

Iron perchlorophthalocyanine and tetrasulfophthalocyanine catalyzed oxidation of cyclohexane using hydrogen peroxide, chloroperoxybenzoic acid and *tert*-butylhydroperoxide as oxidants

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Abstract

Polychlorophthalocyanine ($\text{Cl}_{16}\text{PcFe}^{\text{II}}$) and tetrasulfophthalocyanine ($[\text{Fe}^{\text{II}}\text{TSPc}]^{4-}$) complexes of iron are employed as catalysts for the oxidation of cyclohexane using *tert*-butyl hydroperoxide (TBHP), *m*-chloroperoxybenzoic acid (*m*-CPBA) and hydrogen peroxide as oxidants. Catalysis using the $\text{Cl}_{16}\text{PcFe}^{\text{II}}$ was performed in a dimethylformamide:dichloromethane (3:7) solvent mixture. For the $[\text{Fe}^{\text{II}}\text{TSPc}]^{4-}$ catalyst, a water:methanol (1:9) mixture was employed. The products of the catalysis are cyclohexanone, cyclohexanol and cyclohexanediol. The relative yields of the products depended on oxidant and the catalyst. TBHP was found to be the best oxidant since minimal destruction of the catalyst and higher selectivity in the products were observed when this oxidant was employed. The mechanism of the oxidation of cyclohexane in the presence of the $\text{Cl}_{16}\text{PcFe}^{\text{II}}$ and $[\text{Fe}^{\text{II}}\text{TSPc}]^{4-}$ involves the oxidation of these catalysts, forming an Fe(III) phthalocyanine species as an intermediate. Higher yields were observed when $[\text{FeTSPc}]^{4-}$ was employed as a catalyst, which is more soluble than the perchlorinated iron phthalocyanine catalyst. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Iron phthalocyanine; Cyclohexane; Cyclohexanone; Cyclohexanol; Cyclohexanediol

1. Introduction

The search for biomimetic analogs of cytochrome P-450 [1] for selective oxidation of hydrocarbons has been a subject of several investigations in recent years. Metalloporphyrin complexes have been studied extensively for use as catalysts for hydrocarbon oxidation [2–10]. Halogenated metalloporphyrin complexes have been used successfully as catalysts for hydrocarbon oxidation due to increased stability (induced by the halogens) of the porphyrin ring towards degradation. Metallophthalocyanine (MPc) complexes have a

similar structure to the porphyrins, but the former are more stable to degradation. MPc complexes are also cheaper and more readily available than porphyrins. Both the porphyrins and phthalocyanines are useful catalysts that allow control of the active form of oxygen, resulting in selectivity of the products formed.

The use of MPc complexes as catalysts for the chlorinated phenols, using oxidants such as hydrogen peroxide, has received considerable attention in recent years [11–17]. Iron(II) tetrasulfophthalocyanine was in particular found to efficiently catalyze the oxidation of trichlorophenol with high turnover rates. Studies on the use of MPc complexes as catalysts for the oxidation of alkanes or alkenes has received less attention [6,18,19]. The use of supported PdPc as a catalyst for the partial oxidation of methane resulted in the

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formation of ethane rather than methanol, whereas when RuPc, or tetraphenylporphyrin (TPP) complexes of cobalt (CoTPP) and manganese (MnTPP) were employed, methanol was produced [18]. The only observable products for the oxidation of methane using FeTPP, RuTPP, FePc and CoPc as catalysts were carbon dioxide and water [18]. Thus selectivity of the MPc and metalloporphyrin complexes for the oxidation of hydrocarbons may be introduced by changing the nature of the central metal. The oxidation state of the central metal and the substituents on the ring may also affect the selectivity and efficiency of oxidation of hydrocarbons. The catalytic activity of iron porphyrins towards the oxidation of cyclohexane was found to be dependent on the solvent [20]. When FePc was employed as a catalyst for iodobenzene oxidation of cyclohexane, cyclohexanol was obtained [6]. Perfluorinated iron phthalocyanine was found to have less catalytic activity than FePc towards the formation of cyclohexanol from cyclohexane, this was

attributed to the low solubility of the former catalyst in dichloromethane [6]. The use of halogenated MPcs as heterogeneous catalysts for the oxidation of cyclohexane has been reported in a patent application [19]. Aluminosilicate supported perfluorinated CoPc was found to be more active and selective for cyclohexane oxidation than the unsupported complex [21]. Higher activity for cyclohexane oxidation was also observed when CuPc was incorporated inside a Y zeolite [21]. Carbo black-supported FePc has been employed for selective oxidation of cyclohexane [22]. Tetrasulfo MPcs have not yet been explored for the catalytic oxidation of alkanes. In this work, we compare iron polychlorophthalocyanine ($\text{Cl}_{16}\text{PcFe}$) and iron tetrasulfophthalocyanine ($[\text{FeTSPc}]^{4-}$) complexes, Fig. 1, as homogeneous catalysts for the oxidation of cyclohexane.

Products obtained through metalloporphyrin catalyzed oxidation of cyclohexane using iodobenzene, oxygen or hydrogen peroxide as oxidants, include

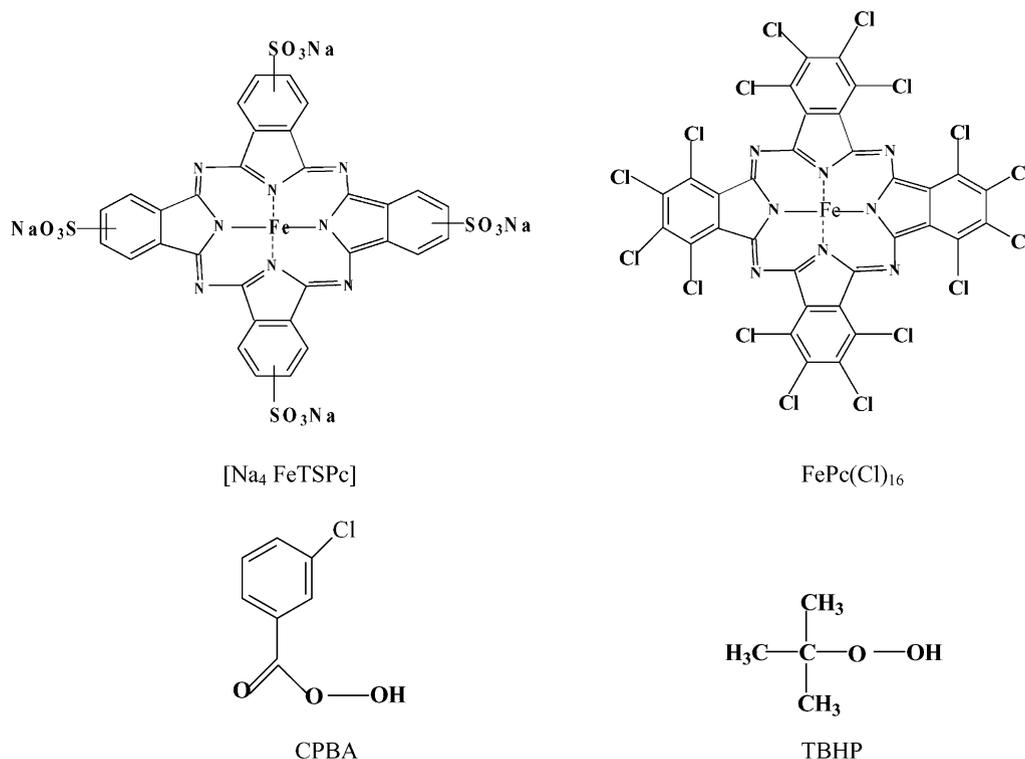


Fig. 1. Molecular structure of Fe(II) tetrasulfophthalocyanine ($\text{Na}_4[\text{FeTSPc}]$), Fe(II) perchlorinated phthalocyanine ($(\text{Cl})_{16}\text{FePc}$), TBHP and *m*-CPBA.

cyclohexanol and cyclohexanone [3,5,6,23]; cyclohexanol being the prominent product [6,23]. The selectivity of iron porphyrin catalyzed oxidations also depends on the nature of the oxidant [4]. Oxidation of alkanes using the biologically important hydrogen peroxide oxidant is desirable, hence this oxidant is employed in this work to oxidize cyclohexane in the presence of MPc catalysts. The effectiveness of hydrogen peroxide as an oxidant for the oxidation of cyclohexane is compared to that of *tert*-butyl hydroperoxide (TBHP) and *m*-chloroperoxybenzoic acid (*m*-CPBA), shown in Fig. 1.

2. Experimental

2.1. Materials

The sodium salt of iron tetrasulfophthalocyanine ($\text{Na}_4[\text{FeTSPc}]$) was prepared (using ferrous chloride) and purified according to the method of Weber and Busch [24]. Iron(II) hexadecochlorophthalocyanine ($\text{Cl}_{16}\text{PcFe}$) was synthesized, purified and characterized according to literature methods [25]. Hydrogen peroxide (33%) was purchased from SAARTECH, *m*-CPBA, TBHP (70%), cyclohexane, cyclohexanone, 1,4-cyclohexanediol and cyclohexanol 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. Triply distilled deionized millipore was employed.

2.2. Oxidation reactions

The oxidation reactions were performed at room temperature (20–25 °C). When $\text{Cl}_{16}\text{PcFe}$ was employed as a catalyst, a solvent mixture containing DMF and dichloromethane was employed. The ratio of DMF to dichloromethane which gave the highest yields of the products was found to be 3:7 and this solvent mixture was used for subsequent studies. The $\text{Cl}_{16}\text{PcFe}$ complex and cyclohexane were dissolved in the solvent mixture, the respective oxidant (H_2O_2 , *m*-CPBA or TBHP) was then added and the reaction monitored with time using GC and UV/visible absorption spectroscopy. The water:methanol (1:9) solvent mixture was employed when $[\text{FeTSPc}]^{4-}$

was used as a catalyst. All reported yields are based on the weight percent of the products. All reactions were run at least in triplicates and not always using the same batches of the catalysts, oxidants or substrates. Studies involving different amounts of the catalyst, oxidants and substrate were undertaken. The molar extinction concentration of $\text{Cl}_{16}\text{PcFe}$ catalyst was determined in the DMF/ CH_2Cl_2 mixture to be $7.4 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and used for the determination of concentration. The published [26] molar extinction coefficient of $4.8 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ for $[\text{FeTSPc}]^{4-}$ was used for determination of its concentration.

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

2.3. Physical measurements

GCs 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 μm film thickness). The parameters for analysis were: carrier gas N_2 at 30.7 cm s^{-1} , injector temperature = 225 °C, detector temperature = 280 °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 μm film thickness. UV/visible spectra was recorded with the Cary 500 UV/Visible/NIR Spectrophotometer.

3. Results and discussion

Varying amounts of cyclohexanol, cyclohexanone and cyclohexanediol were identified from GC analysis as the products obtained on oxidation of cyclohexane using the $\text{Cl}_{16}\text{PcFe}$ or $[\text{FeTSPc}]^{4-}$ catalysts. To our knowledge, this is the first time that cyclohexanediol has been reported as one of the products of cyclohexane oxidation catalyzed by phthalocyanines. There have been reports of the formation of adipic acid, cyclohexanol and cyclohexanone from cyclohexane using halogenated phthalocyanine complexes as

heterogeneous catalysts [19]. The yield of each product was strongly dependent on the nature of the catalyst and the oxidant.

3.1. Catalytic oxidation of cyclohexane using $[\text{FeTSPc}]^{4-}$ catalyst

Phthalocyanine complexes are more stable and readily available catalysts compared to porphyrins. However, the former have relatively lower solubility. This may explain why there has been less attention of the use of phthalocyanine as homogeneous catalysts. $[\text{FeTSPc}]^{4-}$ like all $[\text{MTSPc}]^{4-}$ complexes is soluble in water. In order to get all the components of the reaction mixture into solution, it was necessary to use a methanol:water solvent mixture. The three oxidants (H_2O_2 , TBHP and *m*-CPBA) were tested for cyclohexane oxidation using $[\text{FeTSPc}]^{4-}$ catalyst. Fast degradation of the phthalocyanine ring in $[\text{FeTSPc}]^{4-}$ was observed when *m*-CPBA was employed as an oxidant. In fact, the solution went from the blue-green color of the $[\text{FeTSPc}]^{4-}$ catalyst to colorless, immediately following addition of this oxidant, hence oxidation using this oxidant and $[\text{FeTSPc}]^{4-}$ catalyst was not studied. A degradation of the ring was also observed for hydrogen peroxide, though to a lesser extent compared to *m*-CPBA. Less degradation of the phthalocyanine ring was observed when TBHP was employed as an oxidant, but some degradation was still evident. TBHP has been reported before [21] to be a more convenient oxidant for MPc catalyzed oxidation of cyclohexane. The results of the catalytic oxidation of cyclohexane by TBHP in the presence of $[\text{FeTSPc}]^{4-}$ catalyst are shown in Fig. 2, which shows the variation of product yield with reaction

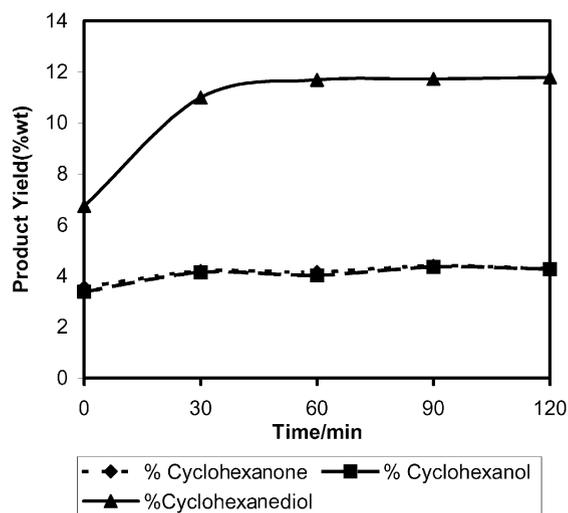


Fig. 2. Variation of product yield with time for the oxidation of 0.2 mol dm^{-3} cyclohexane in the presence of $1.4 \times 10^{-3} \text{ mol dm}^{-3}$ $[\text{FeTSPc}]^{4-}$ catalyst; oxidant = TBHP (0.8 mol dm^{-3}).

time. The leveling off in Fig. 2 is most likely due to the degradation of the phthalocyanine catalyst by the TBHP oxidant, with time. According to Fig. 2, the yield of the three products increased relatively fast initially but soon level off with time. Higher yields were obtained for cyclohexanediol than for cyclohexanol or cyclohexanone. The yields for cyclohexanol and cyclohexanone were nearly similar. Product yields reported in Fig. 2 and Table 1, are slightly higher (in some cases) than those reported for perhalogenated iron phthalocyanine as heterogeneous catalysts and oxygen as an oxidant [19]. Higher selectivity for cyclohexanediol was observed for the $[\text{FeTSPc}]^{4-}$ catalyst and using TBHP oxidant, Table 1.

Table 1

Product yields and selectivities for the oxidation of cyclohexane by the various oxidants in the presence of the $\text{Cl}_{16}\text{PcFe}$ and $[\text{FeTSPc}]^{4-}$ complexes as catalysts^a

Catalyst	Oxidant	Product selectivity (%)			Product yield (%)		
		Cyclohexanol	Cyclohexanone	Cyclohexanediol	Cyclohexanol	Cyclohexanone	Cyclohexanediol
$[\text{FeTSPc}]^{4-}$	TBHP	21	21	58	4.3	4.3	11.8
$\text{Cl}_{16}\text{PcFe}$	<i>m</i> -CPBA	54	38	–	1.6	1.0	–
	TBHP	10	90	–	0.02	0.2	–
	H_2O_2	40	60	–	0.01	0.02	–

^a For experiments involving $\text{Cl}_{16}\text{PcFe}$ catalysts, a solvent mixture of DMF/ CH_2Cl_2 (3:7) was employed. For the $[\text{FeTSPc}]^{4-}$ catalysts, water/methanol (1:9) was employed. Product yield based on the substrate.

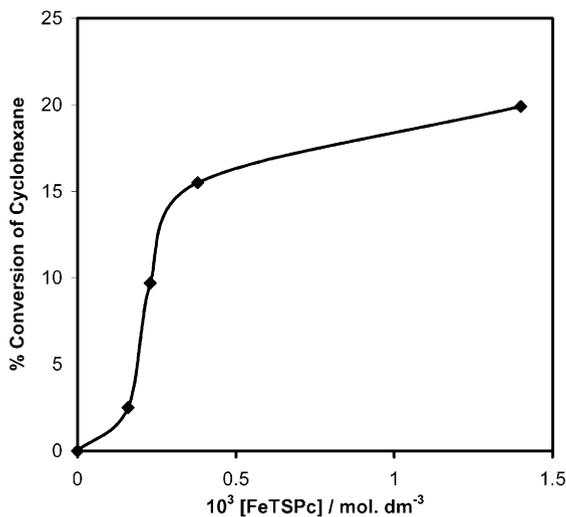


Fig. 3. The effect of $[\text{Fe}^{\text{II}}\text{TSPc}]^{4-}$ catalyst loading on the percentage conversion of 0.2 mol dm^{-3} cyclohexane; oxidant = THBP (0.8 mol dm^{-3}); reaction time = 2 h.

Fig. 3 shows the effect of $[\text{FeTSPc}]^{4-}$ catalyst loading on the percent conversion of cyclohexane for a reaction mixture consisting of a constant concentration of cyclohexane (0.2 mol dm^{-3}) and 0.8 mol dm^{-3} of the TBHP oxidant. There is an increase in the percent conversion with increase in the concentration of the catalyst within the concentration range shown in Fig. 3. There is a fast increase in percent conversion at low concentrations of the catalyst, and a more gradual increase at higher concentrations. Aggregation of the phthalocyanine complexes is known to occur at high concentrations, lowering the catalytic activity of the catalyst at high concentrations, hence the leveling off of percent conversion in Fig. 3. It has also been reported [6] for porphyrins that at high catalyst concentrations, the catalyst effectively competes with the substrate for oxidation. We cannot rule out this possibility for the MPc catalysts. Fig. 4 shows the variation of the percent conversion of cyclohexane with time for three different concentrations of this substrate for a reaction mixture containing 0.8 mol dm^{-3} of the TBHP oxidant and $3.8 \times 10^{-4} \text{ mol dm}^{-3}$ $[\text{FeTSPc}]^{4-}$. The percent conversion is not affected much by changes in the concentration of the substrate for the concentration employed in Fig. 4. Oxidation of cyclohexane was not observed in the absence of the $[\text{FeTSPc}]^{4-}$ catalyst,

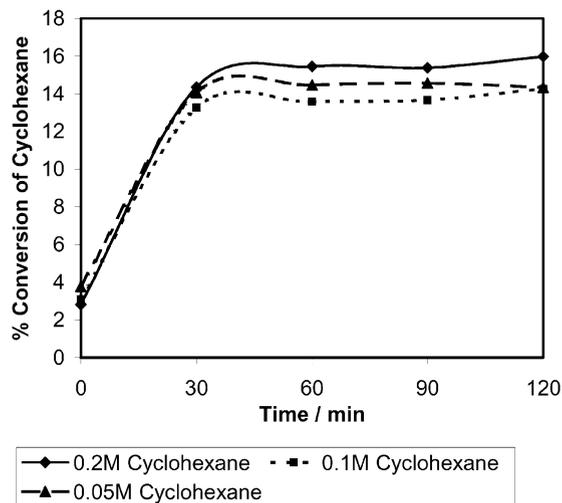


Fig. 4. Effect of substrate concentration on percent conversion in the presence of $3.8 \times 10^{-4} \text{ mol dm}^{-3}$ $[\text{Fe}^{\text{II}}\text{TSPc}]^{4-}$ catalyst. Cyclohexane concentrations: (a) 0.2 mol dm^{-3} ; (b) 0.1 mol dm^{-3} ; (c) 0.05 mol dm^{-3} ; oxidant = THBP (0.8 mol dm^{-3}).

confirming that the catalyst plays a prominent role in the oxidation process. The observed lack of change of the conversion with changes in the oxidant:substrate ratio, is due to the fact that the catalyst concentration was kept constant as this ratio was changed.

Fig. 5 shows the spectral changes observed for the $[\text{FeTSPc}]^{4-}$ catalyst during the course of the oxidation of cyclohexane in the presence of the THBP oxidant. The reaction was exothermic; the temperature of the solution was found to increase by 40°C immediately following addition of the oxidant to solutions containing the catalyst and the substrate. The spectra of MPc complexes is well known and it consists of an intense band called the Q band in the visible region, and a Soret or B band in the ultraviolet region. The spectral changes shown in Fig. 5 consisted of a drastic decrease in both the Q and B bands (only the Q band area is shown in Fig. 5) and the splitting of the Q band. No changes in the spectra of $[\text{FeTSPc}]^{4-}$ were observed in the absence of the oxidant. The lower energy band in Fig. 5(b) was observed at 678 nm and the higher energy band at 636 nm . The Q band of the Fe(II) phthalocyanine complex was observed at 664 nm . The 636 nm band increased in intensity with time as shown in Fig. 5(c), as the band at 678 nm decreased. The band at 636 nm has been observed before

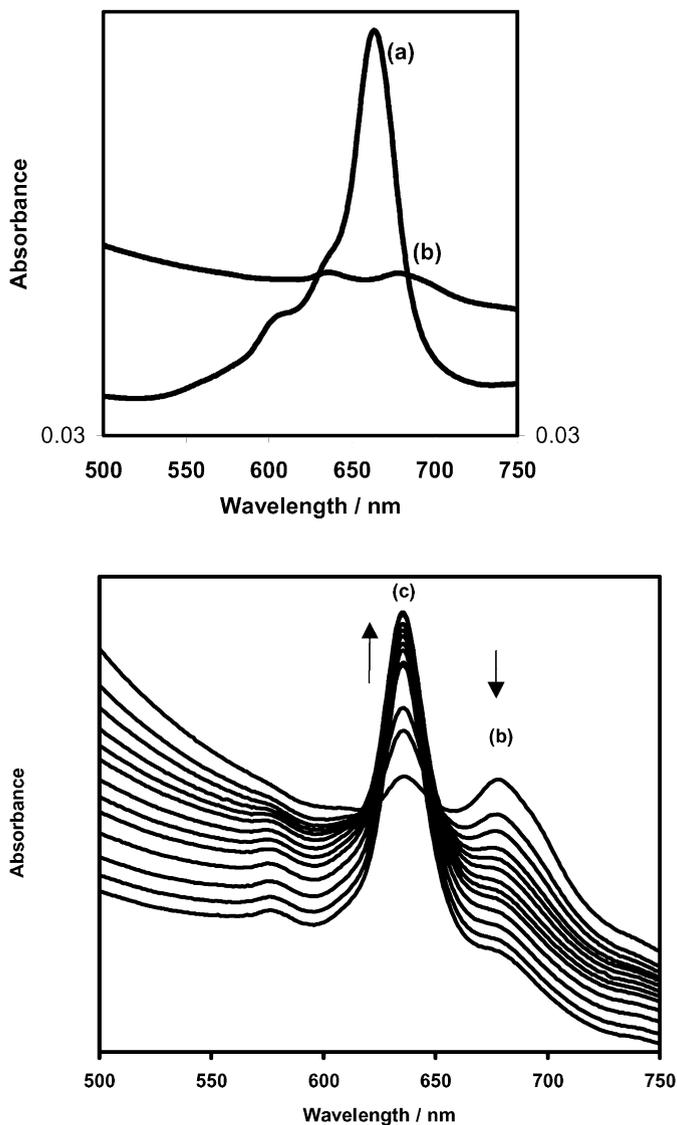


Fig. 5. Electronic absorption spectral changes observed on addition of TBHP oxidant (0.8 mol dm^{-3}) to a reaction mixture containing $3.8 \times 10^{-4} \text{ mol dm}^{-3}$ $[\text{Fe}^{\text{II}}\text{TSPc}]^{4-}$ catalyst and 0.2 mol dm^{-3} cyclohexane. Spectra (a) before, (b) immediately after and (c) 2 h after, addition of the TBHP oxidant.

and has been associated with the formation of stacked monomers [14].

The nature of the $[\text{FeTSPc}]^{4-}$ complex has been a subject of several investigations. Like all $[\text{MTSPc}]^{4-}$ complexes, the spectra of $[\text{FeTSPc}]^{4-}$ in aqueous solutions consists of a dimer in equilibrium with a monomer, with the dimeric peak being observed near

630 nm and the monomeric peak near 670 nm [14]. The ratio of monomer to dimer is dependent of many factors including, the ionic strength, pH and temperature. In the presence of non-aqueous solvents, the monomeric species predominates. Thus, since the solvent mixture used for the catalytic studies in this work contained methanol, the spectra shown

before addition of the oxidant in Fig. 5(a) is that of the monomeric $[\text{FeTSPc}]^{4-}$ species. The nature of $[\text{FeTSPc}]^{4-}$ species prepared according to the method used in this work [24] has been found to vary with each preparation batch. A wide range of iron phthalocyanine complexes have been obtained with different preparation batches [14], with some authors reporting on the formation of μ -oxo complexes, while other authors found no evidence for dimeric μ -oxo species. The μ -oxo species becomes monomeric in the presence of organic solvents. The formation of $[\text{Fe}^{\text{III}}\text{TSPc}]^{3-}$ is common in many preparations [14,24]. The original spectra in Fig. 5(a) before addition of the oxidant to solutions containing the $[\text{FeTSPc}]^{4-}$ catalyst and the substrate (cyclohexane) is due to the $[\text{Fe}^{\text{II}}\text{TSPc}]^{4-}$ species and not the $[\text{Fe}^{\text{III}}\text{TSPc}]^{3-}$ species. This is evidenced by the fact that oxidation of this $[\text{Fe}^{\text{II}}\text{TSPc}]^{4-}$ complex using ferric chloride resulted in the formation of the $[\text{Fe}^{\text{III}}\text{TSPc}]^{3-}$ species, Fig. 6, with a split Q band and a shifting of one of the Q band components to longer wavelengths as is typical of the oxidation of Fe(II)Pc to Fe(III)Pc [27].

The spectral changes observed for the $[\text{Fe}^{\text{II}}\text{TSPc}]^{4-}$ catalyst during the oxidation of cyclohexane using the TBHP oxidant, suggest that the mechanism for the transformation of the catalyst is as outlined in Scheme 1.

Routes 1 and 2 are proposed on the basis of the split in the Q band on addition of the oxidant, with the formation of bands at 678 and 636 nm, respectively. Route 3 is proposed on the basis of the observation of a decrease in the band at 678 nm and the increase in the band at 636 nm associated with the formation of the stacked monomer, and not the

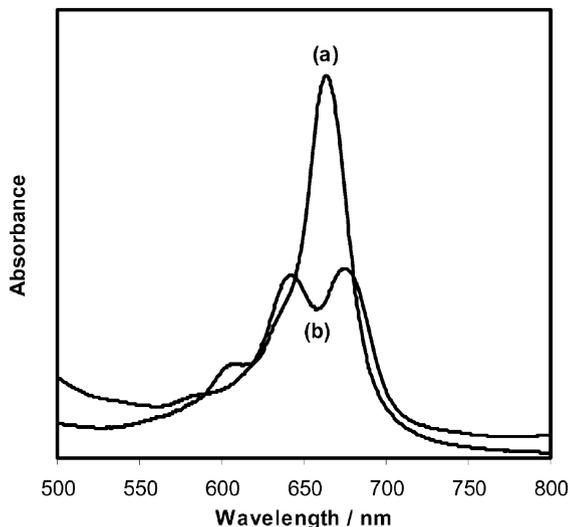
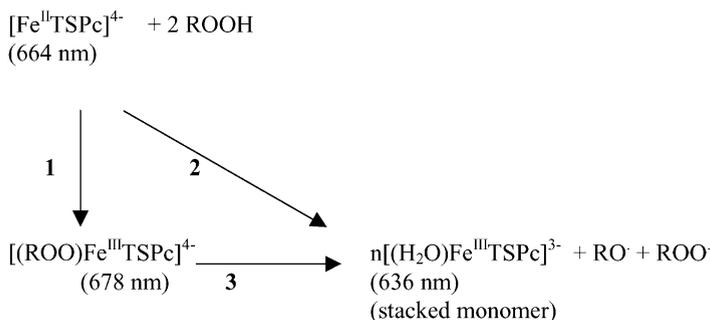
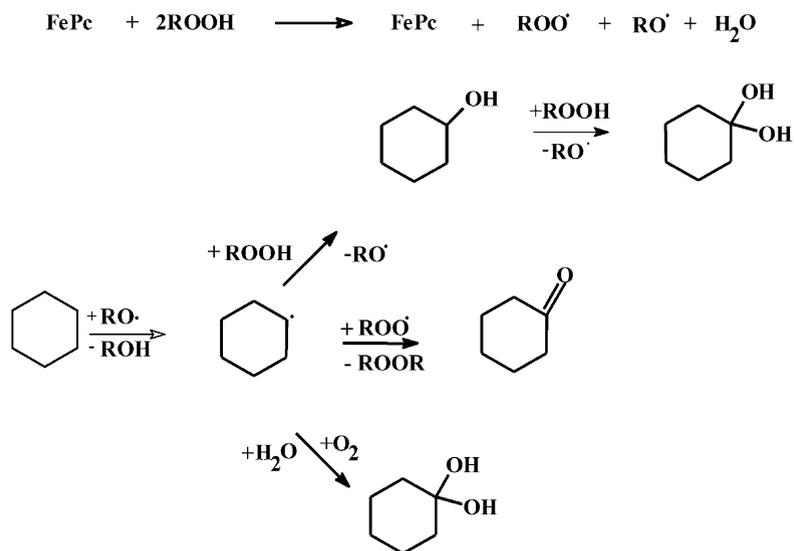


Fig. 6. Electronic absorption spectral changes observed on addition ferric chloride to $[\text{Fe}^{\text{II}}\text{TSPc}]^{4-}$ in water:methanol solvent mixture.

original Fe(II) phthalocyanine species as the Q band for this species was located at 664 nm. The RO^\bullet and ROO^\bullet radicals formed then react with cyclohexane according to Scheme 2 [28]. The suggested presence of the $[(\text{ROO})\text{Fe}^{\text{III}}\text{TSPc}]^{4-}$ intermediate is based on the fact that the Fe(III)(OOR) phthalocyanine species has been proposed as a key species for the ring cleavage of chlorophenols [14]. Also oxidations of alkanes catalyzed by iron porphyrin have been described as being mediated by porphyrin species containing oxo iron porphyrin species and a high oxidation state iron [6,9,29]. Scheme 2 (adopted from Ref. [28] for alcohol and ketone formation) shows only the main products of cyclohexane oxidation. Cyclohexanediol



Scheme 1.



Scheme 2.

may be formed via the alcohol and as a primary product by direct reaction of the cyclohexyl radical in the presence of residual oxygen and oxygen produced from ROOH [30]. It is also possible for the ketone to be formed as a secondary product from the alcohol.

3.2. Catalytic oxidation of cyclohexane using $\text{Cl}_{16}\text{PcFe}$ catalyst

Dichloromethane has been used successfully as a solvent for the catalytic oxidation of cyclohexane using metalloporphyrins [3,6]. However, the $\text{Cl}_{16}\text{PcFe}$ catalyst is not soluble in dichloromethane, but is more soluble in DMF. Thus, the DMF:dichloromethane solvent mixture was employed for studies involving the $\text{Cl}_{16}\text{PcFe}$ catalyst. When DMF was employed in the absence of dichloromethane for the catalytic oxidation of cyclohexane in the presence of any of the oxidants employed in this work, no oxidation products were obtained. The yield of oxidation products increased with the dichloromethane content of the solvent mixture, however, the solubility of the catalyst decreased with decrease in the DMF content. The best results in terms of product yield and solubility were obtained with a DMF: CH_2Cl_2 ratio of 3:7.

Fig. 7 shows the variation of the product yields for a reaction mixture consisting of a constant concentra-

tion of the $\text{Cl}_{16}\text{PcFe}$ catalyst ($6 \times 10^{-6} \text{ mol dm}^{-3}$), 0.2 mol dm^{-3} cyclohexane and varying amounts of the *m*-CPBA oxidant in a 3:7 DMF: CH_2Cl_2 solvent mixture. As the concentration of *m*-CPBA was increased, the yields of cyclohexanone and cyclohexanol increased. Amounts of cyclohexanediol were insignificant for the $\text{Cl}_{16}\text{PcFe}$ catalyst.

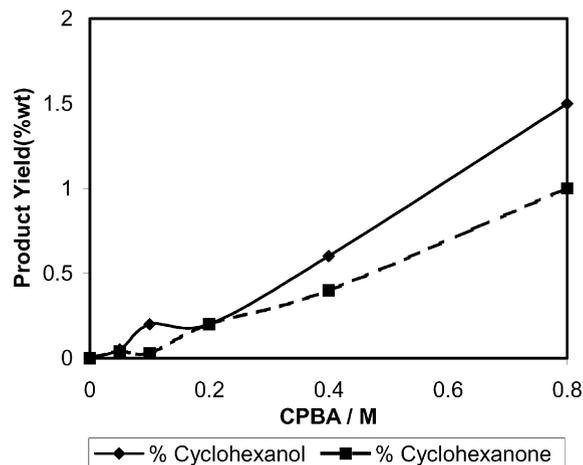


Fig. 7. Variation of product yield with *m*-CPBA oxidant concentration for the oxidation of 0.2 mol dm^{-3} cyclohexane in the presence of $6 \times 10^{-6} \text{ mol dm}^{-3}$ $(\text{Cl})_{16}\text{FePc}$ catalyst.

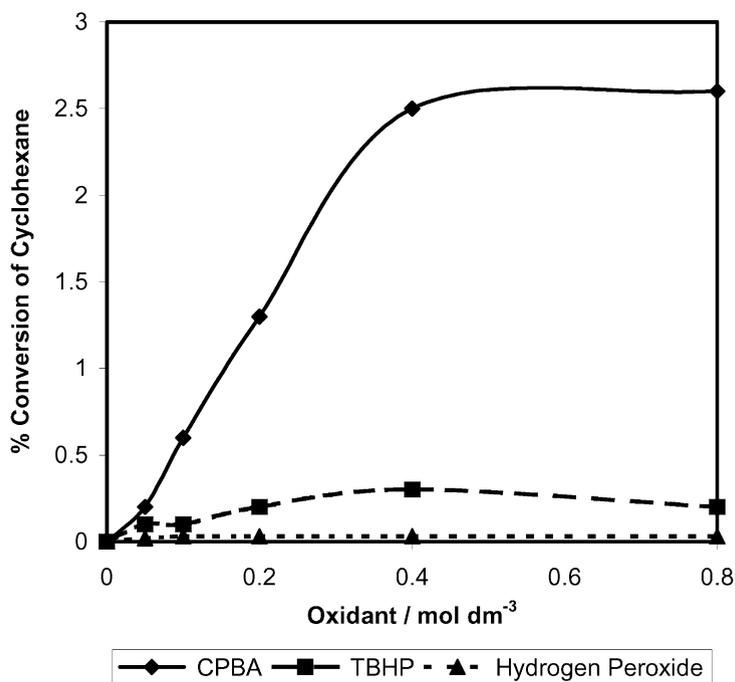


Fig. 8. Variation of percentage conversion of 0.2 mol dm^{-3} cyclohexane with oxidant concentration for $6 \times 10^{-6} \text{ mol dm}^{-3}$ $(\text{Cl})_{16}\text{PcFe}$ catalyst.

The yields shown in Fig. 7 are smaller than those reported above for the $[\text{FeTSPc}]^{4-}$ catalyst. This is most likely due to the low solubility of $\text{Cl}_{16}\text{PcFe}$ compared to $[\text{FeTSPc}]^{4-}$. Product yields of 3% have been reported using halogenated MPc complexes as heterogeneous catalysts and oxygen as an oxidant [19]. The product yields are highly dependent on the nature of the oxidant. Fig. 8 shows the variation of percent conversion of cyclohexane with increase in the concentration of the oxidant for the three oxidants under consideration in this work. A relatively high increase in conversion of cyclohexane was observed as the concentration of the *m*-CPBA oxidant was increased, but leveled off at high concentrations of the oxidant. The percent conversion was the lowest for hydrogen peroxide, with TBHP showing a slightly higher percent conversion compared to hydrogen peroxide.

Table 1 shows that the selectivity for the cyclohexanol was slightly higher than that for cyclohexanone using the *m*-CPBA oxidant. Table 1 also shows that even though the product yields using TBHP oxidant were lower than that for *m*-CPBA, a much higher

selectivity for one of the products (cyclohexanone) was obtained for TBHP oxidant compared to either *m*-CPBA or hydrogen peroxide. The selectivity towards cyclohexanone was also higher for hydrogen peroxide when compared to *m*-CPBA. Selectivity of the products was found not to vary with the solvent in that when methanol or acetonitrile were employed instead of dichloromethane in the solvent mixture, no changes in selectivity were observed. The results presented here show that of the three oxidants chosen, *m*-CPBA, TBHP and hydrogen peroxide, *m*-CPBA is the most efficient in the presence of the $\text{Cl}_{16}\text{PcFe}$ catalyst, in terms of giving higher yields of the products. Hydrogen peroxide gave the lowest yields.

Fig. 9 shows electronic spectral changes of the $\text{Cl}_{16}\text{PcFe}$ catalyst observed during the course of the oxidation of cyclohexane in the presence of the *m*-CPBA oxidant. The Q band of the $\text{Cl}_{16}\text{PcFe}$ catalyst in the DMF: CH_2Cl_2 solvent mixture was observed at 629 nm, Fig. 9(a). On addition of the *m*-CPBA oxidant to solutions of $\text{Cl}_{16}\text{PcFe}$ catalyst and 0.2 mol dm^{-3} of the substrate (cyclohexane), the Q band maxima

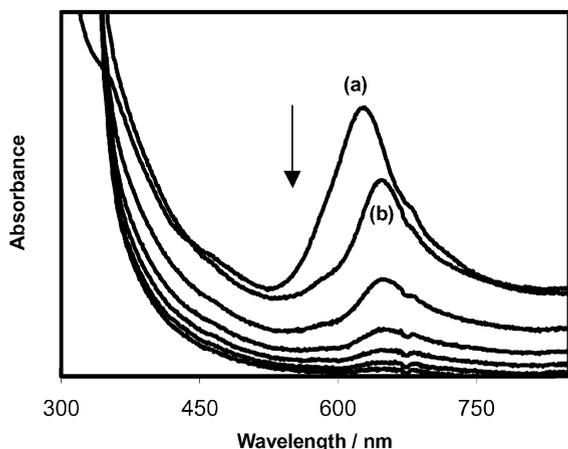


Fig. 9. Electronic absorption spectral changes observed on addition of *m*-CPBA oxidant (0.8 mol dm^{-3}) to a reaction mixture containing $2 \times 10^{-6} \text{ mol dm}^{-3}$ $(\text{Cl})_{16}\text{FePc}$ catalyst and 0.2 mol dm^{-3} cyclohexane: (a) before and (b) immediately after addition of oxidant.

of $(\text{Cl})_{16}\text{PcFe}$ catalyst shifted from 639 to 647 nm, Fig. 9(b). The new spectra is similar to the spectra obtained following chemical oxidation of $(\text{Cl})_{16}\text{PcFe}$ using bromine. Oxidation of iron phthalocyanine complexes occurs at the central metal prior to ring-based oxidation. Shifts of the Q band to higher wavelengths occur following the central metal oxidation in FePc complexes [27]. As discussed above, a split in the Q band and its shifting to longer wavelengths following oxidation of Fe(II)Pc to the Fe(III)Pc species has been reported [27]. The splitting is not observed in Fig. 9, and was also not observed when other oxidants such as bromine, were employed. The split in the Q band was, however, observed for the oxidation of the $[\text{Fe}^{\text{II}}\text{TSPc}]^{4-}$ as discussed above. Following the formation of the Fe(III) perchlorophthalocyanine complex in Fig. 9, a decrease in the Q band is observed without any new bands being formed, showing that the phthalocyanine complex degrades as the oxidation proceeds. Decomposition of the phthalocyanine ring was not observed in the absence of the oxidant.

Spectral changes shown in Fig. 9 give evidence for the involvement of the Fe(III) phthalocyanine species. The mechanism which has been proposed [28] for the oxidation of cyclohexane catalyzed by iron phthalocyanine complexes is shown by Scheme 2. Changes which the catalyst undergoes during the catalysis were,

however, not described by the authors [28]. As mentioned above for the $[\text{Fe}^{\text{II}}\text{TSPc}]^{4-}$ catalyst, we propose that the Fe(III)(OOR) phthalocyanine species is an intermediate in the oxidation of cyclohexane catalyzed by $(\text{Cl})_{16}\text{PcFe}$ complex. The decomposition of the phthalocyanine complex during the oxidation of cyclohexane, Fig. 9, is a result of the attack of the phthalocyanine ring by the RO^\bullet and ROO^\bullet radicals.

When TBHP was used as an oxidant, the formation of the Fe(III) phthalocyanine complex was not observed. Spectral changes observed during the oxidation of cyclohexane by TBHP consisted of a small decrease in the Q band without much shift the wavelength. As discussed above, shifts to longer wavelength shown in Fig. 9 are associated with central metal oxidation and the formation of an Fe(III) phthalocyanine species. Such shifts were not observed when using TBHP as an oxidant. It is possible that the Fe(III)(OOR) phthalocyanine intermediate is formed as proposed above when *m*-CPBA is employed as an oxidant, but that this intermediate is readily reduced back to an Fe(II) phthalocyanine species when TBHP was employed as an oxidant. Also the phthalocyanine ring is not destroyed by the radicals when TBHP is employed as an oxidant as judged by lack of a significant decrease in the Q band even after prolonged reaction times. The TBHP oxidant contains electron-donating methyl groups, whereas the *m*-CPBA oxidant contains electron-withdrawing groups in its molecule, Fig. 1. Ring destruction in phthalocyanines has been reported to be through oxidative degradation [31]. The RO^\bullet and ROO^\bullet radicals generated from the TBHP oxidant contain electron-donating groups hence these radicals are less destructive to the phthalocyanine ring. Whereas the radicals from the *m*-CPBA oxidant contain electron-withdrawing substituents, hence the phthalocyanine ring is more readily degraded through an oxidative mechanism. The fact that the spectra for the Fe(III) phthalocyanine species is not observed when TBHP is employed as an oxidant, suggests that this intermediate is not stable in the presence of the electron-donating TBHP oxidant, but is stable in the presence of electron-withdrawing *m*-CPBA oxidant.

When hydrogen peroxide was employed as an oxidant, total destruction of the phthalocyanine ring was observed, without formation of the intermediate Fe(III) phthalocyanine species, using the $(\text{Cl})_{16}\text{PcFe}$

catalyst. Thus this catalyst is not stable to hydrogen peroxide and to a lesser extent, to *m*-CPBA oxidants, but is stable to TBHP.

In conclusion, we have shown in this work that iron phthalocyanine complexes containing peripheral substituents catalyze the oxidation of cyclohexane. The success of the catalytic process depends on the stability and solubility of the catalyst. For some oxidants, the radicals generated during the catalytic process attack the phthalocyanine ring, destroying it. For both (Cl)₁₆FePc and [Fe^{II}TSPc]⁴⁻ catalysts, the largest degradation of the ring was observed when the *m*-CPBA and hydrogen peroxide oxidants were employed. The stability of the ring in the presence of the TBHP oxidant is attributed to the electron donating nature of the oxidant, which stabilizes the ring from oxidative degradation. The [Fe^{II}TSPc]⁴⁻ complex showed higher catalytic activity compared to the perchlorinated iron phthalocyanines. This could be a reflection of the greater solubility of the former. The products formed from catalytic oxidation of cyclohexane are cyclohexanone, cyclohexanol and cyclohexanediol. The relative yields of each product depended on the oxidant and catalyst employed. The selectivity in the products decreased as the overall product yield increased.

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References

- [1] P.R. Ortiz de Montellano (Ed.), *Cytochrome P-450: Structure, Mechanism and Biochemistry*, 2nd Edition, Plenum Press, New York, 1995.
- [2] E.R. Birnbaum, J.A. Labinger, J.E. Bercaw, H.B. Gray, *Inorg. Chim. Acta* 270 (1998) 433.
- [3] P. Battioni, E. Cardin, M. Louloudi, B. Schöllhorn, G.A. Spyroulias, D. Mansuy, T.G. Traylor, *Chem. Commun.* (1996) 2037.
- [4] W. Nam, Y.M. Goh, Y.J. Lee, M.H. Lim, C. Kim, *Inorg. Chem.* 38 (1999) 3238.
- [5] W. Nam, H.J. Ham, S.Y. Oh, Y.J. Lee, M.H. Choi, S.-Y. Han, C. Kim, S.K. Woo, W. Shin, *J. Am. Chem. Soc.* 122 (2000) 8677.
- [6] M.J. Nappa, C.A. Tolman, *Inorg. Chem.* 24 (1985) 4711.
- [7] C.M.C. Prado-Manso, E.A. Vidoto, F.S. Vinhado, H.C. Sacco, K.J. Ciuffi, P.R. Martins, A.G. Ferreira, J.R. Lindsay-Smith, O.R. Nascimento, Y. Iyanamoto, *J. Mol. Catal. A* 150 (1999) 251.
- [8] A. Thellend, P. Battioni, D. Mansuy, *J. Chem. Soc., Chem. Commun.* (1994) 1035.
- [9] W. Nam, H.J. Lee, S.-Y. Oh, C. Kim, H.G. Jang, *J. Inorg. Biochem.* 80 (2000) 219.
- [10] A.M.d'A. Rocha Gonsalves, A.C. Serra, *J. Porphyr. Phthalocya.* 4 (2000) 598.
- [11] B. Meunier, A. Sorokin, *Acc. Chem. Res.* 30 (1997) 470.
- [12] A. Sorokin, S. De Suzzoni-Dezard, D. Poullain, J.-P. Noël, B. Meunier, *J. Am. Chem. Soc.* 118 (1996) 7418.
- [13] A. Hadasch, A. Sorokin, A. Rabion, L. Fraise, B. Meunier, *Bull. Soc. Chim. Fr.* 134 (1997) 1025.
- [14] A. Hadasch, A. Sorokin, A. Rabion, L. Fraise, B. Meunier, *New J. Chem.* (1998) 45.
- [15] A. Sorokin, B. Meunier, *J. Chem. Soc., Chem. Commun.* (1994) 1799.
- [16] K. Kasuga, K. Mori, T. Sugimori, M. Handa, *Bull. Chem. Soc. Jpn.* 73 (2000) 939.
- [17] A. Sorokin, J.-L. Séris, B. Meunier, *Science* 268 (1995) 1163.
- [18] Y.-W. Chan, R.B. Wilson Jr., *ACS National Meeting*, Vol. 33, 1988, p. 453.
- [19] P. Ratnasamy, R. Raja, *European Patent*, EP 0 784 045 A1.
- [20] J.-W. Huang, W.-Z. Huang, W.-J. Mei, J. Liu, S.-G. Hu, L.-N. Ji, *J. Mol. Catal. A* 156 (2000) 275.
- [21] E. Armengol, A. Corma, V. Fornés, H. García, J. Primo, *Appl. Catal. A* 181 (1999) 305.
- [22] P.E. Neys, R.F. Parton, P.A. Jacobs, R.C. Sosa, O. Lardinois, P.G. Rouxhet, *J. Mol. Catal. A* 110 (1996) 141.
- [23] C.-C. Guo, H.-P. Li, J.-B. Xu, *J. Catal.* 185 (1999) 345.
- [24] J.H. Weber, D.H. Busch, *Inorg. Chem.* 4 (1965) 469.
- [25] J. Mertz, O. Scheider, M. Hanack, *Inorg. Chem.* 23 (1984) 1065.
- [26] J. Oni, T. Nyokong, *Polyhedron* 19 (2000) 1355.
- [27] M.J. Stillman, T. Nyokong, in: C.C. Leznoff, A.B.P. Lever (Eds.), *Phthalocyanines: Properties and Applications*, Vol. 1, VCH, New York, 1989.
- [28] O.L. Kaliya, E.A. Lukyanets, G.N. Vorozhtsov, *J. Porphyr. Phthalocya.* 3 (1999) 592.
- [29] K.T. Moore, I.T. Horváth, M.J. Therien, *Inorg. Chem.* 39 (2000) 3125.
- [30] C.L. Hill, *Activation and Functionalization of Alkanes*, 1st Edition, Wiley, New York, 1989, p. 192.
- [31] S.A. Borisenkova, E.P. Denisova, E.A. Batanove, E.G. Girenko, O. Kaliya, E.A. Lukyanets, G.N. Vorozhtsov, *J. Porphyr. Phthalocya.* 4 (2000) 684.