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Model reaction related to cytochrome P-450: effect of substitution on the rate of naphthalene oxidation

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Abstract

A kinetic method for measuring the relative rates of hydroxylation of naphthalene derivatives/cyclohexene has been developed. With this technique a linear relationship between the logarithm of the rates of oxidation products and the oxidation potentials of the naphthalene derivatives has been observed. Plots of σ Hammett and σ^+ Hammett–Brown with logarithm of relative rates have been linear and shown $\rho = -0.98$ and $\rho^+ = -0.58$, respectively. This contrast aromatic oxidation in protic solvents in which the oxidation products are naphthoquinones and provides further evidence for the intermediacy of carbocation in the hemin catalyzed hydroxylation of aromatic rings.

Keywords: Ironporphyrin; Relative rates; Kinetics; Naphthalene derivatives

1. Introduction

In the past three decades, one of the major goals of bioinorganic chemistry of monooxygenases enzymes was elucidation of the "oxidized intermediate" and "mechanistic pathways" in natural enzymes and in metalloporphyrins as cytochrome P-450 models [1–6]. Most proposed mechanisms involve high-valent iron(IV) oxo porphyrin cation radical intermediate (4 in Scheme 1) as the substrate oxidant [7–17]. Recently, the involvement of hydroperoxo and alkylperoxo intermediates (2 and 3 in Scheme 1) as electrophilic oxidants in alkene epoxidation and aromatic oxidation were reported by peracids and hydrogen peroxide [13–17]. In spite of the wide studies on the effects of substrate structure, porphyrin ring substituents, central metal, solvent and axial ligands on the mechanism and the nature of intermediate formed in hydroxylation of alkanes and epoxidation of olefins [18–26], little attention has been made on the oxidation of aromatic and polyaromatic hydrocarbons [27,28].

Recently, we have reported the catalytic-oxidation of naphthalene by various oxidants and axial ligands in protic and aprotic solvents and have shown that both intermediates 3 and 4 in Scheme 1 functioned as reactive species in the aromatic ring oxidation by iron porphyrins at room temperature. We have shown that participation of 3 and 4 was controlled mainly by the solvent system (protic or aprotic solvents) [29].

During the course of our systematic studies on the simulation of the enzymatic function of cytochrome P-450 with metalloporphyrins, and in order to determine the extent to which electronic effects determine the rate of oxygen transfer, we have studied the relative rates of aromatic ring hydroxylation of a series of naphthalene derivatives by *m*-CPBA and $F_{20}TPPFe^{III}Cl$ in aprotic CH_3CN:CH_2Cl_2 (1:1) solvent. To accomplish the relative rate measurements, we have used a competitive kinetic method.

2. Experimental

2.1. Materials

The 5,10,15,20-tetrakis(2,3,4,5,6-pentafluorophenyl)porphyrin ($H_2F_{20}TPP$) was prepared from 2,3,4,5,6-pentafluorobenzaldehyde by the procedure used by Lindsey et al. [30]. Insertion of iron into $H_2F_{20}TPP$ was performed in acetonitrile under inert N_2 atmosphere, according to liter-

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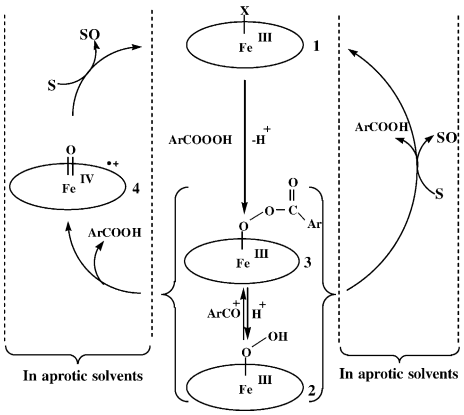


Scheme 1.

ature methods [31]. Metachloroperbenzoic acid, *m*-CPBA, was purchased from Aldrich and purified by washing with phosphate buffer (pH 7.4) followed by water and dried under reduced pressure. Purity of *m*-CPBA was determined by iodometeric analysis. All reagents such as naphthalene derivatives, cyclohexene and cyclohexene oxide purchased from Merck and Fluka were the best available purity and used without further purification. Acetonitrile (anhydrous, Merck) and dichloromethane (anhydrous, Merck) were distilled from calcium hydride before used. Imidazole was prepared from Riedel-deHaën.

Phenolic compounds produced in oxidation of some naphthalene derivatives (Table 1) were isolated and identified by chromatography and their spectral properties. Thin-layer chromatography (TLC) analysis was performed on precoated aluminum oxide TLC cards. Column chromatography was carried out on Fluka aluminum oxide (type 5016 A basic).

2.2. Instrumentation

The GC–MS analysis was performed on a Shimadzu gas chromatograph with a DB5 column, interfaced to a QP MS detector. IR spectra were obtained with an IR-470 Shimadzu spectrophotometer. The ^{1}H NMR spectra were recorded with a Bruker 300-Avance NMR spectrometer using CD_2Cl_2 as the solvent and tetramethylsilane (TMS) as an internal standard. The UV–vis spectra have been done by a Shimadzu 2100 spectrophotometer. Cyclohexene and cyclohexene oxide were detected and qualified using Varian gas chromatograph fitted with a SE-30 packed column (3 m × 1.6 mm) and flame ionization detector. All peaks were identified by co-injection with the known compounds. Quantification of substrate and product were performed by comparison with *n*-octane as internal standard. The electrochemical experiments were performed on a Metrohm 746 VA Trace Analyzer. Cyclic voltametry was carried out in CH_2Cl_2 solution using tetrabutylamonium perchlorate (0.1 M) as supporting electrolyte, a glassy carbon working electrode, a Pt-wire counter electrode and an Ag/AgCl (KCl, 3 M) reference electrode. The typical sweep rate was 100 mV s^{-1} and the window used was from 0.0 to +1.75 V. All melting points were measured on an Electrothermal 9100 apparatus and are uncorrected.

2.3. General procedure for isolation and characterization of products on naphthalene oxidation

The products composition for the oxidation of 1-nitronaphthalene, 1-methylnaphthalene, 2-naphthaldehyde and 2-methylnaphthalene were obtained by caring out a large scale run. A typical procedure is as follows. To dry CH_3CN:CH_2Cl_2 (1:1) solvent mixture (55 ml) at ambient temperature was added 3 × 10^{-3} mole of substrate, 2.04 × 10^{-6} mole of $F_{20}TPPFe^{III}Cl$ and 2.04 × 10^{-5} mole of imidazole. To this solution, 3.6 × 10^{-3} mole of *m*-CPBA in 5 ml solvent was slowly added over 10 min. The mixture was stirred until completion of the reaction by TLC monitoring. Then, solvent was evaporated in vacuum and the crude reaction mixture was solved in toluene and filtered for separation of metachlorobenzoic acid and no reacted *m*-CPBA. Again, the solvent was removed by evaporation,

Table 1
Oxidation of naphthalene derivatives by $F_{20}TPPFe^{III}Cl$/imidazole in CH_3CN:CH_2Cl_2 (1:1) solvent with *m*-CPBA

Run	Substrate	Yields (%)[a]		Conversion (%)	Selectivity (%)[b]
		4-hydroxy	3-hydroxy		
1	1-Methylnaphthalene	42.5	20.0	70.0	89.3
2	1-Nitronaphthalene	5.0	0.0	8.0	62.5
3	2-Methylnaphthalene	31.0	9.1	45.0	89.1
4	2-Naphthaldehyde	32.8	3.4	56.5	64.1
5	Naphthalene[c]	31.9	1.8	56.1	60.1

Reaction was carried out in air at room temperature. Molar ratio for naphthalene:oxidant:catalyst:imidazole was 1:1.2:6.8 × 10^{-4}:6.8 × 10^{-3} and *m*-CPBA was 0.06 M. The reaction time for 1-methylnaphthalene, 1-nitronaphthalene, 2-methylnaphthalene, 2-naphthaldehyde and naphthalene was 10, 24, 10, 10 and 24 h, respectively.

[a] The organic products and the unreacted naphthalenes were separated by column chromatography and analyzed by spectroscopic methods and melting points by comparison with literature. The yields calculated based on starting naphthalenes.

[b] Selectivity is [(3-hydroxy (%) + 4-hydroxy (%))/conversion (%)] × 100.

[c] From our previous work [29], naphthalene:oxidant:catalyst:midazole were 1:1:10^{-3}:10^{-2} and the yield calculated based on starting oxidant by HPLC.

Table 2
Relative reaction rates of oxidation of naphthalenes by *m*-CPBA with $F_{20}TPPFe^{III}Cl$ as catalyst

No.	Naphthalene derivatives	$\Delta[S_{a/b}]_\infty$ (M)[a]	Naphthalene concentration (M)[a]	$k_1 = k_b/k_{cyclohexene}$ ($\times 10^{-3}$)	$k_2 = k_1/k_{nap}$
1	Naphthalene	0.0377	0.180	62.2509 ± 2.14	1.000
2	1-Fluoronaphthalene	0.0361	0.346	39.7352 ± 0.34	0.638
3	1-Chloronaphthalene	0.0397	0.380	23.6570 ± 3.01	0.380
4	1-Bromonaphthalene	0.0405	0.302	23.8807 ± 1.78	0.384
5	1-Methylnaphthalene	0.0353	0.225	66.9784 ± 0.56	1.076
6	1-Methoxynaphthalene	0.0317	0.135	167.1205 ± 1.68	2.685
7	1-Naphthylamine	0.0294	0.151	193.3670 ± 8.22	3.106
8	1-Naphthol	0.0326	0.108	191.7486 ± 2.53	3.080
9	1-Nitronaphthalene[b]	–	0.487	9.4788 ± 1.00	0.152
10	1-Naphthoic acid	0.0376	0.250	47.1126 ± 2.83	0.757
11	2-Bromonaphthalene	0.0397	0.260	31.2537 ± 1.04	0.502
12	2-Methynaphthalene	0.0345	0.187	95.5103 ± 6.81	1.534
13	2-Methoxynaphthalene	0.0319	0.232	99.6288 ± 5.57	1.600
14	2-Naphthol	0.0286	0.147	213.0069 ± 6.52	3.422
15	2-Naphthalenethiol	0.0306	0.100	250.3092 ± 0.77	4.021
16	2-Naphthaldehyde	0.0374	0.215	56.5154 ± 3.31	0.908
17	2-Naphthoic acid	0.0438	0.244	10.9223 ± 1.13	0.175

[a] For lower concentration of naphthalenes.
[b] Relative rate was calculated according to change of epoxide.

and the residue were washed thoroughly with H_2O and then extracted with CH_2Cl_2 (3 × 20 ml). The organic layer was dried under $MgSO_4$ and the solvent was evaporated under reduced pressure. Separation and purification carried out by aluminum oxide column chromatography eluting with chloroform:*n*-hexane (1.5:1) mixture, giving compounds in yields and selectivity reported in Table 1. All of these products were identified by IR, ^{1}H NMR and melting point measurement and the results were compared with literature reports [32]:

3-Methyl-1-naphthol; IR(KBr): ν, cm^{-1} 3440 (–OH, stretch), mp (°C): 155 (lit; 155–156), GC/MS (*m*/*z*) 158 (M^+), 3-methyl-2-naphthol; IR(KBr): ν, cm^{-1} 3435 (–OH, stretch), mp (°C): 83–85 (lit; 87), GC/MS (*m*/*z*) 158 (M^+), 4-methyl-1-naphthol; IR(KBr): ν, cm^{-1} 3425 (–OH, stretch), mp (°C): 80 (lit; 81–82), 4-methyl-2-naphthol; IR(KBr): ν, cm^{-1} 3420 (–OH, stretch), mp (°C): 88 (lit; 84–85), 4-nitro-1-naphthol; IR(KBr): ν, cm^{-1} 3491 (–OH, stretch), mp (°C): 162 (lit; 166.5–167), ^{1}H NMR (CD_2Cl_2) δ (ppm) 7.53–7.77 (3H, m, aromatic CH and phenolic OH), 7.97(1H, d, $J = 8.0$ Hz, aromatic CH), 8.14 (1H, d, $J = 8.2$ Hz, aromatic CH), 8.25(1H, d, $J = 7.6$ Hz, aromatic CH), 8.59 (1H, d, $J = 7.6$ Hz, aromatic CH), 3-hydroxy-2-naphthaldehyde; IR(KBr): ν, cm^{-1} 3360 (–OH, stretch), 1678 (C=O, stretch), mp (°C): 95 (lit; 99–100), 4-hydroxy-2-naphthaldehyde; IR(KBr): ν, cm^{-1} 3245 (–OH, stretch), 1625 (C=O, stretch), mp (°C): 173 (lit; 169–170).

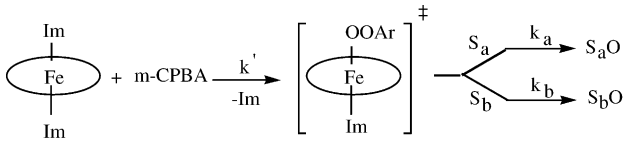
2.4. Competitive oxidation and relative rates

The relative rates of naphthalenes reactions were determined by competitive method. Competitive reaction between cyclohexene as a reference substrate and naphthalene derivative were carried out under homogeneous condition in $F_{20}TPPFe^{III}Cl$/imidazole/*m*-CPBA system. The rates were determined by gas chromatography, following decreasing of the cyclohexene in the presence of naphthalene derivatives using *n*-octane as internal standard. Rate calculation was performed for at least three different concentrations of each substrate and results were averaged.

In a typical procedure, a fresh solution of 6.25×10^{-2} M cyclohexene, 6.25×10^{-5} M $F_{20}TPPFe^{III}Cl$ and 6.25×10^{-4} M imidazole in CH_3CN:CH_2Cl_2 (1:1) solvent was prepared. The above solution (200 μl) was charged into a small test tube with a silicon stopper, and the corresponding amount of *m*-CPBA (50 μl, 1.25×10^{-5} mole) in CH_3CN:CH_2Cl_2 (1:1) was added. After 15 h, the rate of decreasing of the reference alkene was determined by GC. This experiment was repeated in the presence of three different concentrations of each naphthalenes. Concentration of naphthalene derivatives were varied on the basis of reactivity and solubility from 0.48 M for non-reactive substituted naphthalenes such as 1-nitronaphthalene to 0.1 M for reactive ones such as 2-naphthalenethiol. The rates calculated relative to that of cyclohexene and naphthalene oxidation are listed in Table 2.

3. Results

The reaction between cyclohexene, *m*-CPBA and $F_{20}TPPFe^{III}$-Im at 25 °C in CH_3CN:CH_2Cl_2 (1:1) results in the conversion of 91.8% and formation of cyclohexene oxide in 70.0% yield (71.4% selectivity) based on oxidant during reaction time. In the presence of a second substrate such as naphthalene, the conversion of cyclohexene (and the yield of cyclohexene oxide) was decreased. In the presence



Scheme 2.

of a second substrate, the reactions were assumed to occur as in Scheme 2 and Eq. (1).

$$\frac{\Delta[S_b]_\infty}{\Delta[S_a]_\infty} = \frac{k_b}{k_a}\left(\frac{[S_b]_0}{[S_a]_0}\right) \quad (1)$$

where S_a is the concentration of cyclohexene (the reference alkene), S_b is the concentration of naphthalene derivative, ∞ means the end of reaction and 0 means the start of the reaction. Decreasing of the conversion of cyclohexene in the presence of a second substrate is equal to conversion of the second substrate. Therefore,

$$\Delta[S_b] \approx \Delta[S_a] - \Delta[S_{a/b}] \quad (2)$$

where $S_{a/b}$ is the concentration of S_a in the presence of S_b. So, relative reaction rate, k_b/k_a, can be calculated according to the following equation (Eq. (3)):

$$\frac{k_b}{k_a} = \frac{\Delta[S_a]_\infty - \Delta[S_{a/b}]_\infty}{\Delta[S_{a/b}]_\infty}\left(\frac{[S_a]_0}{[S_b]_0}\right) \quad (3)$$

Thus, by measuring the conversion of cyclohexene with and without the second substrate, the relative reaction rates can be calculated. Calculation of the relative rates obtained for various naphthalenes were based upon conversion of S_a and S_b. Products of naphthalene oxidation were estimated as the sum of 3-naphthol and 4-naphthol. At least three different concentrations of each test substrate were used to determine the relative rates. Table 1 demonstrates products of oxidation of naphthalene derivatives in our system. High selectivity toward hydroxylation in 3 and 4 positions on naphthalene ring is observed.

4. Discussion

4.1. Product and selectivity of naphthalene by hemin oxidation

The oxidation of aromatics generally lack selectivity because of coupling reaction caused by phenoxy radicals and hence novel practical methods for hydroxylation of aromatic compounds could be very interesting. Aromatic hydroxylation by metalloporphyrins usually results in low yields. The first report returns to 1982, that Smith and Sleath has reported, that toluene, anisole and naphthalene hydroxylation gives related phenols less than 5% by Fe^{III}TPPCl/iodosylbenzen in CH_2Cl_2 [33]. Better yield in aromatic oxidation was reported by Mansuy and co-workers. They have found that all iron porphyrins result in low yields of aromatic hydroxylation, although they have reported relatively higher yields for anisole and naphthalene hydroxylation by Mn^{III}meso-tetraarylporphyrin bearing halogen and nitro substituents on the meso-aryl and pyrrole groups with H_2O_2 oxidant [34,35]. For other polyaromatic hydrocarbons, there are little reports and generally quinonic compounds are major products [36,37]. Also, conversion of some naphthalene derivatives to related quinonic products with metalloporphyrins was reported [38–40].

The hydroxylation of naphthalene and some naphthalene derivatives (1-nitronaphthalene, 1-methylnaphthalene, 2-naphthaldehyde and 2-methylnaphthalene) by $F_{20}TPPFe^{III}$Cl and *m*-CPBA in the presence of imidazole in aprotic solvent, CH_3CN:CH_2Cl_2 (1:1), yielded the naphthol products, Table 1. Notably, hydroxylation of naphthalene ring occurred on the 3 and 4 positions. According to adequate differences between melting point of all of probable phenolic and quinonic products, we used melting point for appointment of position of hydroxyl group in naphthalene ring. Although infra red spectroscopy for all of products was recorded and O–H stretching band in all of products shows presence of phenolic compounds. For 4-nitro,1-naphthol, ^{1}H NMR spectrum shows two doublets peaks in 8.2–8.6 ppm region for CH_a and CH_b on hydroxylated ring that confirmed the major products in 1-nitronaphthalene oxidation is 4-hydroxy product. Comparison between conversion of 1-nitronaphthalene which is 8% with 5% of yield of 4-hydroxy product shows formation of other hydroxylated products such as 5-hydroxy and 8-hydroxy (that in most electrophilic reaction are major products) are negligible. This fact shows special selectivity in our system. For some oxidation mixture systems such as 2-methylnaphthalene and 1-fluoronaphthalene GC/MS spectra show all detected products are phenolic compounds and no quinonic compounds was detected.

We have previously shown that the nature of solvent have profound effect upon quinonic or phenolic products in oxidation of naphthalene [27,29]. The reaction of naphthalene with iron(III) porphyrin complexes and *m*-CPBA did not produce phenolic products in good yield in protic solvents whereas in aprotic solvent, phenolic compounds are major products. We have proposed two different mechanistic pathways and two different active intermediates in protic and in aprotic solvents. In protic solvents, high oxo intemediate produced quinonic compounds but in aprotic solvents, phenolic products were produced from peroxo active oxidant [29]. Here, that observation was reconfirmed with various substituted naphthalene because the solvent is aprotic and the major products are naphthols.

Notably, with electron-withdrawing or -donating in α and β position of naphthalene ring, hydroxylation occurred on 3 and 4 positions, chemoselectively. The yield of none-reactive substituted naphthalenes, 1-nitronaphthalene and 2-naphthaldehyde is lower than the reactive substituted naphthalenes derivatives. Although selectivity toward formation of naphtholic compound conserved. For example,

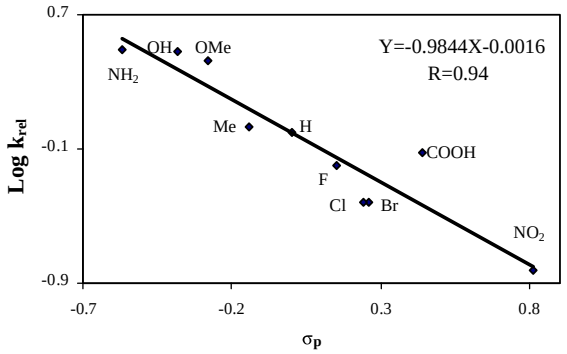


Fig. 1. Plot of logarithm of relative rate constant vs. σ_p for α-naphthalene derivatives.

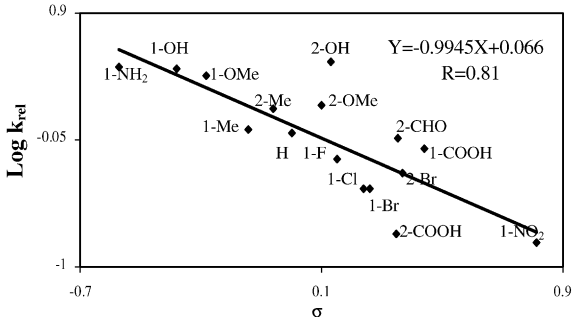


Fig. 2. Plot of logarithm of relative rate constant vs. σ_p for α-naphthalene derivative and σ_m for β-naphthalene derivative.

1-methylnaphthalene by 70.0% conversion produced 42.5% + 20.0% = 62.5% phenolic products, so only about 7.5% of initial reagent converted to quinonic and polymeric compounds. Although in 2-naphthaldehyde difference between conversion of starting 2-naphthaldehyde and total yield of naphtholic products is ∼20.0%. This can be due to other oxidation product such as 2-naphthoic acid or due to lose of the products during purification method. However, we were not able to isolate any other product from reaction vessel.

4.2. Relative rates and mechanistic insight

In order to investigate substrate effects, we have studied the relative rates of hydroxylation of a series of naphthalene derivatives with different electron-donating and -withdrawing groups. To accomplish the relative rate measurements, we have used a competitive method [27,28]. The assumption is made that oxidation of cyclohexene as reference alkene, S_a, and naphthalene derivatives, S_b, are the only pathways for oxygen transfer from the peroxo intermediate. So, we assumed that oxidation of solvents and oxidative degradation of catalyst was negligible in the presence of excess amount of substrates.

Table 2 demonstrates the resulting relative rates, $k_1 = k_b/k_a$. The data were standardized to be the ratios to naphthalene in column 6. It is clear, with all of substituents, the oxidation of naphthalenes are slower than oxidation of cyclohexene. The rate of naphthalene oxidation versus cyclohexene oxidation is varied on the basis of reactivity from 0.01 for electron-withdrawing substituent such as 1-nitronaphthalene to 0.25 for electron-donating ones, such as 2-naphthalenethiol.

For the investigation of mechanistic details, we used Hammett parameters in our systems. According to Table 2, major products of monosubstituent naphthalenes in α or β position are *para*-hydroxylated products. So, we used σ_P and σ_m Hammetts parameters for α-naphthalene and β-naphthalene derivatives, respectively. The plot of $\log k_{rel}$ against Hammetts σ_P [41] for α-naphthalenes is presented in Fig. 1 and the plot for σ_P and σ_m [41] for α-naphthalenes and β-naphthalenes, respectively, are presented in Fig. 2. Both two graphs show a linear relationship between $\log k_{rel}$ and $\sigma_{Hammetts}$, indicated the substituent affected the hydroxylation of naphthalenes. In Fig. 1, 1-naphthoic acid does not fit with the graphs. This returned to acid catalytic activity of this compound in metalloporphyrin oxidation [24]. In benzylic compounds, $R = 0.98$ were accepted for linearity of the plot. Since all data for calculation of reaction and substituent constant did not come from the same investigation and the medium and condition of the reaction are different especially in naphthalenes which are different systems, this linearity is surprising well and confirm electronic effect in this system.

We compared the plot of Hammett σ and Hammett–Brown σ^+ for α-naphthalene derivatives. The ρ and ρ^+ were −0.98 and −0.58, respectively, and the correlation factors, R, were 0.94 and 0.86 for σ and σ^+, respectively. However, the linear relationship between relative rates with σ were better than with σ^+. We found no relationship in the $\sigma_p^\bullet$ [42] plot, but with the dual parameter analyses of $\rho_p{}^\bullet\sigma_p{}^\bullet + \rho_p{}^+\sigma_p{}^+$, a linear behavior with $R = 0.86$ was observed. No clear evidence to support an electron transfer mechanism was obtained since improve correlation in dual parameters are not significant. The plot of $\log k_{rel}$ for α-naphthalene and β-naphthalene against E_p (oxid.) are presented in Fig. 3. There is a linear correlation between E_p (oxid.) and $\log k_{rel}$. Practically, any process in which an electrophilic species reacts with an unsaturated bond responds to electron density.

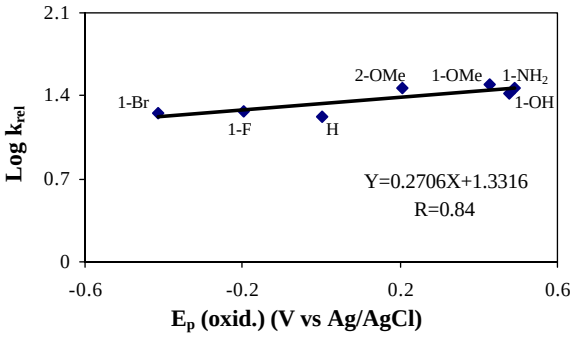
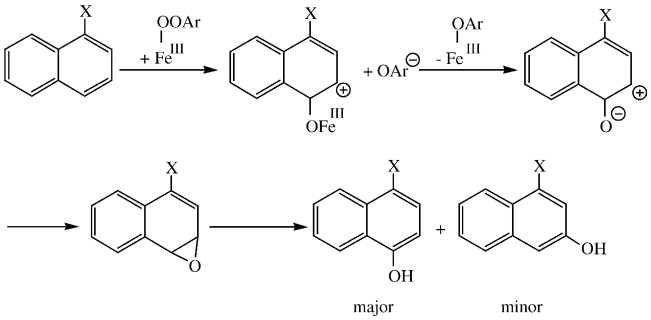


Fig. 3. Correlation of $\log k_{rel}$ for hydroxylation with solution oxidation potential of naphthalene derivatives.



Scheme 3.

4.3. Proposed mechanistic pathway

Two different active oxidants were proposed in hemin catalyzed oxidation with peracids and iodosylbenzen. Nam et al. showed that both high-oxo and peroxo intermediate were formed in the catalytic-oxidation of olefins and some factors such as presence of proton source in solvent controlled the nature of intermediate [15]. Collman et al. have also reported peroxo intermediacy in hemin catalyzed epoxidation [13]. We have shown recently that for aromatic ring oxidation protic solvents result in high oxo intermediate and production of quinonic products, whereas, in aprotic solvents, the intermediate is peroxo iron complexes and the products are phenolic. In contrast, we have shown that in protic solvent, both electron-donating and -withdrawing groups result in increasing the relative rate, and we proposed a radical pathway [27].

In this study, based upon the result obtained from Hammett plots, oxidation potentials plot, yield and specificity of products in naphthalene oxidation, which is consistent with peroxo iron intermediacy, a mechanism based upon the electrophilic addition with a carbocation intermediate were proposed, Scheme 3.

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