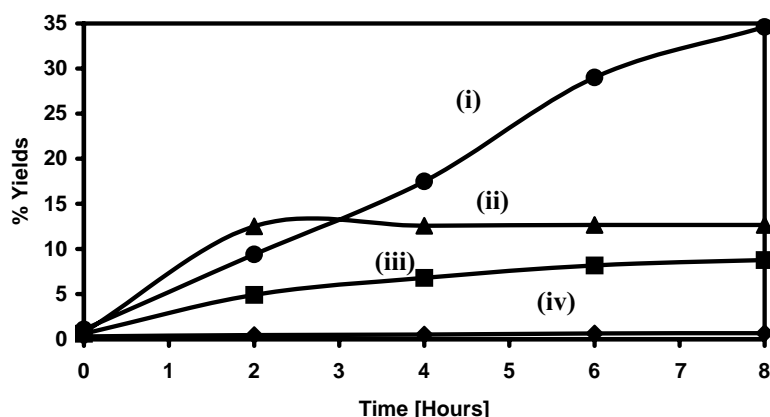


Fig. 5. Effect of the nature of catalyst on the cyclohexene-1-one product yield. (i)  $(\text{Cl})_{16}\text{PcFe}$ , (ii) FePc, (iii) CoPc and (iv) no catalyst. Catalyst concentration =  $1.7 \text{ mg/ml}$  in all cases. Starting concentrations: cyclohexene =  $1.6 \text{ mol dm}^{-3}$  and TBHP =  $0.5 \text{ mol dm}^{-3}$ . Dimethylformamide/dichloromethane (3:7) solvent mixture.

the form  $\text{Cl}_{16}\text{PcFe}^{\text{III}}-\text{O}-\text{FePcCl}_{16}$  [27]. Fig. 6a shows spectral changes observed for the catalyst  $\text{Cl}_{16}\text{PcFe}$  during the catalytic oxidation of cyclohexene in the presence of TBHP as oxidant. The spectrum in Fig. 6a(i) is typical of the monomeric form of the  $\text{Cl}_{16}\text{PcFe}^{\text{II}}$  complex before the

start of the catalytic process with a Q band at 681 nm. Immediately after addition of oxidant, the Q band reduces in intensity and it becomes split (Fig. 6a (i)). The split components are observed at 648 and 678 nm. The split in the Q band is typical of the oxidation of  $\text{Fe}(\text{II})\text{Pc}$  to  $\text{Fe}(\text{III})\text{Pc}$

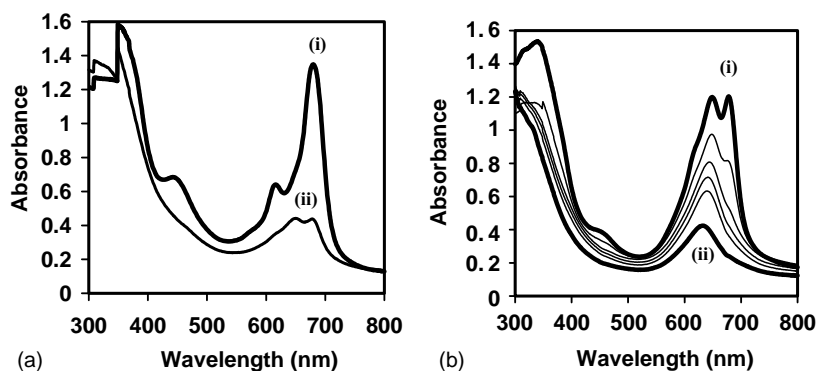
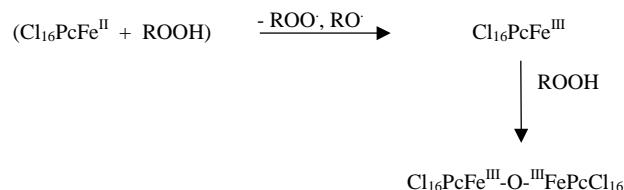


Fig. 6. Electronic absorption spectral changes observed on addition of TBHP oxidant ( $0.5 \text{ mol dm}^{-3}$ ) to a reaction mixture containing  $(\text{Cl})_{16}\text{PcFe}$  catalyst cyclohexene. Initial concentrations:  $(\text{Cl})_{16}\text{PcFe}$  =  $1.7 \text{ mg/ml}$ , cyclohexene =  $1.6 \text{ mol dm}^{-3}$ . For spectral measurements, the solution made of these reagents was diluted hundred fold. (a) (i) before addition and (ii) immediately after addition of TBHP to catalyst/substrate mixture. (b) (i) same as spectrum (ii) in Fig. 6(a) and (ii) spectrum 8 h after addition of TBHP to catalyst/substrate mixture.

species [29]. Thus, spectral changes shown in Fig. 6a are consistent with the oxidation of the  $\text{Cl}_{16}\text{PcFe}^{\text{II}}$  and the formation  $\text{Cl}_{16}\text{PcFe}^{\text{III}}$  species. Following the split in the Q band, the 678 nm band decreased in intensity and finally disappears as the catalytic process proceeds. The 648 nm band on the other hand gradually shifts to lower wavelength and after about 8 h, this band is observed at 636 nm, Fig. 6b (ii). Oxidants such as iodosobenzene are known to convert  $\text{PcFe}^{\text{II}}$  species to the  $\mu$ -oxo species,  $\text{PcFe}^{\text{III}}\text{--O--}^{\text{III}}\text{FePc}$  [29], which is characterized by a low intensity broad Q band at  $\sim 630$  nm. Thus, the final spectrum in Fig. 6b is typical of  $\mu$ -oxo species, confirming that the final form of the catalyst following the oxidation of cyclohexene using TBHP oxidant, is the  $\text{Cl}_{16}\text{PcFe}^{\text{III}}\text{--O--}^{\text{III}}\text{FePcCl}_{16}$  species. The oxidation is probably accompanied by some degradation of the catalyst as judged by the decrease in the Q band intensity, though the  $\text{PcFe}^{\text{III}}\text{--O--}^{\text{III}}\text{FePc}$  species typically show a weak Q band. The catalyst was still present even after 4 weeks of catalysis, with the yields of the products still increasing. The solution turned from blue to brown, even though the 636 nm band was still present after 4 weeks of catalysis. When CPBA was employed as an oxidant for cyclohexene oxidation using  $\text{Cl}_{16}\text{PcFe}^{\text{II}}$  catalyst, fast degradation of the catalyst was observed, with the final formation of a weak high energy band at 636 nm, Fig. 7, hence confirming the formation the  $\mu$ -oxo species as was the case for TBHP. However, complete disappearance of 636 nm band was observed within 2 h when CPBA was employed as an oxidant, showing that this oxidant degrades the phthalocyanine molecule more readily than TBHP.

Oxidation of cyclohexane [17] using the  $\text{Cl}_{16}\text{PcFe}$  catalyst and chloroperoxybenzoic acid oxidant, showed different



Scheme 1. The mechanism for  $\text{Cl}_{16}\text{PcFe}^{\text{II}}$  transformation during the catalytic oxidation of cyclohexene. ROOH—represents the oxidants, TBHP or CPBA.

spectral features from those reported here in that the  $\mu$ -oxo dimer was not formed only the  $\text{Fe}^{\text{III}}\text{Pc}$  species was observed. Thus, the formation of the  $\mu$ -oxo species following oxidation of  $\text{Fe}^{\text{II}}\text{Pc}$  species may be determined by both the nature of the substrate and the oxidant.

The  $\text{PcCo}$  and  $\text{PcFe}$  catalysts were readily deactivated, with the solutions changing from blue to brown in a very short time (within 2 h). For  $\text{PcFe}$  catalysis of cyclohexene oxidation, the Q band of  $\text{PcFe}$  at 660 nm split into bands at 674 and 637 nm on addition of TBHP oxidant, consistent with the formation of the  $\text{PcFe}^{\text{III}}$  species. However, the latter degraded very fast. For the  $\text{PcCo}$  catalyst, an initial shift of the Q band from 662 nm to 666 nm, typical [29] of oxidation of  $\text{PcCo}^{\text{II}}$  to  $\text{PcCo}^{\text{III}}$ , was observed followed by total disappearance of the Q band. Thus, for both  $\text{PcCo}$  and  $\text{PcFe}$ , the  $\text{PcM}^{\text{III}}$  species are implicated in the catalytic process. However, both of these catalysts are readily degraded and hence the unsubstituted  $\text{PcCo}$  and  $\text{PcFe}$  catalysts are not efficient for the catalytic oxidation of cyclohexene.

Spectral changes shown in Fig. 6 suggest the following mechanism for the  $\text{Cl}_{16}\text{PcFe}^{\text{II}}$  catalyst, Scheme 1.

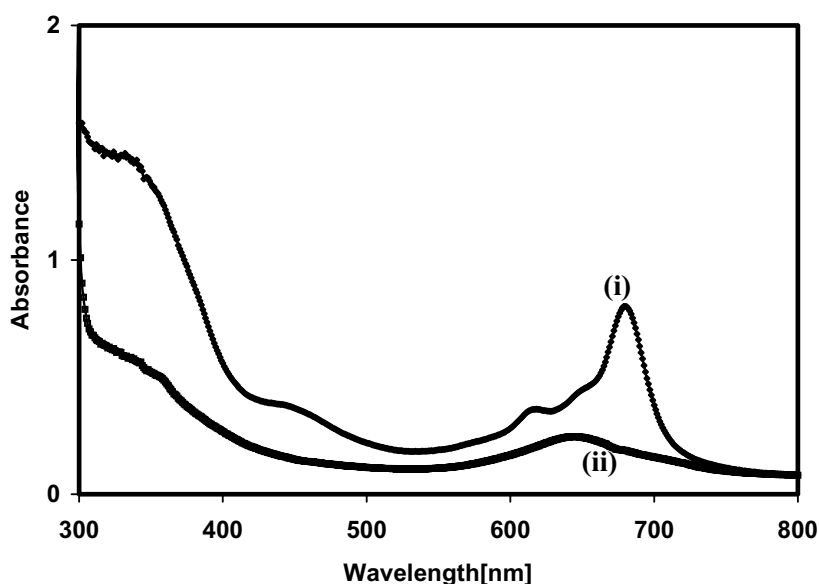
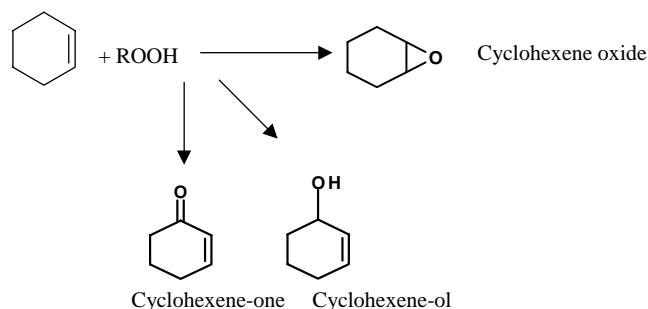


Fig. 7. Electronic absorption spectral changes observed on addition of CPBA oxidant ( $0.5 \text{ mol dm}^{-3}$ ) to a reaction mixture containing  $(\text{Cl})_{16}\text{PcFe}$  catalyst and cyclohexene. Initial concentrations:  $[(\text{Cl})_{16}\text{PcFe}] = 1.7 \text{ mg/ml}$ ,  $[\text{cyclohexene}] = 1.6 \text{ mol dm}^{-3}$ . For spectral measurements, the solution made of these reagents was diluted hundred fold. (i) before addition and (ii) immediately after addition of CPBA to catalyst/substrate mixture.





Scheme 2. Products formed through oxidation of cyclohexene by TBHP or CPBA in the presence of  $(\text{Cl})_{16}\text{PcFe}$ ,  $\text{CoPc}$  or  $\text{FePc}$  catalysts.

It is expected that  $\text{ROO}^\bullet$  and  $\text{RO}^\bullet$  radicals will be formed, since these have been suggested as the species involved in the catalytic processes involving phthalocyanines and porphyrins [30]. When DABCO (a radical scavenger) was added to the reaction mixture, there was a decrease in product yield, confirming the involvement of radicals in the mechanism for the catalytic oxidation of cyclohexene. It has also been shown [26] that when  $\text{PcFe}^{\text{III}}$  is employed as a catalyst, with iodosylbenzene as an oxidant, a  $\text{PcFe}^{\text{IV}}=\text{O}$  species is an intermediate in the epoxidation of alkenes. However, we have no spectroscopic evidence for the formation of an  $\text{PcFe}^{\text{IV}}$  intermediate in this work.

Product formation for the transformation of cyclohexene in the presence of  $(\text{Cl})_{16}\text{PcFe}$  and TBHP (or CPBA) oxidant may be represented by Scheme 2.

In conclusion, we have shown in this work that oxidation of cyclohexene using the TBHP or CPBA oxidants and in the presence of  $\text{Cl}_{16}\text{PcFe}$ ,  $\text{PcFe}$  and  $\text{PcCo}$  as catalysts leads to the formation of cyclohexene oxide, 2-cyclohexene-1-ol and 2-cyclohexene-1-one as products. The product selectivity varied with the nature of the catalyst and oxidant, with  $\text{Cl}_{16}\text{PcFe}$  and  $\text{PcCo}$  showing selectivity towards cyclohexene-one, while  $\text{PcFe}$  favours the formation of cyclohexene-ol. When  $\text{Cl}_{16}\text{PcFe}$  was employed as catalyst and TBHP as oxidant, the highest yields were obtained for the 2-cyclohexene-1-one. The  $\text{Cl}_{16}\text{PcFe}$  catalyst is transformed to the  $\text{Cl}_{16}\text{PcFe}^{\text{III}}-\text{O}-^{\text{III}}\text{FePcCl}_{16}$  species during the catalytic process.  $\text{PcFe}^{\text{III}}$  and  $\text{PcCo}^{\text{III}}$  species were implicated as intermediates when the  $\text{PcFe}$  and  $\text{PcCo}$  complexes were employed as catalysts. The active form of the  $\text{Cl}_{16}\text{PcFe}$  catalyst was stable to degradation in that it was still active even after 4 weeks of catalysis.

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