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Oxidation of 1-naphthol and related phenols with hydrogen peroxide and potassium superoxide catalysed by 5,10,15,20-tetraarylporphyrinatoiron(III)chlorides in different reaction conditions

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Abstract

Reaction of 1-naphthol and related phenols with hydrogen peroxide catalysed by 5,10,15,20-tetra(pentafluorophenyl)porphyrinatoiron(III)chloride gives corresponding quinones and oxidative phenol coupled products, whereas the reaction of naphthols with hydrogen peroxide catalysed by 5,10,15,20-tetramesitylporphyrinatoiron(III)chloride give above products along with quinone epoxides in moderate yields. The reaction of quinone with potassium superoxide catalysed by Me_{12}TPPFe(III)Cl and *p*-MeOTPPFe(III)Cl give higher yields of quinone epoxides than the reaction of quinone with hydrogen peroxide catalysed by 5,10,15,20-tetraarylporphyrinatoiron(III)chlorides.

Keywords: Naphthols; 5,10,15,20-Tetraarylporphyrinatoiron(III)chlorides; Hydrogen peroxide; Potassium superoxide; Coupling; Peroxo complex; Epoxidation

1. Introduction

Chemical and enzymatic oxidation of phenols have been implicated in cellular oxidation, fruit browning, pulp delignification, oxidative phenol coupling and in the biosynthesis of complex phenolics [1]. Oxidative phenol coupling and formation of quinones from phenols have been mimicked by chemical models for cytochrome P450 and related heme containing monooxygenase [2,3]. Different reactive species formed from the reaction of monooxygen donors and 5,10,15,20-tetraarylporphyrinatoiron(III)chlorides have been implicated in the reaction of specific isoenzymes of cytochrome P450 [4,5]. Herein, we report the oxidation of selected phenols with hydrogen peroxide and potassium superoxide catalysed by electron donating and electron withdrawing substituents in the aryl ring of 5,10,15,20-tetraarylporphyrinatoiron(III)chlorides in order to understand the molecular mechanism of different isoforms of cytochrome P450.

2. Experimental

Melting points were determined on Thomas Hoover Unimelt capillary melting point appara-

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tus. IR spectra were recorded on a Perkin Elmer FT 1710 spectrophotometer and absorption maxima was expressed in nanometers. ^{1}H NMR spectra were recorded on a Perkin Elmer R-32 (90 MHz) spectrophotometer using TMS as an internal reference. HPLC analyses were performed on Shimadzu SPD-2AS detector (set at 254 nm) on a Zorbax ODS column (150 mm × 4.6 mm) using methanol as eluent at a flow rate of 0.2 ml/min.

2.1. Materials and methods

The different tetraarylporphyrinatoiron-(III)chlorides including 5,10,15,20-tetra(2′, 3′,4′,5′,6′-pentafluorophenyl)porphyrinatoiron-(III)chloride (**1a**), 5,10,15,20-tetra(2′,4′,6′-trimethylphenyl)porphyrinatoiron(III)chloride (**1b**) [6], 5,10,15,20-tetra(4′-methoxyphenyl)porphyrinatoiron(III)chloride (**1c**) [7] were prepared by known literature procedures. 1-Naphthol (**8**), 2-naphthol (**18**), 1,5-dihydroxynaphthalene (**22**), 8-hydroxy quinoline (**25**) were obtained from SD Fine Chemicals, Bombay. Potassium superoxide and 18-Crown-6 were obtained from Fluka, Switzerland. The oxidation products including 1,4-dihydroxynaphthalene (**13**), 1,4-naphthoquinone (**16**), m.p. 124°C, lit. m.p. 125°C [8]; 4,4′-dihydroxy-1,1′-binaphthyl (**11**), m.p. 264°C, lit. m.p. 268°C [9]; 1,2-dihydroxynaphthalene (**19**), m.p. 104°C, lit. m.p. 103–104°C [10]; 1,2-naphthoquinone (**20**), m.p. 145°C, lit. m.p. 145–147°C [11]; 2,2′-dihydroxy-1,1′-binaphthyl (**21**), m.p. 214°C, lit. m.p. 218°C [12]; 1,4,5-trihydroxynaphthalene (**23**), m.p. 168°C, lit. m.p. 168–170°C [13]; 5-hydroxy-1,4-naphthoquinone (**24**), m.p. 154°C, lit. m.p. 154°C [14]; 5,8-dihydroxyquinoline (**26**), m.p. 270°C, lit. m.p. 270°C (dec) [15]; 5,8-dioxoquinoline (**27**), m.p. 119°C, lit. m.p. 121–122°C [16]; 8-hydroxy-quinoline-*N*-oxide (**28**), m.p. 136°C, lit. m.p. 138°C [17] were isolated by column chromatography on silica gel using petrol:ethylacetate as the eluent and characterised. 1,4-Naphthoquinone epoxide (**17**) was prepared by known literature procedure [18], m.p. 132°C, lit. m.p. 133°C, UV (MeOH): 251.8 and 334.2 nm; IR (KBr): 3000, 2900, 1700, 1680, 1600, 1400, 1373, 1000, 860, 785, 720; ^{1}H NMR (acetone-d^6): 3.98 (s, H-2, H-3), 7.61 (brs, H-4, H-5, H-6, H-7 and H-8); EIMS *m/z* (%): 174 (100), 146 (38), 105 (88), 89 (30), 76 (40), 57 (8).

2.2. Oxidation of selected phenols with hydrogen peroxide catalysed by TAPFe(III)Cl (*1*) in dichloromethane

Hydrogen peroxide (0.01 mmol) was added to a stirred solution of phenols (0.1 mmol) and TAPFe(III)Cl (0.001 mmol) in dichloromethane (20 ml). The reaction was stirred at room temperature for 1 h. After 1 h, the solvent was evaporated under reduced pressure and the residue was dissolved in methanol and subjected to HPLC for the analysis of products and results are presented in Tables 1 and 3.

2.3. Oxidation of 1-naphthol with hydrogen peroxide catalysed by TAPFe(III)Cl in the presence of N-methylimidazole / pyridine / alcohol

Hydrogen peroxide was added to a stirred solution of 1-naphthol (0.1 mmol), TAPFe(III)Cl

Table 1
Oxidation of 1-naphthol (**8**) and 1,4-dihydroxynaphthalene (**13**) with hydrogen peroxide/potassium superoxide catalysed by TAPFe(III)Cl under different reaction conditions

Entry system	Products (% yield)			
	13	**11**	**16**	**17**
	7.05[a]	7.95[a]	9.25[a]	8.56[a]
(1) **8**/F_{20}TPPFe(III)Cl/H_2O_2	4.0	32.8	24.0	–
(2) **8**/F_{20}TPPFe(III)Cl/H_2O_2–NMeIm	4.2	34.0	32.0	–
(3) **8**/Me_{12}TPPFe(III)Cl/H_2O_2	5.1	34.0	29.3	0.3
(4) **8**/Me_{12}TPPFe(III)Cl/H_2O_2–NMeIm	5.4	34.2	39.1	3.2
(5) **13**/F_{20}TPPFe(III)Cl/H_2O_2	–	–	42.4	–
(6) **13**/F_{20}TPPFe(III)Cl/H_2O_2–NMeIm	–	–	49.6	–
(7) **13**/Me_{12}TPPFe(III)Cl/H_2O_2	–	–	47.8	5.9

[a] Retention times.
Substrate:catalyst:oxidant = 100:1:10.

Table 2
Oxidation of 1,4-naphthoquinone (**16**) with hydrogen peroxide/potassium superoxide catalysed by TAPFe(III)Cl in different reaction conditions

Entry system	Product (% yield)
	17
	8.56[c]
(1) **16**/F_{20}TPPFe(III)Cl/$H_2O_2^b$/pyridine (CH_2Cl_2)	–
(2) **16**/F_{20}TPPFe(III)Cl/KO_2^a/18-Crown-6 (CH_3CN)	2.0
(3) **16**/KO_2^a/18-Crown-6 (CH_3CN)	12.0
(4) **16**/Me_{12}TPPFe(III)Cl/$H_2O_2^b$/NMeIm (CH_2Cl_2)	12.8
(5) **16**/Me_{12}TPPFe(III)Cl/KO_2^a/18-Crown-6 (CH_3CN)	57.3 (42.8)[d]
(6) **16**/Me_{12}TPPFe(III)Cl/$H_2O_2^a$ (CH_3OH)	6.8
(7) **16**/Me_{12}TPPFe(III)Cl/$H_2O_2^a$ (*n*-butanol)	4.9
(8) **16**/Me_{12}TPPFe(III)Cl/$H_2O_2^a$ (*n*-octanol)	2.5
(9) **16**/*p*-MeOTPPFe(III)Cl/KO_2^a/18-Crown-6 (CH_3CN)	66.4

Substrate:catalyst:oxidant = [a]100:1:10; [b]100:1:100.
[c]Retention times.
[d]Isolated yield.

(0.001 mmol) and *N*-methylimidazole or pyridine (0.05 mmol) in dichloromethane (20 ml). The reaction was stirred for 1 h. After 1 h, the solvent was removed under reduced pressure and the residue was dissolved in methanol and subjected to HPLC for the analysis of products and results are presented in Table 1.

2.4. Oxidation of naphthoquinone with potassium superoxide catalysed by TAPFe(III)Cl in different reaction conditions

Potassium superoxide (0.01 mmol) was added to a stirred solution of naphthoquinone (0.1 mmol) and TAPFe(III)Cl (0.001 mmol) in the presence of 18-Crown-6 (0.01 mmol) in acetonitrile (20 ml). The reaction was stirred at room temperature for 10 min. After 10 min, the solution was subjected to HPLC for the analysis of products and results are presented in Table 2.

3. Results

The reaction of 1-naphthol (**8**) with hydrogen peroxide catalysed by F_{20}TPPFe(III)Cl (**1a**) gave 4.0% of 1,4-dihydroxynaphthalene (**13**), 32.8% of 2,2′-dihydroxy-1,1′-binaphthyl (**11**) and 24.0% of 1,4-naphthoquinone (**16**). The same reaction catalysed by Me_{12}TPPFe(III)Cl (**1b**)

Table 3
Oxidation of selected phenols with hydrogen peroxide catalysed by 5,10,15,20-tetra(2′,3′,4′,5′,6′-pentafluorophenyl)porphyrinatoiron-(III)chloride in dichloromethane

Entry substrate	Products	% Isolated yield
(1) 2-Naphthol (**18**)	1,2-Dihydroxynaphthalene (**19**)	5.0
	1,2-Naphthoquinone (**20**)	30.0
	2,2′-Dihydroxy-1,1′-binaphthyl (**21**)	20.0
(2) 1,5-Dihydroxynaphthalene (**22**)	1,4,5-Trihydroxynaphthalene (**23**)	10.0
	5-Hydroxy-1,4-naphthoquinone (**24**)	45.0
(3) 8-Hydroxy quinoline (**25**)	5,8-Dihydroxyquinoline (**26**)	4.0
	5,8-Dioxoquinoline (**27**)	30.0
	8-Hydroxyquinoline-*N*-oxide	5.0

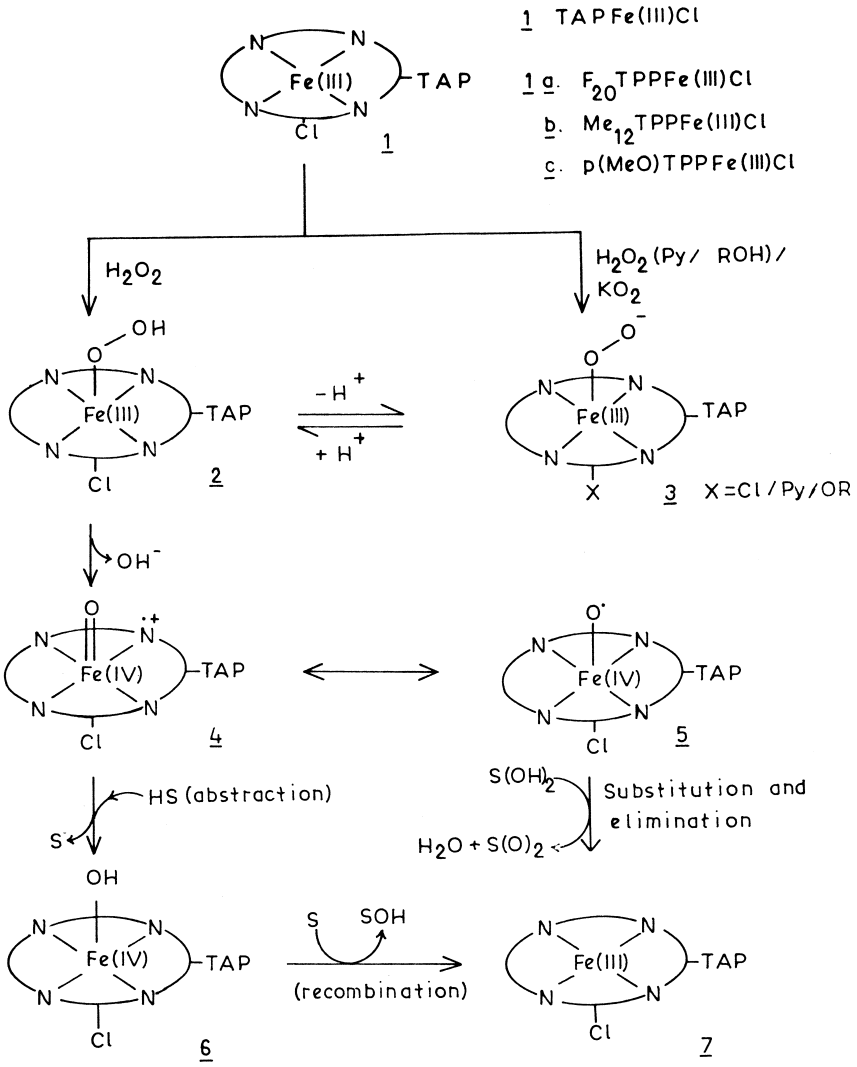
[a]Reaction time = 1 h.
Substrate:catalyst:oxidant = 100:1:10.

gave 5.1% of **13**, 34.0% of **11** and 29.3% of **16** along with 0.3% of 1,4-naphthoquinone epoxide (**17**). The yield of **17** was increased to 3.2% by the use of *N*-methyl imidazole in the above reaction (Table 1).

The reaction of **13** with hydrogen peroxide catalysed by **1a** gave 49.6% of **16** whereas the same reaction catalysed by **1b** gave 47.8% of **16** along with 5.9% of **17** (Table 1).

The reaction of **16** with potassium superoxide in acetonitrile in the presence of 18-Crown-6 gave 12.0% of **17**. The reaction of **16** with hydrogen peroxide catalysed by Me_{12}TPP-Fe(III)Cl in methanol gave 6.8% of **17**. However, relatively lower yield of **17** were observed with higher alcohols. The yield of **17** was 4.9% and 2.5% in *n*-butanol and *n*-octanol, respectively (Table 2).

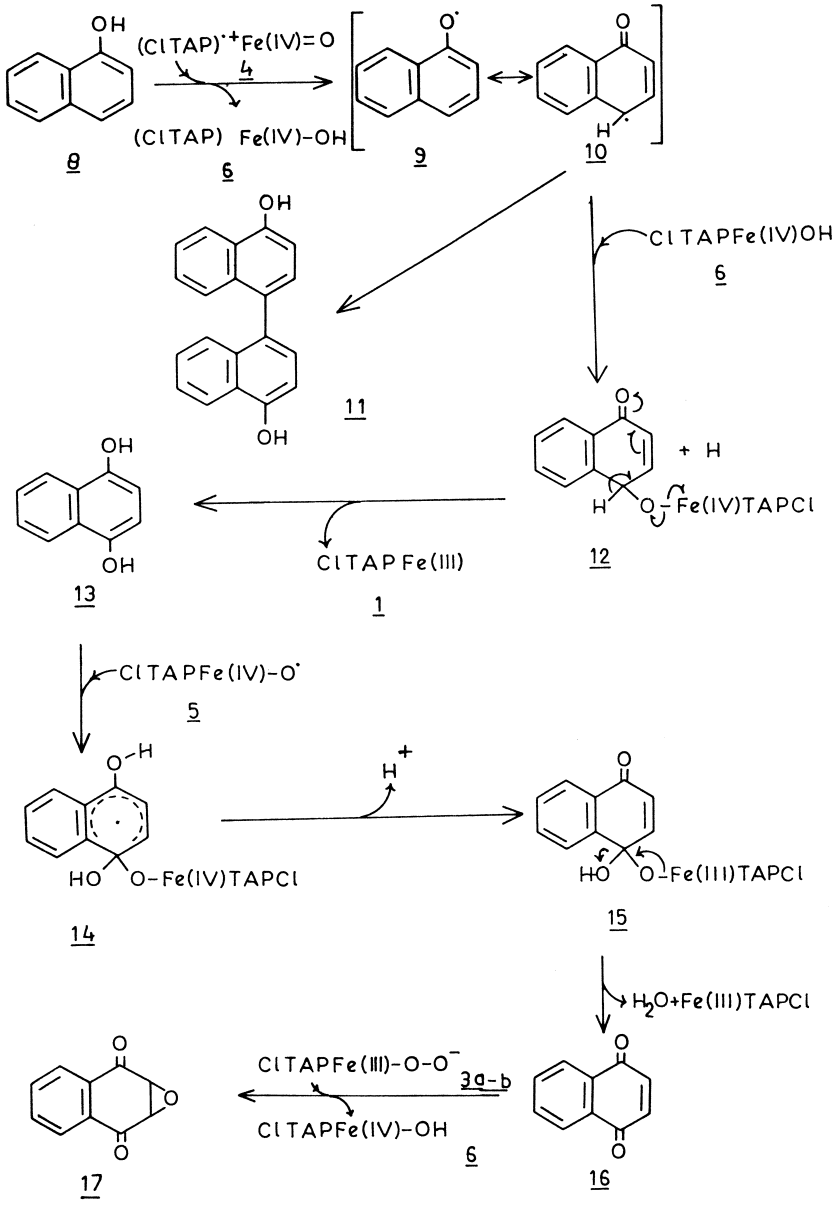
The reaction of **16** with potassium superoxide catalysed by F_{20}TPPFe(III)Cl did not give quinone epoxide. However, the oxidation of **16** with potassium superoxide catalysed by Me_{12}TPPFe(III)Cl in acetonitrile in the presence of 18-Crown-6 gave **17** in 57.3% yield. The



Scheme 1.

reaction of **16** with potassium superoxide catalysed by *p*-MeOTPPFe(III)Cl (**1c**) in acetonitrile using 18-Crown-6 gave 66.4% of **17** (Table 2).

The oxidation of 2-naphthol (**18**) with hydrogen peroxide catalysed by F_{20}TPPFe(III)Cl gave 1,2-dihydroxynaphthalene (**19**), 1,2-naphthoquinone (**20**) and 2,2′-dihydroxy-1,1′-binaphthyl (**21**) in 5%, 30% and 20% yields, respectively. The oxidation of 1,5-dihydroxynaphthalene (**22**) with hydrogen peroxide catalysed by **1a** gave 1,4,5-trihydroxynaphthalene (**23**) and 5-hydroxy-1,4-naphthoquinone (juglone) (**24**) in 10% and 45% yields, respectively. The oxidation of 8-hydroxyquinoline (**25**) with hydrogen peroxide catalysed by **1a** gave 5,8-dihydroxyquinoline (**26**), 5,8-dioxoquinoline (**27**) and 8-hydro-



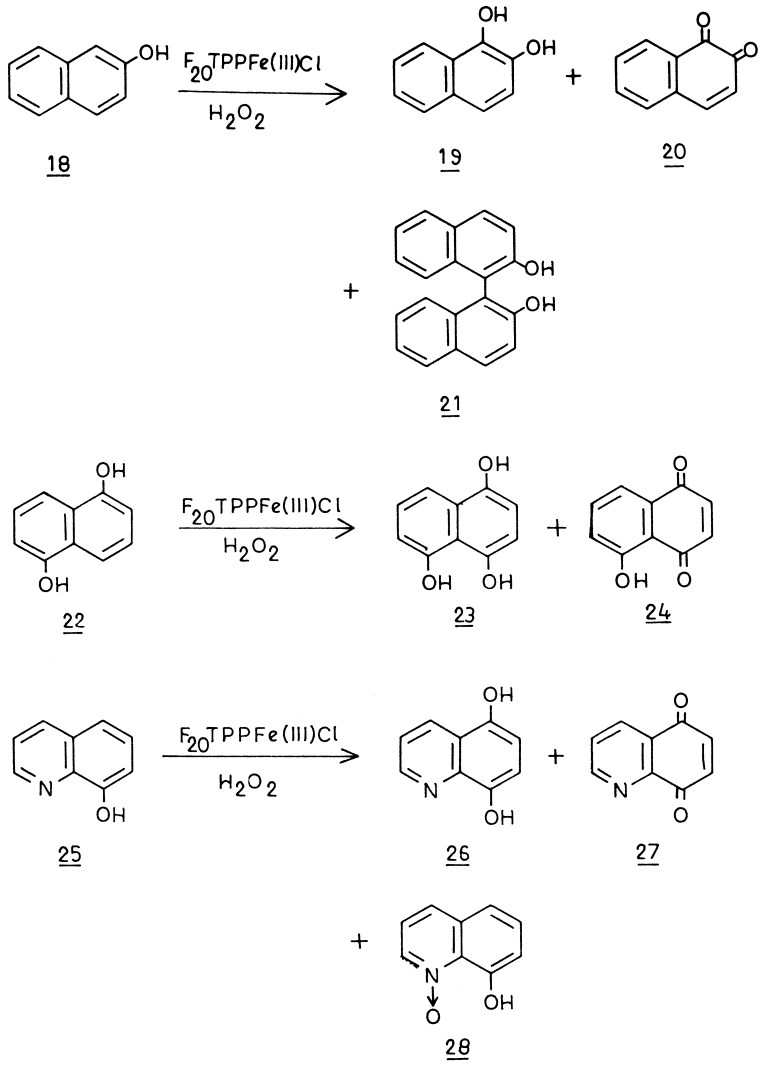
Scheme 2.

xyquinoline *N*-oxide (**28**) in 4%, 30% and 5% yields, respectively (Table 3; Scheme 1).

4. Discussion

Oxidation of phenols with monooxygen donors catalysed by sulphonated metallopthalocyanines [19–21], iron porphyrins [22–25] and non-heme iron complexes [26,27] is of current research interest. The formation of high valent *oxo*-iron(IV) radical cation and related reactive species have been implicated in the above biomimetic oxidation reactions.

The reaction of hydrogen peroxide and F_{20}TPPFe(III)Cl (**1a**) form hydroperoxy intermediate (**2**) which on heterolytic cleavage gives high valent *oxo*-iron(IV) radical cation (**4**). The abstraction of hydrogen atom from substrate by **4** give high valent *oxo*-iron(IV) intermediate [F_{20}TPPFe(IV)-OH] (**6**) (Scheme 2). The recombination of substrate radical and **6** form the hydroxylated substrate. The intermediate **4** also equilibrate to intermediate **5** depending on the



Scheme 3.

substituents on the phenyl ring of porphyrins as well as axial ligands [32,34] (Scheme 2). The reaction of 1-naphthol (**8**) with hydrogen peroxide catalysed by metalloporphyrin (**1a**) in the formation of 1,4-dihydroxynaphthalene (**13**) may be explained by above hydrogen abstraction from **8** to form **9** ↔ **10** and recombination of **10** with **6** and subsequent decomposition of intermediate **12** to **13** (Scheme 2). The oxidative *p,p*-phenol coupling of **10** led to formation of **11**. This type of oxidative phenol coupling is known in the reaction of phenol with hydrogen peroxide catalysed by iron(III)porphyrins [22–25] and with natural cytochrome P450 [5]. However, corresponding oxidative phenol coupled products are not formed in the oxidation of 1,5-dihydroxynaphthalene and 8-hydroxyquinoline.

The *ipso*-substitution of intermediate **5** at position 4 of 1,4-dihydroxynaphthalene forms the intermediate **14** which on elimination of a proton give the intermediate **15**. The release of iron(III)porphyrin from **15** lead to the formation of 1,4-naphthoquinone (**16**) (Scheme 3). This type of *ipso*-substitution and subsequent formation of quinone has been proposed in the reactions of substituted phenols with monooxygen donors catalysed by iron(III)porphyrins [25,34]. The intramolecular hydrogen bonding in **23** and **26** may be responsible for the higher yield of corresponding quinones **24** and **27** than the formation of **16** from **8**.

Oxidative addition of superoxide to synthetic iron(III)porphyrins form high spin ferric peroxo complexes [28,29] and have been used in the oxidation of organic substrates [30,31]. The formation of high spin ferric porphyrin peroxo complex **3a** and **3b** have been confirmed by the appearance of a low energy Soret band at 430–434 nm and two maxima between 500–600 nm in their UV–visible spectra. The iron(III)peroxotetramesitylporphyrin **3b** epoxidise electron poor olefins like 1,4-naphthoquinone by transferring one oxygen atom to the electron poor olefin. This type of nucleophilic oxygen atom transfer mimicks the direct nucleophilic attack on the enzyme bound substrate proposed for certain types of P450 enzyme [32,33]. The iron(III)peroxo - tetrakis(pentafluorophenyl)porphyrin **3a** is unable to epoxidise the electron poor olefin. The strong electron withdrawing fluorine substituents probably reduce the nucleophilic character of oxygen atom in iron(III)peroxo complexes, thus unable to epoxidise the quinone.

The hydrogen abstraction and recombination mechanism involved during the oxidation of phenols with monooxygen donors and iron(III)porphyrins depends on the different substituents on the phenols and electron withdrawing groups in aryl ring of 5,10,15,20-tetraarylporphyrinatoiron(III)chlorides. The formation of naphthoquinone epoxide depends on the monooxygen donor and electron donating substituents on the phenyl ring of 5,10,15,20-tetraarylporphyrinatoiron(III)chloride.

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