ELSEVIER

Journal of Molecular Catalysis A: Chemical 188 (2002) 115–122

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

Remarkable solvent effect on the yield and specificity of oxidation of naphthalene catalyzed by iron(III)porphyrins

Hamid Reza Khavasi, S. Saeed Hosseiny Davarani, Nasser Safari*

Chemistry Department, Shahid Beheshti University, Evin, Tehran 19839, Iran

Received 26 March 2002; accepted 20 June 2002

Abstract

Oxidation of naphthalene was performed with tetrakis(pentaflourophenyl)porphyrin iron(III)chloride ($F_{20}TPPFe^{III}Cl$), or tetrakis(2,6-dichlorophenyl)porphyrin iron(III)chloride ($TDCPPFe^{III}Cl$), or tetramesitylporphyrin iron(III)chloride ($TMPFe^{III}Cl$) as catalyst and metachloroperbenzoic acid or pentafluoroiodosylbenzene or *tert*-butylhydroperoxide as oxidant in different media in the presence of imidazole as cocatalyst. In aprotic solvent (CH_3CN:CH_2Cl_2, 1:1) and in the presence of $F_{20}TPPFe^{III}Cl$, 1-naphthol, 2-naphthol and 1,4-naphthoquinone yields based on metachloroperbenzoic acid oxidant were 77.7, 2.1 and 5.6%, respectively. The best yield for 1,4-naphthoquinone in methanol with $F_{20}TPPFe^{III}Cl$ was 52.8%. The effect of bases on the yield and specificity of the naphthalene oxidation were studied. When imidazole changed to pyridine in $F_{20}TPPFe^{III}Cl$, the yield of 1-naphthol decreased from 77.7 to 55.3%, whereas for $TDCPPFe^{III}Cl$ catalyst, the yield changed from 61.1 to 18.3%.

Keywords: Cytochrome P-450; Iron-porphyrin; Metachloroperbenzoic acid oxidation; Polycyclic aromatic hydrocarbon; Naphthalene

1. Introduction

The metabolic conversion of aromatic hydrocarbons to hydroxyarenes or/and quinones in mammals has been considered a means for the detoxification and excretion of a variety of foreign substances, including many drugs and environmental pollutants. Ligninases are capable of oxidizing aromatic compounds to quinones followed by ring cleavage [1]. Dioxygenases enzymes incorporate both atoms of molecular oxygen into the aromatic ring to form *cis*-dihydrodiols [2]. Third pathway is oxidation of these compounds to arene oxides by cytochrome P-450 monooxygenases, and the arene oxides then transformed to phenols or epoxy-dioles derivative [3]. Extensive studies have been carried out using of metalloporphyrins, as model for oxygenases, for oxidation of organic compounds [3–13], but polycyclic aromatic hydrocarbons have received little attention [14–18]. Also recently Bartoli et al. [19] have shown that the Mn-porphyrins bearing one to five β-nitro groups are particularly good catalyst for hydroxylation of aromatic compounds with H_2O_2, and Sorokin and Tuel [20] have employed metallophthalocyanines/H_2O_2 system for this purpose; however, iron-porphyrins systems efficient for aromatic oxidations remain to be found.

Because of the quantity of phenolic compounds produced industrially ranks near the top of the list of synthetic aromatics, and it is well known that quinones posses pronounced bioactivity and are important for

* Corresponding author. Tel.: +98-21-240-3155.
E-mail address: n-safari@cc.sbu.ac.ir (N. Safari).

1381-1169/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S1381-1169(02)00354-0

medicine and versatile starting materials in the synthesis of many natural products, and due to severe condition for chemical oxidation of aromatics which needs elevated temperature and/or powerful oxidants, e.g. chromium compounds, we have searched for the catalytic oxidation of aromatics and in this report, we present oxidation of naphthalene by various oxidants in protic and aprotic solvents with iron-porphyrins.

2. Experimental

2.1. Instrumentation

High performance liquid chromatography (HPLC) analyses were performed with a Shimadzu HPLC liquid chromatograph equipped with UV–VIS detector and an ODS column (15 cm × 6 mm). Eluents were a mixture of methanol and water (50:50 (v/v) for detection of 1-naphthol, 2-naphthol and 1,4-naphthoquinone and 80:20 (v/v) for detection of naphthalene) at a flow rate of 1 ml/min. The detection wavelength was 254 nm. All the chromatograms were compared with authentic samples and the yields were calculated from standard curves. UV–VIS spectra were recorded with a Shimadzu 2100 spectrophotometer.

2.2. Materials

The tetrakis(2,6-dichlorophenyl)porphyrin iron-(III)chloride (TDCPPFe^{III}Cl) and tetramesitylporphyrin iron(III)chloride (TMPFe^{III}Cl) were synthesized according to literature methods [21,22]. The tetrakis(pentaflourophenyl)porphyrin iron(III)-chloride (F_{20}TPPFe^{III}Cl) were obtained from Fluka. Metachloroperbenzoic acid (*m*-CPBA) was purchased from Aldrich Chemical Co. and purified by washing with phosphate buffer (pH 7.4) followed by water and then dried under reduced pressure. H_2O_2 (30% aqueous) and *tert*-butylhydroperoxide (*tert*-BuOOH 70% aqueous) were obtained from Merck and Fluka, respectively. Pentafluoroiodosylbenzene (PFIB) was prepared by hydrolysis of pentafluoroiodobenzen-bis(trifluoroacetate) with saturated sodium hydrogen carbonate [23]. The resulting precipitate was collected and carefully dried under reduce pressure and kept at 5 °C. Naphthalene, 1-naphthol, 2-naphthol, 1,4-naphthoquinone and other substances such as axial bases used in these studies, were of the highest grade commercially available from Merck and

Table 1
Oxidation of naphthalene in various solvents and with various Fe-porphyrins under excess amount of substrate

Solvent	Catalyst	Yields (%)[a]			Products/catalyst (M/M)
		1-Naphthol	2-Naphthol	1,4-Naphthoquinone	
CH_3CN:CH_2Cl_2 (1:1)	F_{20}TPPFe^{III}Cl	77.7 ± 2.6	2.1 ± 0.2	5.6 ± 0.3	854
	TDCPPFe^{III}Cl	61.1 ± 1.0	3.4 ± 0.5	8.3 ± 0.3	728
	TMPFe^{III}Cl	5.4	Trace	Trace	54
	None	Trace	Trace	Trace	–
CH_3OH:CH_2Cl_2 (1:3)	F_{20}TPPFe^{III}Cl	27.2 ± 0.9	Trace	7.0 ± 1.4	342
	TDCPPFe^{III}Cl	15.1 ± 0.5	Trace	13.7 ± 0.6	288
	TMPFe^{III}Cl	2.5	1.5	Trace	40
	None	Trace	Trace	Trace	–
CH_2Cl_2	F_{20}TPPFe^{III}Cl	38.2	Trace	6.6	448
	TDCPPFe^{III}Cl	14.4	5.5	Trace	199
CH_3CN	F_{20}TPPFe^{III}Cl	65.9	9.1	5.1	801
	TDCPPFe^{III}Cl	45.9 ± 0.1	Trace	5.1 ± 0.3	510
CH_3OH	F_{20}TPPFe^{III}Cl	29.1 ± 1.0	2.0 ± 0.3	49.5 ± 0.3	806
	TDCPPFe^{III}Cl	34.1	2.0	7.4	435

[a] Reaction is carried out in air at room temperature. Molar ratio for naphthalene:oxidant:Fe-porphyrin:imidazole are $180:1:10^{-3}:10^{-2}$ and *m*-CPBA is 2.4×10^{-3} M. The yield was calculated based on *m*-CPBA.

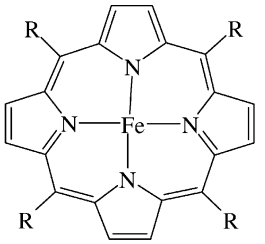
Riedel-deHaën. Solvents for all of these studies were from Merck (spectra grade).

2.3. Typical procedure for oxidation using an excess naphthalene relative to oxidant

A solution of 10.8 mmol of naphthalene and 0.06 μmol of iron-porphyrin and 0.6 μmol of axial bases such as imidazole in 20 ml of solvent such as methanol was prepared. To this solution, 60 μmol of *m*-CPBA in 5 ml solvent was added over 10 min and reaction mixture was left to stir under air at ambient temperature, unless otherwise mentioned. The reaction mixture was analyzed by HPLC after 24 h (Table 1). Most of the reactions were run at least three times and the reported data are averages.

2.4. Typical procedure for oxidation using equal amount of naphthalene and oxidant

A solution of 0.3 mmol of *m*-CPBA in 0.2 ml of solvent was slowly added to a solution of 0.3 mmol naphthalene, 0.3 μmol iron-porphyrin and 3 μmol imidazole in 2.8 ml solvent during 10 min. After 24 h, reaction mixture was diluted with 27 ml of solvent and analyzed by HPLC. Results of these studies presented in Table 2.



R= 2,3,4,5,6-pentafluorophenyl (F_{20}TPPFeCl),
2,6- dichlorophenyl (TDCPPFeCl),
2,4,6-tetramesityl (TMPFeCl)

Fig. 1. Structure of the iron-porphyrins.

3. Results

3.1. The effect of solvent on naphthalene oxidation yield

3.1.1. Under excess amount of substrate to oxidant

Oxidation of naphthalene was performed with iron-porphyrins bearing electron withdrawing and electron donating substituents on the porphyrin ring such as $F_{20}TPPFe^{III}Cl$, $TDCPPFe^{III}Cl$, and $TMPFe^{III}Cl$ (Fig. 1). Table 1 demonstrates the yield of oxidation products in five different solvent systems in the presence of metachloroperbenzoic acid.

Table 2
Oxidation of naphthalene in various solvents and with various Fe-porphyrins under stoichiometric amount of substrate

Solvent	Catalyst	Yields (%)[a]			Conversion (%)	Products/catalyst (M/M)
		1-Naphthol	2-Naphthol	1,4-Naphthoquinone		
CH_3CN:CH_2Cl_2 (1:1)	$F_{20}TPPFe^{III}Cl$	31.9	1.8	14.3	56.1	480
	$TDCPPFe^{III}Cl$	12.0	1.0	4.6	44.5	176
	$TMPFe^{III}Cl$	Trace	Trace	Trace	8.9	–
	None	Trace	Trace	Trace	<4.0	–
CH_3OH:CH_2Cl_2 (1:3)	$F_{20}TPPFe^{III}Cl$	16.7 ± 0.5	Trace	21.3 ± 0.5	49.8 ± 1.1	380
	$TDCPPFe^{III}Cl$	10.3	1.4	8.3	65.0	200
	$TMPFe^{III}Cl$	Trace	Trace	1.7	6.2	17
	None	Trace	Trace	Trace	<3.0	–
CH_3CN	$F_{20}TPPFe^{III}Cl$	25.0 ± 1.5	Trace	9.2 ± 0.7	67.0 ± 0.7	342
	$TDCPPFe^{III}Cl$	9.1 ± 0.5	3.9 ± 0.4	3.9 ± 0.2	51.0 ± 0.9	169
CH_3OH	$F_{20}TPPFe^{III}Cl$	27.7 ± 1.2	Trace	52.8 ± 0.1	56.2 ± 1.5	805
	$TDCPPFe^{III}Cl$	1.8 ± 0.5	Trace	4.0 ± 0.1	13.3 ± 1.0	58

[a] Reaction is carried out in air at room temperature. Molar ratio for naphthalene:oxidant:Fe-porphyrin:imidazole are $1:1:10^{-3}:10^{-2}$ and *m*-CPBA is 0.1 M. The yield was calculated based on *m*-CPBA.

Reaction were carried out under air and concentration of reactants naphthalene:oxidant:porphyrin catalyst:imidazole were $180{:}1{:}10^{-3}{:}10^{-2}$, respectively. Three different products: 1-naphthol, 2-naphthol and 1,4-naphthoquinone were obtained and characterized with HPLC using authentic samples. We have found that the solvent system has profound effect on the both yield of total oxidation products and specificity of the products.

In aprotic solvent ($CH_3CN{:}CH_2Cl_2$, 1:1) and in the presence of $F_{20}TPPFe^{III}Cl$ the 1-naphthol yield based on oxidant is 77.7%, whereas the amount of 2-naphthol 2.1% and 1,4-naphthoquinone 5.6% gained were low in these conditions. $TDCPPFe^{III}Cl$ showed the same trend as $F_{20}TPPFe^{III}Cl$ with slightly lower yields and specificity. These catalysts have also shown high turnover. $TMPFe^{III}Cl$ indicated little catalytic activity by comparison with the former catalyst. Change of solvent from aprotic to protic in the same condition resulted in increasing in the yield of quinone. The best yield for 1,4-naphthoquinone obtained in methanol was 49.5% with $F_{20}TPPFe^{III}Cl$.

3.1.2. Under stoichiometric amount of substrate to oxidant

The yield of oxidation of naphthalene in 1:1 ratio of oxidant to substrate in different solvent system and iron-porphyrin catalyst, is presented in Table 2. The concentration of metachloroperbenzoic acid was 0.1 M and the ratio of naphthalene:oxidant:porphyrin catalyst:imidazole were $1{:}1{:}10^{-3}{:}10^{-2}$. The reaction mixture was chromatographed after 24 h to search for 1-naphthol, 2-naphthol and 1,4-naphthoquinone. In accordance to Table 2, the best solvent system for specific formation of 1-naphthol is 1:1 mixture of $CH_3CN{:}CH_2Cl_2$ (31.9%) and for 1,4-naphthoquinone is protic solvent, methanol, with $F_{20}TPPFe^{III}Cl$ as catalyst (52.8%). Again in every reaction condition, production of 2-naphthol is minor, between 1 and 4%.

Comparison between conversion percent and the total yields of (1-naphthol + 1,4-naphthoquinone) shows selectivity of these catalytic conversions. For instances $F_{20}TPPFe^{III}Cl$ catalyst in methanol produces in 27.7% 1-naphthol and 52.8% 1,4-naphthoquinone that accounts for 54.1% consumption of oxidant. Comparison of 54.1% with conversion of 56.2% of naphthalene proves specificity of this system. In contrary, other solvent systems result in conversion of 40–60% whereby the total yield of naphthol + quinone are around 20% and shows that huge amount of naphthalene has been converted into uncharacterized compounds. These results confirm that solvent and catalyst together have profound effects on the selectivity of naphthalene oxidation. In all of the experiments, conversion of naphthalene in the absence of catalyst was negligible and electron rich iron-porphyrins such as $TMPFe^{III}Cl$ were poor catalysts.

3.2. The effect of oxidant on the yield of oxidation products of naphthalene

Table 3 indicates effect of different oxidants on the reaction products of naphthalene oxidation. The *m*-CPBA produce 77.7% of 1-naphthol, where PFIB result in production of 22%. Other peroxides such as *tert*-butylhydroperoxide and H_2O_2 are not good candidates for these catalytic oxidation in our experimental conditions. The surprising results were obtained when the solvent system has changed to $CH_3OH{:}CH_2Cl_2{:}H_2O$ in the ratio of 18:80:2, in which PFIB acted as better oxidant than *m*-CPBA. The yields of 1-naphthol with PFIB and *m*-CPBA as oxidant are 30.7 and 7.5%, respectively, in this solvent. Traylor and Miksztal [24] have shown that these solvent system are best for alkene epoxidation with PFIB in the presence of electron withdrawing iron-porphyrins.

None of these oxidants other than *m*-CPBA produced considerable amount of 1,4-naphthoquinone.

3.3. The effect of axial ligands on the specificity and the yield of naphthalene conversion

The effect of bases on the yields and specificity of the naphthalene conversion were studied and the results are indicated in Table 4. All iron-porphyrins employed in these studies are poor catalysts in the absence of bases as cocatalyst. Both $F_{20}TPPFe^{III}Cl$ and $TDCPPFe^{III}Cl$ have similar catalytic ability in the absence of bases and produced around 8% of 1-naphthol and trace of other products. Imidazole is best cocatalyst under our reaction conditions both from point of high conversion and high selectivity. The role of imidazole to increase the yield and specificity of products of naphthalene oxidations was more pronounced in $TDCPPFe^{III}Cl$ than $F_{20}TPPFe^{III}Cl$. For instance, when imidazole changed to pyridine

Table 3
Effect of oxidant in the oxidation of naphthalene in air at room temperature

Solvent	Catalyst	Oxidant	Yields (%)[a]		
			1-Naphthol	2-Naphthol	1,4-Naphthoquinone
$CH_3CN:CH_2Cl_2$ (1:1)[b]	$F_{20}TPPFe^{III}Cl$	*m*-CPBA	77.7 ± 2.6	2.1 ± 0.2	5.6 ± 0.3
		PFIB	22.0	1.8	2.9
		tert-BuOOH	1.1	Trace	Trace
		H_2O_2	Trace	Trace	Trace
	$TDCPPFe^{III}Cl$	*m*-CPBA	61.1 ± 1.1	3.4 ± 0.5	8.3 ± 0.2
		PFIB	Trace	Trace	12.5
		tert-BuOOH	Trace	Trace	Trace
		H_2O_2	1.3	Trace	Trace
$CH_3OH:CH_2Cl_2$ (1:3)[b]	$F_{20}TPPFe^{III}Cl$	*m*-CPBA	27.2 ± 0.9	Trace	7.0 ± 1.4
		PFIB	30.4	1.4	4.6
		tert-BuOOH	4.3	Trace	9.9
		H_2O_2	Trace	Trace	Trace
	$TDCPPFe^{III}Cl$	*m*-CPBA	15.1 ± 0.5	Trace	13.7 ± 0.6
		PFIB	7.1	Trace	3.2
		tert-BuOOH	Trace	Trace	3.5
		H_2O_2	Trace	Trace	Trace
$CH_3OH:CH_2Cl_2$ (1:3)[c]	$F_{20}TPPFe^{III}Cl$	*m*-CPBA	16.7 ± 0.6	Trace	21.3 ± 0.5
		PFIB	10.0	Trace	11.0
CH_3OH[c]	$F_{20}TPPFe^{III}Cl$	*m*-CPBA	27.7 ± 1.2	Trace	52.8 ± 0.1
		PFIB	6.7	Trace	16.6

[a] The yield was calculated based on *m*-CPBA.
[b] Molar ratio for naphthalene:oxidant:Fe-porphyrin:imidazole are: $180:1:10^{-3}:10^{-2}$ and oxidant is 2.4×10^{-3} M.
[c] Molar ratio for naphthalene:oxidant:Fe-porphyrin:imidazole are: $1:1:10^{-3}:10^{-2}$ and oxidant is 0.1 M.

Table 4
Effect of axial bases in the oxidation of naphthalene in air and at room temperature in $CH_3CN:CH_2Cl_2$ (1:1) medium with *m*-CPBA

Catalyst	Axial ligand	Yields (%)[a]		
		1-Naphthol	2-Naphthol	1,4-Naphthoquinone
$F_{20}TPPFe^{III}Cl$	None	8.4	1.5	3.7
	Quinoline	55.9	3.3	10.8
	2-Picoline	47.3	1.6	6.7
	Imidazole	77.7	2.1	5.6
	Pyridine	53.3	4.4	10.5
	Collidine	43.8	1.3	5.6
$TDCPPFe^{III}Cl$	None	8.1	Trace	Trace
	Quinoline	12.0	Trace	1.1
	2-Picoline	14.9	Trace	1.1
	Imidazole	61.1	3.5	8.3
	Pyridine	18.3	Trace	4.6
	Collidine	8.7	Trace	2.0
$TMPFe^{III}Cl$	None	Trace	Trace	Trace
	Imidazole	5.4	Trace	Trace

[a] Molar ratio for naphthalene:oxidant:Fe-porphyrin:imidazole are $180:1:10^{-3}:10^{-2}$ and *m*-CPBA is 2.4×10^{-3} M. The yield was calculated based on *m*-CPBA.

in $F_{20}TPPFe^{III}Cl$, the yield of 1-naphthol decreased from 77.7 to 53.3%, whereas in $TDCPPFe^{III}Cl$ the yield changed from 61.1 to 18.3%.

4. Discussion

The oxidation of aromatics generally lacks selectivity because of coupling reactions caused by phenoxy radicals and hence a novel practical method for oxidation of aromatics could be very interesting. So during the course of our systematic study on the simulation of the enzymatic function of cytochrome P-450 with metalloporphyrins, we have found a biomimetic method for selective oxidation of naphthalene to 1-naphthol or 1,4-naphthoquinone.

In this work, oxidation of naphthalene were investigated with *m*-CPBA as oxidant and iron-porphyrins catalysts for selective production of naphtholic and quinonic compounds with high turnover number in different media. We have found that the $F_{20}TPPFe^{III}Cl$ is better oxidant for oxidation of naphthalene than $TDCPPFe^{III}Cl$ and the latter is much better than electron rich porphyrins, $TMPFe^{III}Cl$. $TMPFe^{III}Cl$ is very poor catalyst in our reaction conditions and was destroyed very fast, whereas electron withdrawing substituent porphyrins have high turnover and their degradation in our reaction conditions is low. UV–VIS of the reaction mixture proves that after around 720–850 turnovers, more than 85% of the catalyst was still intact (Fig. 2) [25].

4.1. Effect of solvent and oxidant

Effect of metalloporphyrins structure on the specificity and the yield of oxidation products widely investigated by others [17,24], but effects of solvents and media have gained less attention in the literature [26,27]. We have found that solvents have profound effect on the yield and selectivity of the naphthalene oxidation. For instance, $F_{20}TPPFe^{III}Cl$ in methanol, produce 27.7% 1-naphthol and 52.8% 1,4-naphthoquinone that accounts for 54.1 ((27.7/1) + (52.8/2)) of *m*-CPBA as oxidant. Comparison between conversion of naphthalene which is 56.2 with 54.1% of total yield of 1-naphthol and 1,4-naphthoquinone shows that around 2% of naphthalene is degraded or transferred to coupling products. In comparison, in CH_2Cl_2:CH_3OH in the ratio of 3:1 there is a difference of 23.5%, which shows that this system acts inefficiently from selectivity point of view.

In addition, alkylhydroperoxides are very poor oxidants in our systems. Bartoli et al. [19] have found that H_2O_2 is very efficient oxidant in multi-nitro-porphyrins of manganese(III). Traylor et al. [7], have shown the mixture of CH_3OH:CH_2Cl_2:H_2O_2 (18:80:2) is good solvent for PFIB oxidation with electron withdrawing porphyrins. We have checked these solvent system and although the yield of 30.7% with PFIB for 1-naphthol has gained in comparison with 7.5% yield with *m*-CPBA, but the

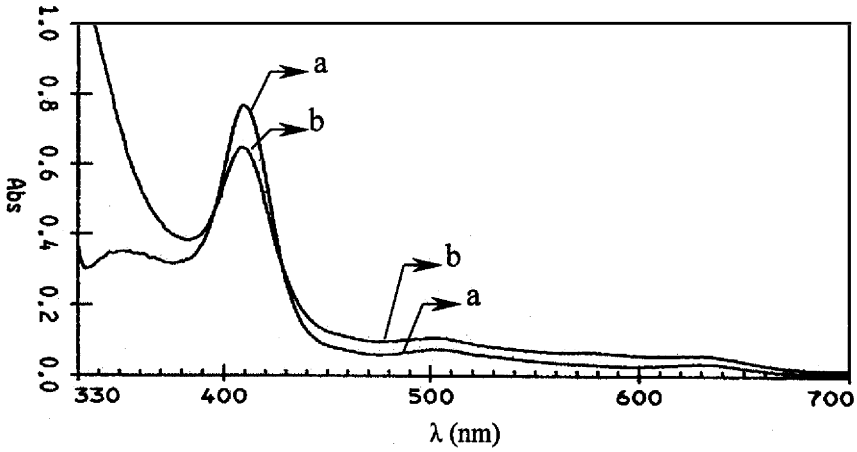
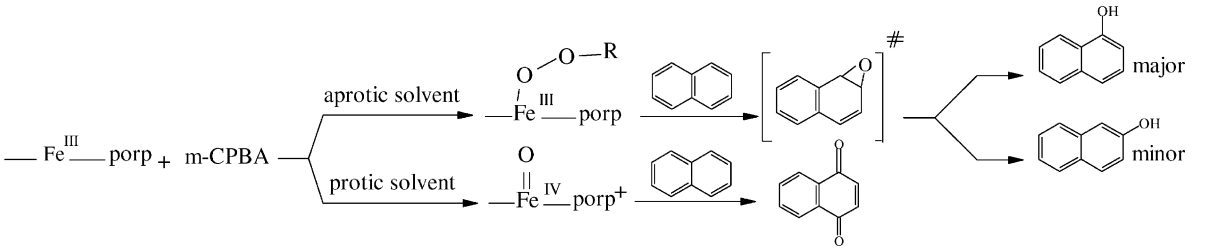


Fig. 2. UV–VIS spectrum of $F_{20}TPPFe^{III}Cl$ (2.4×10^{-6} M), imidazole (2.4×10^{-5} M) and naphthalene (0.432 M) in CH_3CN:CH_2Cl_2 (1:1) solvent: (a) before addition of oxidant, and (b) 24 h after addition of *m*-CPBA (2.4×10^{-3} M).



Scheme 1. Schematic representation of the reaction pathway in naphthalene oxidation with *m*-CPBA in the presence of Fe(III)porphyrin catalyst in protic and aprotic solvents.

condition can be improved with *m*-CPBA on different media (CH_3CN:CH_2Cl_2, 1:1; yield 77.7%).

4.2. Mechanism of naphthols and 1,4-naphthoquinone production

Production of phenols from benzene derivatives and naphthol from naphthalene are believed from intermediacy of arene oxides, due to the nature of NIH shift [28]. But in protic solvents where the 1,4-naphthoquinone is the main product, question was whether 1,4-naphthoquinone forms from further oxidation of phenolic compounds or there is different route to quinone formation. We performed oxidation of 1-naphthol in our experimental conditions. The yield of quinone from naphthalene was 49.5%, whereas the yield of quinone from 1-naphthol was just 6.9% in the same conditions. These result plus our observation which in the ratio of 180:1 of substrate to oxidant in methanol the main product is 1,4-naphthoquinone and changing the mole ratio of naphthalene to oxidant did not dramatically change the amount of quinone, proves formation of 1,4-naphthoquinone directly from naphthalene instead of 1-naphthol or 2-naphthol.

Nam et al. [25] have shown that in protic solvent, high valent oxo intermediate $(PFe^{IV}{=}O)^+$ are reactive oxidant and in aprotic solvent iron peroxy complex is reactive oxidant. So to confirm these for aromatic oxidation, we generate $(PFe^{IV}{=}O)^+$ from reaction of $F_{20}TPPFeNO_3$ with *m*-CPBA in $-45\,^{\circ}C$ in aprotic solvent (CH_3CN:CH_2Cl_2, 1:1). Addition of naphthalene to this oxene resulted in 1,4-naphthoquinone/naphthol ratio of 30 and clearly confirms that 1,4-naphthoquinones formed by this oxidant. We obtained a lower yield for naphthoquinone production in the presence of argon (49.5% in air and 43.0% in argon), so O_2 may take part in the reaction pathway leading to quinone. These results are in accordance with a previously proposed mechanism for the oxidation of polyaromatics when intermediate radicals can be trapped by O_2 to form quinones [29]. We proposed the path of oxidation in Scheme 1.

5. Conclusions

Oxidation of naphthalene *m*-CPBA and in the presence of $F_{20}TPPFe^{III}Cl$ and $TDCPPFe^{III}Cl$ catalyst, result in production of 1-naphthol, 2-naphthol and 1,4-naphthoquinone. This catalytic oxidation exhibits obvious features in the following: (1) the suitable solvent for 1-naphthol production is aprotic solvents and for 1,4-naphthoquinone protic solvents is needed; (2) imidazole as cocatalyst increases the yields more than the other axial ligands that are used in this study; (3) the formation of 1,4-naphthoquinone is directly from naphthalene; and (4) electron withdrawing iron-porphyrins employed in this work indicates high turnover number for aromatic oxidation.

Acknowledgements

We thank the Research and Graduate Study Councils of Shahid Beheshti University for partial financial support and Center of Chemical Services of Shahid Beheshti University for their services.

References

[1] K.E. Hammel, in: H. Sigel, A. Sigel (Eds.), Degradation of Environmental Pollutants by Microorganisms and Their Metalloenzymes. Metal Ions in Biological Systems, Vol. 28, Marcel Dekker, New York, 1992, p. 41.

[2] J.D. Lipscomb, A.M. Orville, in: H. Sigel, A. Sigel (Eds.), Degradation of Environmental Pollutants by Microorganisms and Their Metalloenzymes. Metal Ions in Biological Systems, Vol. 28, Marcel Dekker, New York, 1992, p. 243.
[3] P. Ortiz de montellano, Cytochrome P-450: Structure, Mechanism and Biochemistry, Plenum Press, New York, 1995.
[4] (a) J.T. Groves, T.E. Nemo, J. Am. Chem. Soc. 105 (1983) 5786;
(b) N. Jin, J.T. Groves, J. Am. Chem. Soc. 121 (1999) 2923.
[5] B. Meunier, Chem. Rev. 92 (1992) 1411.
[6] Ö. Almarsson, T.C. Bruice, J. Am. Chem. Soc. 117 (1995) 4533.
[7] T.G. Traylor, J.S. Marsters, T. Nakano Jr, B. Dunlap, J. Am. Chem. Soc. 107 (1985) 5537.
[8] D. Mansuy, Coord. Chem. Rev. 125 (1993) 129.
[9] R.A. Sheldon, Metalloporphyrins in Catalytic Oxidation, Marcel Dekker, New York, 1994.
[10] D. Dolphin, T.G. Traylor, L. Xie, Acc Chem. Res. 30 (1997) 251.
[11] A. Sorokin, J.L. Seris, B. Meunier, Science 268 (1995) 1163.
[12] J.P. Collman, A.S. Chief, T.A. Eberspacher, J.I. Brauman, J. Am. Chem. Soc. 120 (1998) 425.
[13] (a) N. Safari, F. Bahadoran, M.R. Hoseinzadeh, R. Ghiasi, J. Porphyrins Phthalocyanines 4 (2000) 285;
(b) N. Safari, F. Bahadoran, J. Mol. Catal. A: Chem. 171 (2001) 115.
[14] Y. Yan, F.S. Xiao, G. Zheng, K. Zhen, C. Fang, J. Mol. Catal. A: Chem. 157 (2000) 65.
[15] R. Song, A. Sorokin, J. Bernadou, B. Meunier, J. Org. Chem. 62 (1997) 673.
[16] A. Gold, K. Jayaraj, L.M. Ball, K. Brust, J. Mol. Catal. A: Chem. 125 (1997) 23.
[17] M.N. Carrier, C. Scheer, P. Gouvine, J.F. Bartoli, P. Battioni, D. Mansuy, Tetrahedron Lett. 31 (1990) 6645.
[18] S.V. Barkanova, V.M. Derkacheva, O.V. Dolatova, V.D. Li, V.M. Negrimovsky, O.L. Kaliya, E.A. Luk yantes, Tetrahedron Lett. 37 (1996) 1637.
[19] J.F. Bartoli, V.M. Mansuy, K.L.B. Ozette, M. Palacio, P. Battioni, D. Mansuy, Chem. Commun. 10 (2000) 827.
[20] A.B. Sorokin, A. Tuel, Catal. Today 57 (2000) 45.
[21] A.M.D.R. Gonsalves, M.M. Pereira, A.C. Serra, R.A.W. Johnstone, M.L.P.G. Nunes, J. Chem. Soc., Perkin Trans. I 15 (1994) 2053.
[22] A.D. Adler, F.R. Long, F. Kampas, J. Kim, J. Inorg. Nucl. Chem. 32 (1970) 2443.
[23] M. Schemeisser, M.K. Dahmen, P. Sartori, Chem. Ber. 100 (1967) 1633.
[24] T.G. Traylor, A.R. Miksztal, J. Am. Chem. Soc. 111 (1989) 7443.
[25] (a) W. Nam, M.H. Lim, H.J. Lee, C. Kim, J. Am. Chem. Soc. 122 (2000) 6641;
(b) W. Nam, M.H. Lim, S.K. Moon, C. Kim, J. Am. Chem. Soc. 122 (2000) 10805.
[26] T.G. Traylor, F. Xu, J. Am. Chem. Soc. 112 (1990) 178.
[27] Y. Watanabe, K. Yamaguchi, I. Morishima, K. Takehira, M. Shimizu, T. Hayakawa, H. Orita, Inorg. Chem. 30 (1991) 2581.
[28] G. Guroff, J.W. Daly, D.M. Jerina, J. Renson, B. Witkop, S. Udenfriend, Science 158 (1967) 1524.
[29] A. Sorokin, B. Meunier, Eur. J. Inorg. Chem. 9 (1998) 1269.