



Active species formed in a Fenton-like system in the medium of triethylammonium acetate ionic liquid for hydroxylation of benzene to phenol

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ABSTRACT

High-valent iron(IV)-oxo species was proved to be the main oxidizing species for hydroxylation of benzene to phenol by a Fenton-like reagent in triethylammonium acetate ionic liquid via UV-vis and ESI-MS characterization, while hydroxyl radical was excluded by detailed investigations. It was found that the formation of hydroxyl radical was prohibited by the reduction of redox potential of Fe(III)/Fe(II) couple in triethylammonium acetate medium, leading to a decreased over-oxidation of benzene than that in aqueous solution. The reaction mechanisms for hydroxylation of benzene, as well as for over-oxidation of phenol by iron(IV)-oxo species were proposed. The latter is partly prohibited by the hydrogen-bond interaction between as-produced phenol and acetate anion of the ionic liquid.

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1. Introduction

A Fenton or Fenton-like reaction, which is the course of reaction between iron (II or III) and H_2O_2 , is of great importance in biological [1], environmental [2], and catalytic oxidation [3]. Although the Fenton or Fenton-like system has been extensively investigated for about one hundred years [4–9], the detailed mechanism is still ambiguous and more complicated than what had been proposed [10]. The most popular reaction mechanisms are the radical chain mechanism via intermediates of $\cdot\text{OH}$ and $\cdot\text{OOH}$, and the non-radical mechanism through high-valent iron species. The two types of mechanism had always been a controversy since different conclusions were reached under different reaction conditions, such as ligands, solvent, pH, and the presence of O_2 [11]. This is mostly ascribed to the uncertainty of the active species formed, for example, hydroxyl radical is extensively accepted as the active species in aqueous solution [12,13], while high valent iron(IV) oxo species has been invoked as key reactive intermediate in non-heme iron enzyme [14]. Solvent was found to be an important factor which affected the formation of active species in Fenton-like reactions in previous investigations [15]. As a result, the activity of the catalyst and the selectivity of the reaction might be tuned. For example, the oxidation of cyclohexane was not effective by a simple Fenton reaction in the water medium [16], while the reaction efficiency based on H_2O_2 and the selectivity to the product of cyclohexanone

were both greatly enhanced by the introduction of coupled pyridine/acetic acid [17]. The redox systems of $\text{Fe}^{2+}/\text{Fe}^{3+}/\text{H}_2\text{O}_2$ have been elaborated for the oxidation of saturated hydrocarbons in solvent of pyridine/acetic acid, being titled “Gif system” [11]. Water is the solvent for the traditional aqueous Fenton system. However, aqueous Fenton system is more suitable for degradation reactions rather than synthetic applications because over-oxidation is easy to occur [18]. Only few of the traditional organic solvents, such as acetonitrile, pyridine/acetic acid, dichloromethane and alcohol were proved to be efficient for the oxidation of organic substrates by a Fenton-like reaction [19–22]. On the other hand, a new attractive reaction medium, ionic liquid (IL) [23], has drawn our interest on its application in a Fenton-like reaction. Ionic liquids offer some unique properties as solvents, in addition, they have prospect for design of solvent to meet specific requirements for a particular reaction type [24]. Significant improvements on the catalytic performance in some transition metal-catalyzed reactions have been observed using ILs as the solvents [25]. ILs act not only as innocent solvents, but also as ligand, co-catalyst and catalyst that are involved in the formation of the active species changing the reaction mechanism [26]. For example, the Lewis acidity of a chloroaluminate melts IL, $[\text{cation}][\text{Al}_2\text{Cl}_7]$, was utilized to convert the neutral catalyst precursor into the corresponding cationic active form [27]. Xiao and co-workers demonstrated that a Pd carbene complex was formed in the presence of BMIMBr IL, and it was active and stable in the Pd-catalyzed Heck coupling reaction [28]. They also found that the cationic reaction pathway was promoted by IL in the Heck arylation of olefin reaction, resulting in an improved selectivity to the branched product [29]. As the nature of

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Table 1
Phenol oxidation in aqueous solution and [Et₃NH][OAc] system^a.

Entry	Conversion (%)	Di-phenols		Benzoquinone		Tars	
		Y (%) ^b	S (%) ^b	Y (%)	S (%)	Y (%)	S (%)
1 ^c	70.2	48.0	68.4	0.2	0.2	22.0	31.4
2 ^d	4.8	4.0	83.3	0.8	16.7	0	0

^a Reaction conditions: 10 mL solvent; FeSO₄, 0.08 mmol; phenol, 1 mmol; H₂O₂ (30 wt.%), 1.88 mmol; 323 K, 1 h.

^b Y (%): yield of the product; S (%): selectivity to the product.

^c Water, pH = 3.4 (adjusted by H₂SO₄).

^d [Et₃NH][OAc], pH = 3.4 (adjusted by HOAc).

the active species in a Fenton-like reaction is so dependent on the solvent, it may be adjusted by the diversity of anion/cation combinations of ILs, leading to an expected efficiency and selectivity for the reaction. To the best of our knowledge, there were only very few reports on the application of IL as the solvent for a Fenton-like reaction [30]. It is promising to investigate its application, especially its influence on the nature of active species generated.

In our previous work [31], triethylammonium acetate ([Et₃NH][OAc]), a simple ionic liquid, had been used as the medium for hydroxylation of benzene by a Fenton-like reagent. It was found that [Et₃NH][CH₃COO] IL exhibited retardation performance for the decomposition of H₂O₂ and protection performance for the further oxidation of phenol, however, the molecular aspects of the reaction were not investigated. Systematic investigations about the nature of the reactive species originated in the reaction were carried out in detail in the present work. The possible reaction mechanism for the hydroxylation of benzene was also proposed.

2. Experimental

2.1. Synthesis of ionic liquid

[Et₃NH][OAc] was synthesized according to the literature [32]. In a 250 mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer, glacial acetic acid was dropped slowly to stoichiometric amount of triethylamine in the presence of water with stirring at 353 K for 2 h. The water and little amount of unreacted substrates were separated by rotary evaporator, and then the product was dried at 353 K in vacuum (5 mmHg) until the residue remained constant.

2.2. Catalytic oxidations

All experiments were carried out in a 50 mL round-bottom flask equipped with a reflux condenser and a magnetic stirrer in open air. In a typical procedure, 0.08 mmol FeSO₄ was dissolved in 10 mL solvent ($V_{[\text{Et}_3\text{NH}][\text{OAc}]} / V_{\text{HOAc}} = 1/1$, pH = 3.4), then equivalent organic substrate and H₂O₂ (30 wt.%) were added, and the resulting mixture was stirred at 333 K for 4 h under reflux.

After reaction, the products were identified by GC–MS analysis (Agilent, 5973 Network 6890N) and then quantitatively analyzed by internal standard method through HPLC (Waters, 1525P equipped with 250 mm × 4.5 mm ODS column and UV detector) and GC (FULL, GC-9790 equipped with hydrogen flame ionization detector and a capillary column). The yields of the products were calculated as follows: the amount of product (mol)/the amount of substrate initially added (mol). Selectivity to the specified product was calculated as follows: the amount of the designated product (mol)/the sum of all the products (mol).

2.3. Characterization

Electrochemical measurements were conducted on a three-electrode potentiostat (CHI 610D) in an electrochemical cell with

a nitrogen-purge system to control the presence of O₂. The working electrode was a glassy-carbon (area, 0.09 cm²), the auxiliary electrode was a platinum inlay (area, 0.023 cm²), and the calomel electrode (SCE) was employed as the reference electrode.

UV–vis spectra of the samples were recorded in open air on a TU-1901 UV–vis spectrophotometer equipped with a circulating water bath. The sample cells were quartz with a 10-mm path length. All the UV–vis spectra were background-substituted from a reference sample of solvent.

The electrospray ionization mass spectrometry (ESI-MS) experiments were performed on Q-TOF-MS Premier (Waters). Typical ESI conditions were as follows: source temperature, 363 K; spray voltage, 2.8 kV; capillary voltage, 40 V; tube lens off-set voltage, 4 V; sheath gas (N₂) flow rate, 40 units. The negative ion mode mass spectra of the samples using water–methanol as infusion solvent showed the presence of different ionic species.

3. Results and discussion

In our previous work [31], FeSO₄ had been used as the catalyst precursor for the hydroxylation of benzene. Other iron sources, such as Fe₂(SO₄)₃, FeCl₂, FeCl₃, Fe(NO₃)₃, as well as Fe(OH)(OAc)₂, were also tested in the hydroxylation reactions in the [Et₃NH][OAc] system. Almost the same yield of phenol as that by FeSO₄ was obtained when the reaction was catalyzed by Fe₂(SO₄)₃ or Fe(OH)(OAc)₂. However, it was less by using FeCl₂, FeCl₃ or Fe(NO₃)₃. The results confirmed the importance of the contra ion in this reaction. In order to minimize the influence of the original anion, but focus on the acetate anion of the [Et₃NH][OAc] IL, FeSO₄ or Fe₂(SO₄)₃, which has a weak coordinated anion, was still used as the catalyst precursor in this paper. On the other hand, although a comparable yield of phenol was obtained in [Et₃NH][NO₃] IL, this IL could not be used as a pure solvent, as it is in solid state in the absence of water. Thus, in our present work, we just investigate on the [Et₃NH][OAc]/FeSO₄ system.

3.1. Effect of water on the hydroxylation reaction

Hydroxylation of benzene with excessive H₂O₂ to FeSO₄ (140:1) in open air was carried out in the [Et₃NH][OAc] IL medium. Under the optimal reaction condition, a 12% yield of phenol based on H₂O₂ (also 12% based on benzene) was obtained, with a selectivity of 94% to phenol. Biphenyl was never detected. In contrast, in aqueous solution under the same reaction condition, only about 2% yield of phenol was obtained with large amount of tars formed. It seemed that the selectivity to phenol was much improved in the [Et₃NH][OAc] system than that in aqueous solution. It is generally accepted that the over-oxidation of benzene is caused by the oxidation of the produced phenol [33]. The oxidations of phenol in the two systems were then compared, and the results were listed in Table 1. As we had reported in our previous work [31], under the same reaction conditions, phenol was much more easier to be transformed to di-phenols and tars in aqueous solution than that in [Et₃NH][OAc] system. It was suggested that the solvent water

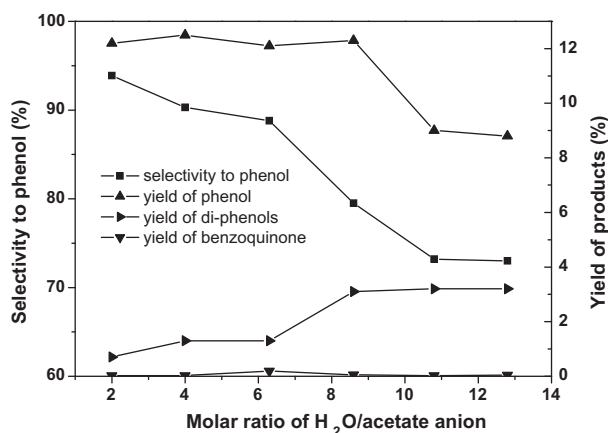


Fig. 1. Hydroxylation of benzene by Fenton reagent in $[\text{Et}_3\text{NH}][\text{OAc}]$ system with addition of water. Reactions conditions: $V_{\text{IL}} + V_{\text{HOAc}} = 5$ mL (pH = 3.4); FeSO_4 , 0.08 mmol; benzene, 1 mL (11.25 mmol); H_2O_2 (30 wt.%), 1.2 mL (11.25 mmol); 333 K, 4 h.

was favorable for the over-oxidation. To test this point, the effect of water on the hydroxylation reaction in the $[\text{Et}_3\text{NH}][\text{OAc}]$ system was then investigated. The yields of the products and the selectivity to phenol were plotted in Fig. 1, as a function of the molar ratio of water to acetate anion. It can be seen that the yield of phenol remained relatively constant at a lower molar ratio of water, while it decreased as the ratio exceeded 8. On the contrary, the yields of the over-oxidation products, di-phenols, increased obviously with the addition of water, resulting in a constantly decrease of the selectivity to phenol. Thus, it could be deduced that the over-oxidation increased in the presence of excessive water, leading to the decrease of the selectivity to phenol.

3.2. Exclusion of the involvement of hydroxyl radical in the triethylammonium acetate system

It has been widely accepted that hydroxyl radical is the active oxidizing species generated by Fenton reagent in aqueous solution, leading to the oxidation of the organic substrates present [12,13]. In order to investigate whether hydroxyl radical was involved in the present reaction, the hydroxylation of benzene with addition of some hydroxyl radical traps such as iso-propanol, tert-butanol, or ammonium formate, was then carried out. From the results listed in Table 2, it can be seen that the yield of phenol was not influenced by adding small amount of the hydroxyl radical scavengers. Only when the amount added was comparable to that of benzene, the prohibiting function on the hydroxylation could be observed. It seemed that the decrease of phenol yield was resulted from the competing oxidation between equivalent amount of foreign organics and benzene, rather than the trapping effect onto the oxidizing species. Therefore, $\cdot\text{OH}$ might not be involved in the reaction.

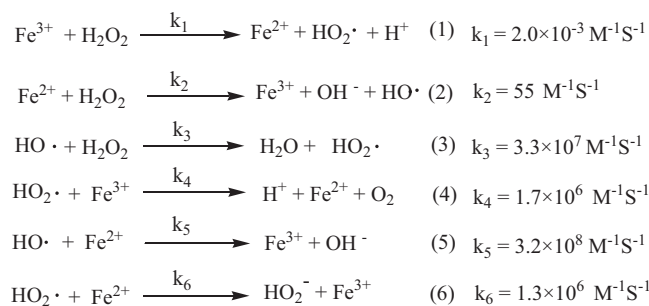
Table 2
Effect of additive on the catalytic oxidation of benzene^a.

Amount added (mmol)	Additive							
	Ammonium formate		Iso-propanol		Tert-butanol		Ascorbic acid	
	Y (%) ^b	S (%) ^b	Y (%)	S (%)	Y (%)	S (%)	Y (%)	S (%)
0	12.0	96.7	12.0	96.7	12.0	96.7	12.0	96.7
0.50	– ^c	–	–	–	–	–	10.5	96.0
1.00	12.0	96.7	12.0	96.8	12.0	96.7	6.8	94.3
11.25	8.0	97.1	9.0	97.3	10.3	97.0	–	–

^a Reaction conditions: $V_{\text{IL}} + V_{\text{HOAc}} = 10$ mL (pH = 3.4); FeSO_4 , 0.08 mmol; benzene, 1 mL (11.25 mmol); H_2O_2 (30 wt.%), 1.2 mL (11.25 mmol); 333 K; 4 h.

^b Y (%): yield of phenol; S (%): selectivity to phenol.

^c Reaction did not be carried out.



Scheme 1. Free radical mechanism for a Fenton reaction.

To further elucidate the impossibility of $\cdot\text{OH}$ involvement, another control experiment with ascorbic acid was carried out. As shown in Table 2, in contrast to the hydroxyl radical scavengers, the decrease of phenol was very obvious when small amount of ascorbic acid was added. It has been known that $\cdot\text{OH}$ formed from the oxidation of ascorbic acid directly by H_2O_2 or catalyzed by iron complexes [34,35]. In that case, an enhanced production of phenol with the addition of ascorbic acid would be expected if the $\cdot\text{OH}$ were the main oxidizing species. However, the result was just on the contrary. It was confirmed that hydroxyl radical was not the corresponding active oxidizing species in this system.

The fact that $\cdot\text{OH}$ is not the main oxidizing species for the Fenton-like reaction in $[\text{Et}_3\text{NH}][\text{OAc}]$ system was also supported by the result of the competitive oxidation between cyclohexane and iso-propanol. When the mixture of cyclohexane and iso-propanol with a molar ratio of 1:1 was oxidized under the standard conditions above, the yield of the oxidation products from cyclohexane showed no decrease, comparing to that obtained in the absence of iso-propanol. The result indicated that saturated hydrocarbons could be oxidized in the presence of alcohol, and it had been presented as a proof to support the hypothesis that $\cdot\text{OH}$ was not the main oxidative species under Gif conditions by Barton and Gloaghec [36].

3.3. Origin of the inhibition effect on hydroxyl radical formation

In aqueous solution, the production of $\cdot\text{OH}$ by Fenton reagent concerns a free radical mechanism (Scheme 1) [12]. As Scheme 1 describes, $\cdot\text{OH}$ is formed from the reduction of H_2O_2 by $\text{Fe}(\text{II})$ via a single electron process in reaction (2). $\text{Fe}(\text{II})$ is recovered through reactions (1) and (4), which is related to the oxidative ability of $\text{Fe}(\text{III})$. It should also be noticed that the consumption of $\text{Fe}(\text{II})$ concurs via reactions (5) and (6), which is influenced by the reductive ability of $\text{Fe}(\text{II})$. Thus, a higher $\text{Fe}(\text{II})$ concentration leads to higher hydroxyl radical concentration [12], and the presence of $\text{Fe}(\text{II})$ is determined by the corresponding redox potential of $\text{Fe}(\text{III})/\text{Fe}(\text{II})$.

The cyclic voltammograms (CV) for FeSO_4 (or $\text{Fe}_2(\text{SO}_4)_3$) in $[\text{Et}_3\text{NH}][\text{OAc}]$ (pH = 6.4) were then recorded, and illustrated in

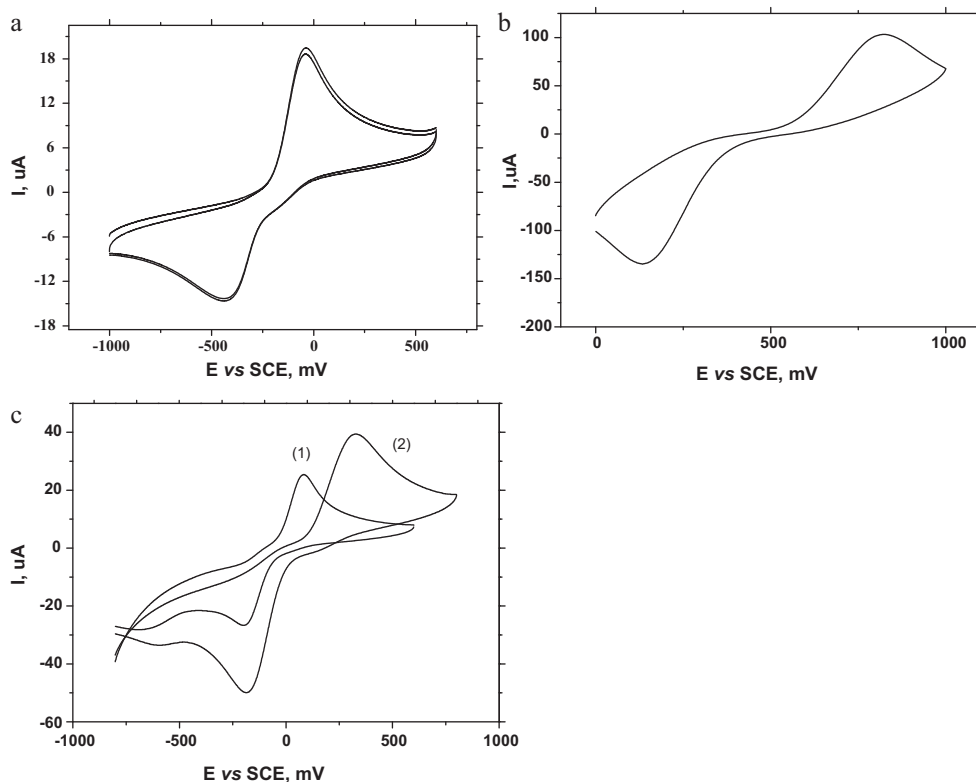


Fig. 2. Cyclic voltammetry of FeSO_4 , or $\text{Fe}_2(\text{SO}_4)_3$ ($C_{\text{Fe(II)}}, C_{\text{Fe(III)}} = 10 \text{ mM}$) in: (a) $[\text{Et}_3\text{NH}][\text{OAc}]$ ($\text{pH} = 6.4$); (b) water ($\text{pH} = 3.4$, adjusted by H_2SO_4); (c) $[\text{Et}_3\text{NH}][\text{OAc}]/\text{H}_2\text{O}$ solution ($\text{pH} = 3.4$, adjusted by HOAc). Curves 1–2: molar ratio of $\text{H}_2\text{O}/\text{OAc}^-$ is 0; 12.8. Scan rate: 50 mV/s .

Fig. 2(a). It is well known that Fe(III) ion could not be present in neutral aqueous solution but precipitated as $\text{Fe}(\text{OH})_3$. While in the present system, Fe(III) ion existed stably in neutral $[\text{Et}_3\text{NH}][\text{OAc}]$ medium. It can be seen that Fe(II) was oxidized to Fe(III) at -40 mV (versus SCE), and Fe(III) was reduced to Fe(II) at -430 mV (versus SCE). A quasi-reversible oxidative wave at $E_{1/2} = -200 \text{ mV}$ (versus SCE) suggested that the potential of the Fe(III)/Fe(II) couple shifted about 700 mV toward more negative potential, comparing to that of 500 mV (versus SCE) measured in aqueous solution ($\text{pH} = 3.4$), **Fig. 2(b)**. Considering the possible effect of acidity on the redox potential of Fe(III)/Fe(II), it was also measured in acidic $[\text{Et}_3\text{NH}][\text{OAc}]$ medium ($\text{pH} = 3.4$, adjusted by acetic acid). As shown in **Fig. 2(c)** (curve 1), the reduction peak of Fe(III) shifted to -200 mV (versus SCE), and the oxidative peak shifted to about 80 mV (versus SCE). There was a new reductive peak at -650 mV (versus SCE), which should be ascribed to the reduction of H^+ of acetic acid to H_2 . The CV characterization results indicated that Fe(II) showed stronger reductive character in $[\text{Et}_3\text{NH}][\text{OAc}]$ than that in aqueous solution, while Fe(III) became a weaker oxidant. The decrease of redox potential of Fe(III)/Fe(II) couple should greatly affect the radical chain reaction of H_2O_2 . In $[\text{Et}_3\text{NH}][\text{OAc}]$, the decreased oxidative ability of Fe(III) is unfavorable for the reformation of Fe(II) via reactions (1) and (4). But for the two competing reactions of (4) and (6), the consumption of Fe(II) through reaction (6) may prevail by the increased reductive ability of Fe(II). Therefore, the recovery of Fe(II) in the catalytic cycling of Fe(III) to Fe(II) was restrained by the decrease of the redox potential of Fe(III)/Fe(II) in $[\text{Et}_3\text{NH}][\text{OAc}]$ medium, which directly led to the limited production of hydroxyl radical. As it has been mentioned, by adding excessive water to the $[\text{Et}_3\text{NH}][\text{OAc}]$ system, the over-oxidation aggravated. It may be related to the formation of hydroxyl radical when the composition of the solvent got close to aqueous solution. The redox potential of Fe(III)/Fe(II) accompanying with the addition of water in $[\text{Et}_3\text{NH}][\text{OAc}]$ medium was further compared. As shown in **Fig. 2(c)**,

the oxidative peak for Fe(II) shifted to positive potential remarkably with the addition of water, while there was no obvious shift for Fe(III). From the results, it can be assumed that the addition of water mainly decreased the reduction ability of Fe(II), and the regeneration of Fe(II) in the radical mechanism would be improved by a lower reductive ability of Fe(II), as it has been discussed, leading to an increased production of hydroxyl radical.

The decrease of redox potential of Fe(III)/Fe(II) couple in $[\text{Et}_3\text{NH}][\text{OAc}]$ should be an effect induced by the σ -donor nature of the coordinated ligand to the Fe ion [37], and this coordination of acetate anion had been proved by UV–vis spectroscopy of FeSO_4 dissolved in $[\text{Et}_3\text{NH}][\text{OAc}]$ medium by our previous work [31]. As shown in **Fig. 3(a)**, an additional intensive band with the maximum absorption located at around 290 nm , being ascribed to the ligand-to-metal charge transfer (LMCT) of O^{2-} to Fe(III), was observed. The shoulder absorption bands at 350 and 410 nm were characteristic for the LMCT transition of the acetate to iron(III) [38]. The spectra also indicated that Fe(II) was inclined to be oxidized to Fe(III) in $[\text{Et}_3\text{NH}][\text{OAc}]$ by atmospheric oxygen, which was consistent with the conclusion about the increased reductive ability of the Fe(II) from the CV characterization. As the CV result showed, the oxidative ability of Fe(III) in $[\text{Et}_3\text{NH}][\text{OAc}]$ medium, however, was hardly influenced by the excessive water present. The electronic spectrum of Fe(III) in $[\text{Et}_3\text{NH}][\text{OAc}]$ with addition of water was scanned to understand the result. As shown in **Fig. 3(b)**, the corresponding ligand to metal charge transfer (LMCT) absorption bands moved slightly to lower wavelength. However, the shift was not substantial even at a higher molar ratio of water to acetate anion (**Fig. 3(c)**). It is well known that the LMCT energy decreases as the ligand becomes more readily oxidisable [39]. On the contrary, the small increase of the energy indicated that the reductive nature of the acetate anion was somehow lowered by the added water. This was mostly ascribed to the H-bonding interaction of water with OAc^- . In such an interaction, the electron density of OAc^- was decreased by the

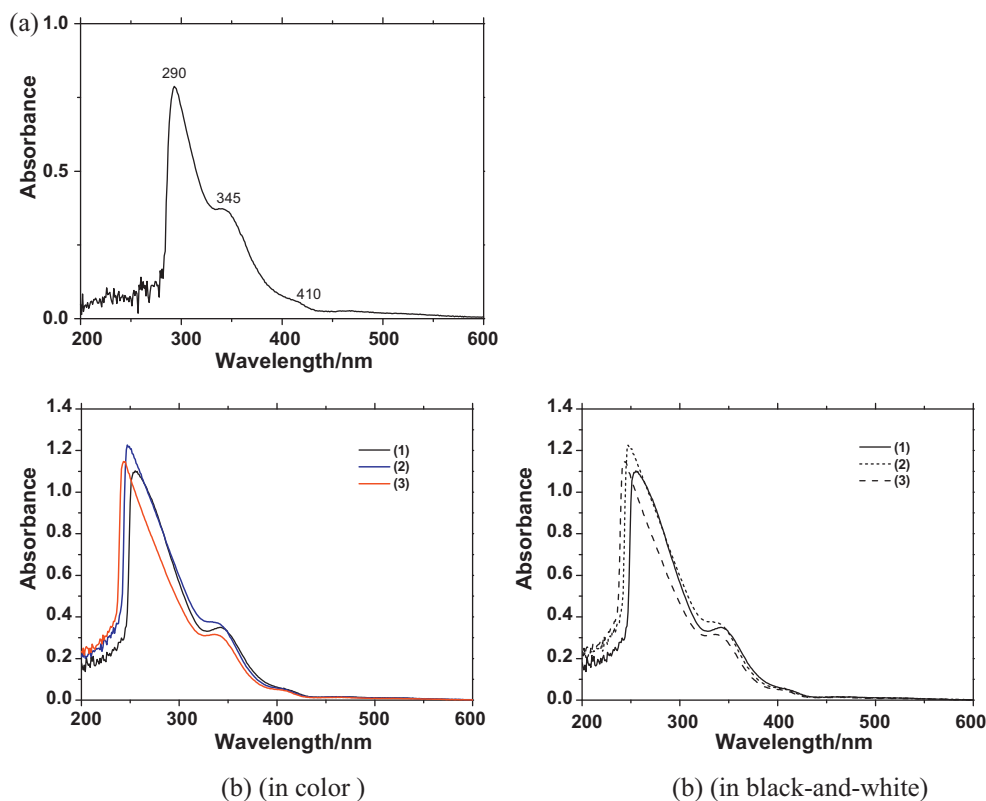


Fig. 3. UV-vis spectra of FeSO_4 , or $\text{Fe}_2(\text{SO}_4)_3$ dissolved in (a) $[\text{Et}_3\text{NH}][\text{OAc}]$ ($\text{pH}=6.4$); (b) $[\text{Et}_3\text{NH}][\text{OAc}]/\text{H}_2\text{O}$ solution ($\text{pH}=3.4$, adjusted by HAc). Curves 1–3: molar ratio of $\text{H}_2\text{O}/\text{OAc}^-$ is 0; 12.8; 44.4.

attraction of water. Considering the rather small shift of the LMCT of acetate anion to $\text{Fe}(\text{III})$ with addition of excessive water, it was suggested that the displacement of acetate anion ligand to $\text{Fe}(\text{III})$ by a weaker electron donor, water, was very difficult. Thus, nearly no shift for $\text{Fe}(\text{III})$ was observed in CV characterization. In contrast, there was a distinct increase of the oxidative potential of $\text{Fe}(\text{II})$, indicating the replacement of OAc^- ligand coordinated to $\text{Fe}(\text{II})$ by water mostly occurred.

From the CV and UV-vis characterizations, we should deduce that, compared to aqueous solution, the coordination of acetate anion of $[\text{Et}_3\text{NH}][\text{OAc}]$ IL to Fe ion resulted in a negative shift for the redox potential of the $\text{Fe}(\text{III})/\text{Fe}(\text{II})$ couple, leading to less recovery of $\text{Fe}(\text{II})$ which is crucial for the production of hydroxyl radical in a radical chain mechanism for a Fenton-like reaction. This is why $\cdot\text{OH}$ was excluded as the oxidizing species in the above-mentioned activity experiments. As expected, the addition of excessive water to $[\text{Et}_3\text{NH}][\text{OAc}]$ IL shifted the oxidative potential of $\text{Fe}(\text{II})$ positively, mostly via substitution of acetate anion to $\text{Fe}(\text{II})$ by water molecule. The production of hydroxyl radical was then increased, leading to a favored over-oxidation.

3.4. Identification of the iron(IV)-oxo species

High-valent iron(IV)-oxo species has frequently been invoked as the key intermediates responsible for oxidation of organic substrates with mononuclear nonheme iron complexes, including alkane hydroxylation, olefin epoxidation, and aromatic hydroxylation, and so on [14]. The iron(IV)-oxo species was deemed to be more selective than those simple radicals (e.g. OH , NO_x , etc.) [40]. In our case, as hydroxyl radical had been excluded as the main active oxidizing species, the involvement of iron(IV)-oxo species was then supposed. The hypothesis agreed well with the prohibiting role of ascorbic acid on hydroxylation reaction mentioned above. As ascor-

bic acid is a good reducing agent, higher oxidation states of the iron ions would be reduced to lower valence states [41]. So the prohibiting role on the hydroxylation was most likely to be induced by the reduction of the iron(IV)-oxo species during the reaction.

In order to further examine whether the $\text{Fe}(\text{IV})$ oxo species was the oxidizing species, tracing experiments on activation of H_2O_2 induced by $\text{Fe}(\text{III})$ with or without the presence of organic substrates were carried out, and monitored by UV-vis and ESI-MS spectra. $\text{Fe}(\text{II})$ precursor should also be transformed to $\text{Fe}(\text{III})$ in open air under experimental conditions.

The UV-vis spectra variations with time for the mixture of $\text{Fe}_2(\text{SO}_4)_3$ and excessive H_2O_2 (30 wt.%) were traced at a absorbance band of $\lambda = 400\text{--}600\text{ nm}$ at 333 K. As shown in Fig. 4(a), upon addition of 100 equiv of H_2O_2 (30 wt.%) to the solution of $\text{Fe}_2(\text{SO}_4)_3$ (5 mM) in $[\text{Et}_3\text{NH}][\text{OAc}]$ ($\text{pH}=3.4$, adjusted by HOAc), the intensity of the absorption bands had some decrease which may be attributed to the decrease of the concentration of $\text{Fe}(\text{III})$. After 5 min of reaction, the intensity of the bands increased to the maximum, and then decayed. For comparison, a control experiment by adding equal amount of water was monitored. As shown in Fig. 4(c), the intensity of the absorption bands initially decreased upon addition of water, however, no change was observed when the mixture was heated at 333 K for 10 min. So it was reasonable to deduce that the spectra changes in $[\text{Et}_3\text{NH}][\text{OAc}]$ were ascribed to the transformation of intermediate species during the reaction of $\text{Fe}(\text{III})$ with H_2O_2 . Since the absorption peaks at $\lambda_{\text{max}} = 520$ and 540 nm were characteristic for the iron(III)-hydroperoxy species [42–44], moreover, the characteristic band at $\lambda_{\text{max}} = 540\text{ nm}$ was also assigned to the presence of the iron(IV) oxo species formed from homolytic cleavage of the $\text{Fe}(\text{III})$ -hydroperoxide by Nam et al. [46] and Stephenson and Bell [45], the spectra changes over the band of 500–600 nm indicated that the intermediate species was iron(III)-hydroperoxy or iron(IV) oxo species. In addition, we observed the same spec-

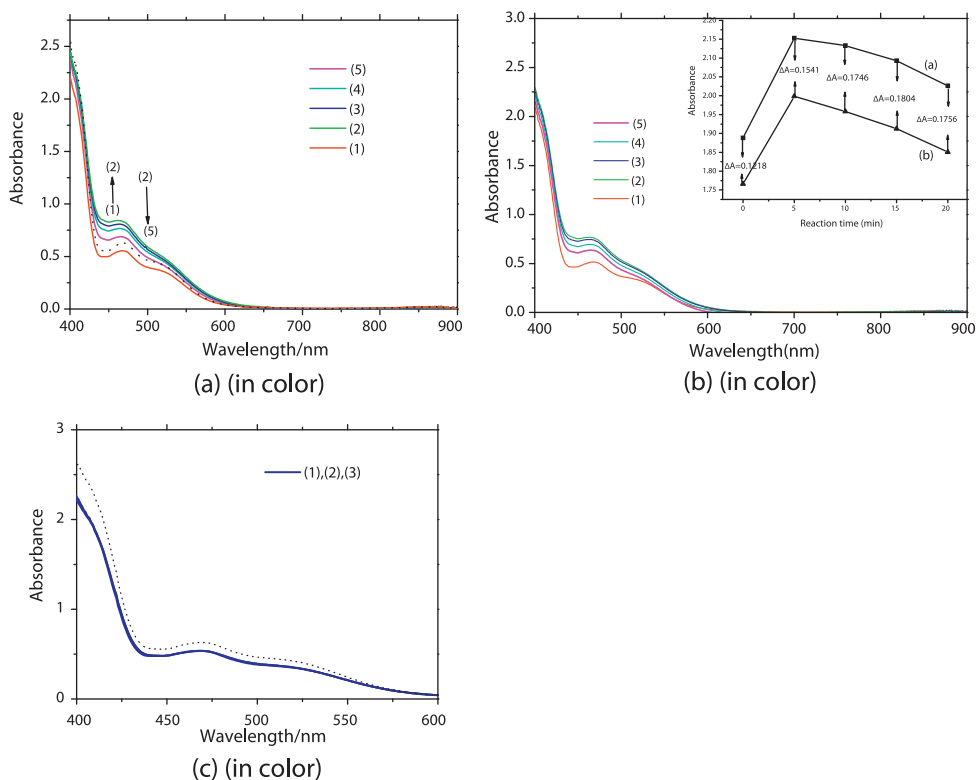


Fig. 4. UV-vis spectra changes of Fe₂(SO₄)₃ (5 mM) in [Et₃NH][OAc] (pH=3.4, adjusted by HOAc), upon addition of (a) H₂O₂ (1 M); (b) H₂O₂ (1 M), in the presence of benzylalcohol (1 M); (c) H₂O (1 M), being heated at 333 K. Curves 1–5: 0, 5, 10, 15, 20 min. Dotted line is no H₂O₂ (or H₂O) being added. Inset: Absorbance-time trace of (a) and (b) at 410 nm.

trum change over the band of 400–500 nm. It is well known that the Scoret band near UV region (400–450 nm) is assigned to oxo-iron(IV) charge transfer transition [47–49]. The spectra changes at 400–500 nm in our experiment were mostly ascribed to the transformation of the corresponding oxo-iron(IV) species. Thus, we suggested that the spectra changes at the band of 400–600 nm were attributed to the formation of the iron(IV) oxo species and its decay in situ. Although the near-IR absorption bands between 650 and 900 nm assigned to low-spin Fe(IV)-oxo species [47] were not observed in our experiment, the suggestion for the formation of Fe(IV)-oxo species is still reasonable. This signature near IR band attributed to the ligand transition [49] was greatly influenced by the ligand environment, and the introduction of anion into Fe(IV) coordination sphere would result in the red shift of the band [50]. We attributed the absence of the corresponding band for the Fe(IV) oxo species in [Et₃NH][OAc] system to its red shift, resulting from the ligand environment of acetate anion.

To confirm the point that the intermediate species was the corresponding oxidizing species, the aforementioned UV-vis spectra characterization in the presence of organic substrate was performed. On account that the Fe(III) phenolate complexes also have the absorption bands in the regions of 400–600 nm [51], benzyl-alcohol was then chosen instead of benzene as the substrate to eliminate the interference of Fe(III) phenolate complexes in the UV-vis spectra. Similar change tendency of the spectra at 400–600 nm was discovered, as shown in Fig. 4(b). The intensity of the absorption bands at each time interval, however, was lower than that with no substrate present after the dilution effect of the substrate being excluded. The intensity difference at $\lambda = 410$ nm was located and plotted as a function of time (Fig. 4(b), inset). The declined intensity indicated the consumption of the active species. Furthermore, the product analysis by GC-MS proved the formation of benzaldehyde as the oxidation product from benzyl-alcohol.

The reaction of Fe₂(SO₄)₃ with excessive H₂O₂ in [Et₃NH][OAc] (pH=3.4, adjusted by HOAc) was also characterized by ESI-MS spectra, and the results were presented in Fig. 5. Compared to the spectrum of pure [Et₃NH][OAc] (Fig. 5(a)), some new peaks appeared in the spectrum of 5 mM Fe₂(SO₄)₃ dissolved in [Et₃NH][OAc] (Fig. 5(b)), indicating the formation of several new species. For example, the peak at $m/z = 292.18$ was assigned to [Fe^{III}(OAc)₄]⁻ (cal. $m/z = 292$), and the peak at $m/z = 264.15$ was corresponding to the [Fe^{III}(OAc)₃(CH₃O)]⁻ species (cal. $m/z = 264$). The main peak at $m/z = 96.74$ should be ascribed to [Fe^{III}(OAc)₇(OH)]⁵⁻ (cal. $m/z = 97.2$), resulting from the polymerization of acetate anion. The result confirmed the coordination of the acetate anion to Fe(III), which was in accordance with the UV-vis result. After addition of 100 equiv of H₂O₂ (30 wt.%) (Fig. 5(c)), the presence of the new peak at $m/z = 160.03$ indicated the formation of the [Fe^{III}(OOH)(OAc)₃(OH)(H₂O)₂]²⁻ (cal. $m/z = 159.5$), an adduct of [Fe^{III}(OOH)(OAc)₃(OH)(H₂O)]²⁻ with a water molecule. It should also be pointed out that the peaks at $m/z = 264.15$, 233.04, 292.18 disappeared, indicating the consumption of the corresponding species. The above mixture was then heated at 333 K for 5 min, and its anionic ESI-MS spectrum (Fig. 5(d)) showed a prominent anion peak of [Fe^{IV}(O)(OAc)₃(OH)₃]⁴⁻ at $m/z = 74.83$ (cal. $m/z = 75$), which was formed from O–O bond cleavage of [Fe^{III}(OOH)(OAc)₃(OH)(H₂O)]²⁻ species and loss of a proton from the adducted water molecule during the ESI-MS experiment. The ESI-MS spectrum of the reaction mixture in the presence of 1 M benzene under the same reaction conditions was also scanned. As shown in Fig. 5(e), the peak at $m/z = 74.83$ was obviously weakened with the appearances of some new peaks, such as $m/z = 92.83$, and 114.84. The peak at $m/z = 92.83$ was ascribed to phenol ($m/z = 92.83$), and the peak at $m/z = 114.84$ was due to the coordination of PhO⁻ with Fe(III) center to form [Fe^{III}(PhO)(OAc)₅(OH)]⁴⁻ (cal. $m/z = 115$). From these

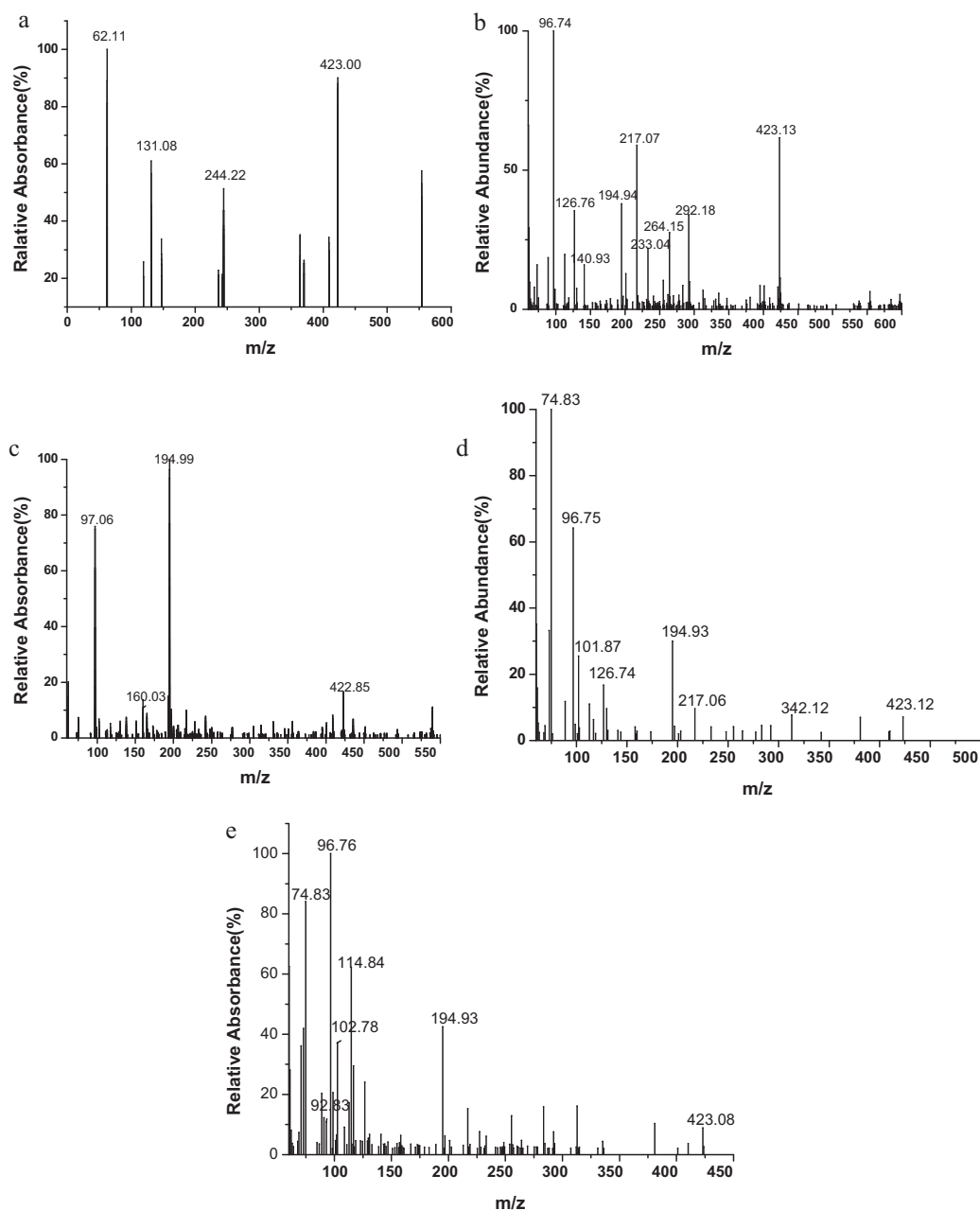


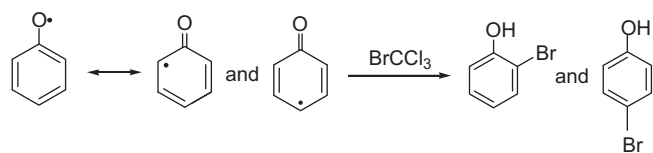
Fig. 5. ESI-MS(–) spectra of (a) $[\text{Et}_3\text{NH}][\text{OAc}]$ (pH = 3.4, adjusted by HOAc); (b) $\text{Fe}_2(\text{SO}_4)_3$ (10 mM) dissolved in (a); (c) upon addition of 100 equiv. H_2O_2 to (b); (d) heating (c) at 333 K for 5 min; (e) heating (c) at 333 K for 5 min, in the presence of benzene (1 M).

results, it may be supposed that iron(IV)-oxo species was the active oxidizing species in the present Fenton-like $[\text{Et}_3\text{NH}][\text{OAc}]$ system.

3.5. The generation of the iron(IV) oxo species

It has been generally accepted that the generation of the iron(IV)-oxo species proceeds via the O–O bond heterolytic cleavage, or homolytic cleavage of the Fe(III)–OOH intermediate [14,52]. The different cleavage mode leads to different product distribution in oxidation of organic substrates. For example, epoxidation of olefins via heterolytic cleavage produced a high yield of epoxide [53], while allylic oxidation products formed via homolytic cleavage. Oxidation of styrene had also been reported to differentiate the two cleavage modes. Heterolysis mainly led to the products of

styrene oxide and phenylacetaldehyde, while the principal product of benzaldehyde was obtained via homolysis [54]. By virtue of these results, the oxidations of cyclohexene, as well as styrene in our system under the typical reaction conditions were then carried out respectively. Oxidation of cyclohexene mainly produced cyclohexenone and cyclohexenol, and in the oxidation of styrene, benzaldehyde was obtained with a selectivity of nearly 90%. From the oxidation products distribution of these two reactions, it could be deduced that the active oxidizing Fe(IV)-oxo species should be resulted from the O–O bond homolysis of the Fe(III)–OOH intermediates in the $[\text{Et}_3\text{NH}][\text{OAc}]$ system. In the above-mentioned UV–vis spectra characterization, the appearance of the band at $\lambda_{\text{max}} = 540 \text{ nm}$ should be a direct proof. The cleavage type of the O–O bond should be related to the stronger electron donors of acetate anionic ligand bounded to Fe ion, since both Nam and Kaizer had



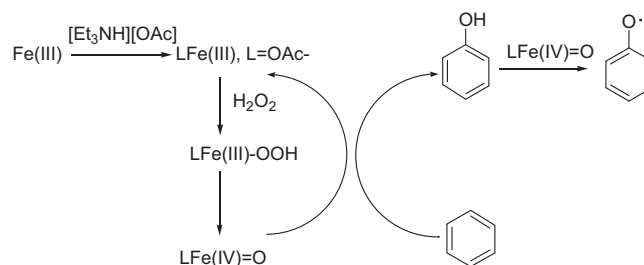
Scheme 2. Mechanism of PhBrOH formation from phenoxy radical.

reported that the donation of electron density to the Fe(III) center by ligand promoted homolytic cleavage of the O–O bond [55,56].

3.6. Reaction mechanism for hydroxylation of benzene

In order to examine whether the reaction mechanism for hydroxylation of benzene included a hydrogen atom abstraction step [57], BrCCl₃, a famous carbon radical scavenger, was added to detect the intermediate of phenyl radical. In the products, PhBr was never detected, while large amount of PhBrOH was obtained with a sharp decrease of the yield of phenol. The absence of PhBr indicated that there was no phenyl radical formed, thus a hydrogen abstraction mechanism for hydroxylation of benzene by the iron(IV)-oxo species could not work. In the reported studies, a hydrogen abstraction mechanism was ruled out by a low kinetic isotope effect (KIE) value obtained in the hydroxylation of aromatic compounds by non-heme iron(IV)–O complexes, and a large negative Hammett ρ implied that the aromatic ring oxidation occurred via electrophilic attack on the aromatic ring [58]. Thus, in our system, it was suggested that the hydroxylation of benzene should also proceed via electrophilic attack on the aromatic ring, but not via a hydrogen atom abstraction mechanism. The electrophilic nature of the corresponding iron(IV)-oxo species is still under investigation.

When phenol was used for hydroxylation reaction in the presence of BrCCl₃, most of phenol was also transformed to PhBrOH. Thus, it was deduced that the produced phenol during hydroxylation of benzene could be further transformed to PhBrOH in the presence of BrCCl₃. The formation of PhBrOH implied the generation of the phenoxy radical. As shown in Scheme 2, the carbon radical of the resonance structure of the phenoxy radical [59] is trapped by BrCCl₃ to form PhBrOH. Phenoxy radical was a common intermediate in the oxidation of phenol by oxidant [59], and its formation in our reaction was suggested through the abstraction of H from O–H of phenol by iron(IV)-oxo species, as it had been proposed in the literature [60]. There was also a quite ordinary reaction path for the hydroxylation of phenol by hydroxyl radical to form di-phenol [59,61,62]. In our experiment, as shown in Table 1, there were little amounts of di-phenols produced in [Et₃NH][OAc] system, indicating the direct hydroxylation of phenol seldom occurred. On the contrary, di-phenols were the main products in aqueous solution. In addition, the amount of di-phenols increased when excessive water was added to [Et₃NH][OAc] system, as shown in Fig. 1. The results again proved the formation of hydroxyl radical was enhanced by introduction of excessive water. Although further oxidation of the produced phenol by the oxidizing species also occurred in the [Et₃NH][OAc] system, the reaction was much prohibited than that in water. Hydrogen-bonding interaction between the phenol (hydrogen-bonding donor, HBD) and the acetate anion (hydrogen-bonding acceptor, HBA) should be responsible for it. As it was reported by MacFaul [63], the hydrogen-bond role between PhOH and HBA could decline the rate constant for hydrogen atom abstraction from phenol by some active oxidative species. Therefore, it was deduced that this hydrogen-bonding role protected phenol from its further oxidation. The reaction mechanism of the hydroxylation of benzene by Fenton reagent, as well as the possible further oxidation in [Et₃NH][OAc] system was then outlined (Scheme 3).



Scheme 3. Mechanism for hydroxylation of benzene in [Et₃NH][OAc] system.

4. Conclusions

Hydroxyl radical, the widely accepted oxidizing species in an aqueous Fenton system, was not the main oxidizing species in [Et₃NH][OAc] system because of the reduction of the redox potential of the Fe(III)/Fe(II) couple. With the addition of excessive water to [Et₃NH][OAc] medium, the reductive ability of Fe(II) was decreased, leading to an enhanced production of hydroxyl radical. That is why over-oxidation of benzene was promoted by water. It was revealed that the main oxidizing active species was the high-valent iron(IV)-oxo species formed from the O–O bond homolysis of a Fe(III)–OOH intermediate. The mechanism for hydroxylation of benzene by the corresponding iron(IV) oxo species was mostly via the electrophilic attack on benzene ring, rather than via hydrogen abstraction to form phenyl radical. Further oxidation of phenol through H-abstraction from O–H of phenol by the iron(IV)-oxo species was partly prohibited by the hydrogen-bond interaction between phenol and acetate anion. Considering the diversity of ILs, tuning the reaction mechanism for better efficiency and selectivity could be greatly expected.

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References

- [1] J. Prousek, *Pure Appl. Chem.* 79 (2007) 2325–2338.
- [2] J. Pignatello, E. Oliveros, A. MacKay, *Crit. Rev. Environ. Sci. Technol.* 36 (2006) 1–84.
- [3] F. Shi, M.K. Tse, Z. Li, M. Beller, *Chem. Eur. J.* 14 (2008) 8793–8797.
- [4] D.T. Sawyer, A. Sobkowiak, T. Matsushita, *Acc. Chem. Res.* 29 (1996) 409–416.
- [5] C. Walling, *Acc. Chem. Res.* 31 (1998) 155–157.
- [6] S. Rachmilovich-Calis, A. Masarwa, N. Meyerstein, D. Meyerstein, *Chem. Eur. J.* 15 (2009) 8303–8309.
- [7] K. Chen, L. Que Jr., *J. Am. Chem. Soc.* 123 (2001) 6327–6337.
- [8] D.R. Barton, *Tetrahedron* 54 (1998) 5805–5817.
- [9] A.E. Anastasi, A. Lienke, P. Comba, H. Rohwer, J.E. McGrady, *Eur. J. Inorg. Chem.* (2007) 65–73.
- [10] S. Rachmilovich-Calis, A. Masarwa, N. Meyerstein, D. Meyerstein, *Eur. J. Inorg. Chem.* (2005) 2875–2880.
- [11] F. Gozzo, *J. Mol. Catal. A: Chem.* 171 (2001) 1–22.
- [12] C.K. Duesterberg, S.E. Mylon, T.D. Waite, *Environ. Sci. Technol.* 42 (2008) 8522–8527.
- [13] O. Pestovskiy, S. Stoian, E.L. Bominaar, X. Shan, E. Münck, L. Que Jr., A. Bakac, *Angew. Chem. Int. Ed.* 44 (2005) 6871–6874.
- [14] W. Nam, *Acc. Chem. Res.* 40 (2007) 522–531.
- [15] T. Paczesniak, A. Sobkowiak, *J. Mol. Catal. A: Chem.* 194 (2003) 1–11.
- [16] G.A. Hamilton, R.J. Workman, L. Woo, *J. Am. Chem. Soc.* 86 (1964) 3390.
- [17] D.R. Barton, D. Doller, *Acc. Chem. Res.* 25 (1992) 504–512.
- [18] D. Bianchi, M. Bertoli, R. Tassinari, M. Ricci, R. Vignola, *J. Mol. Catal. A: Chem.* 200 (2003) 111–116.
- [19] R.R. Fernandes, M.V. Kirillova, J.A.L. da Silva, J.J.R. Fraústo da Silva, A.J.L. Pombeiro, *Appl. Catal. A* 353 (2009) 107–112.
- [20] D.H.R. Barton, T. Li, *Tetrahedron* 54 (1998) 1735.
- [21] A. Thibon, J. Bartoli, R. Guillot, J. Sainton, *J. Mol. Catal. A: Chem.* 287 (2008) 115–120.

- [22] N.A. Stephenson, A.T. Bell, *Inorg. Chem.* 45 (2006) 2758–2766.
- [23] Z. Yang, W. Pan, *Enzyme Microb. Technol.* 37 (2005) 19–28.
- [24] J.S. Wilkes, *J. Mol. Catal. A: Chem.* 214 (2004) 11–17.
- [25] P.J. Dyson, T.J. Geldbach, *Metal Catalysed Reactions in Ionic Liquids*, Springer, 2005, pp. 41–222 (Chapter 3–9).
- [26] H. Olivier-Bourbigou, L. Magna, D. Morvan, *Appl. Catal. A* 373 (2010) 1–56.
- [27] Y. Chauvin, S. Einloft, H. Olivier, *Ind. Eng. Chem. Res.* 34 (1995) 1149–1155.
- [28] L. Xu, W. Chen, J. Xiao, *Organometallics* 19 (2000) 1123–1127.
- [29] X. Wu, J. Mo, X. Li, Z. Hyder, J. Xiao, *Progr. Nat. Sci.* 18 (2008) 639–652.
- [30] J.J. Peng, F. Shi, Y.L. Gu, Y.Q. Deng, *Green Chem.* 5 (2003) 224–226.
- [31] X.K. Hu, L.F. Zhu, B. Guo, Q.Y. Liu, G.Y. Li, C.W. Hu, *Chemical Research in Chinese Universities*, in press.
- [32] C. Wang, L. Guo, H. Li, Y. Wang, J. Weng, *Green Chem.* 8 (2006) 603–607.
- [33] L. Balducci, D. Bianchi, R. Bortolo, R. D'Aloisio, M. Ricci, R. Tassinari, R. Ungarelli, *Angew. Chem.* 115 (2003) 5087–5090.
- [34] T.M. Florence, *J. Inorg. Biochem.* 22 (1984) 221–230.
- [35] A.J. Nappi, E. Vass, *Neurotox. Res.* 2 (2000) 343–355.
- [36] D.R. Barton, V.L. Gloahec, *Tetrahedron Lett.* 39 (1998) 4413–4416.
- [37] E. Vichi, E. Stein, *Inorg. Chim. Acta* 334 (2002) 313–317.
- [38] J.F. Berry, E. Bill, E. Bothe, F. Neese, K. Wieghardt, *J. Am. Chem. Soc.* 128 (2006) 13515–13528.
- [39] A.B.P. Lever, *Inorganic Electronic Spectroscopy*, second ed., Elsevier, Amsterdam, 1984, p. 206 (Chapter 5).
- [40] A. Fokin, P.R. Schreiner, *Chem. Rev.* 102 (2002) 1551–1593.
- [41] G. Tanarungsun, W. Kiatkittipong, P. Prasertthama, H. Yamada, T. Tagawa, S. Assabumrungrat, *Catal. Commun.* 9 (2008) 1886–1890.
- [42] S.L. Jain, P. Bhattacharyya, *Dalton Trans.* (2005) 2696–2701.
- [43] A.M. Awad, A.M. Shaker, A. Zaki, L. Nassr, *Spectrochim. Acta A* 71 (2008) 921–928.
- [44] M.J. Park, J. Lee, Y. Suh, J. Kim, W. Nam, *J. Am. Chem. Soc.* 128 (2006) 2630–2634.
- [45] N.A. Stephenson, A.T. Bell, *J. Am. Chem. Soc.* 127 (2005) 8635–8643.
- [46] W. Nam, S. Park, I.K. Lim, M.H. Lim, J. Hong, J. Kim, *J. Am. Chem. Soc.* 125 (2003) 14674–14675.
- [47] X. Shan, L. Que Jr., *J. Inorg. Biochem.* 100 (2006) 421–433.
- [48] M. Wolak, R. Eldik, *Chem. Eur. J.* 13 (2007) 4873–4883.
- [49] A. Decker, J. Rohde, L. Que Jr., E.I. Solomon, *J. Am. Chem. Soc.* 126 (2004) 5378–5379.
- [50] C.V. Sastri, M.J. Park, T. Ohta, T.A. Jackson, A. Stubna, M.S. Seo, J. Lee, J. Kim, T. Kitagawa, L. Que Jr., W. Nam, *J. Am. Chem. Soc.* 127 (2005) 12494–12495.
- [51] M. Palanandavar, R. Viswanathan, *Proc. Indian Acad. Sci. (Chem. Sci.)* 108 (1996) 235–249.
- [52] N.A. Stephenson, A.T. Bell, *J. Mol. Catal. A: Chem.* 275 (2007) 54–62.
- [53] W. Nam, H.J. Han, 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) 8677–8684.
- [54] J.T. Groves, Z. Gross, M.K. Stern, *Inorg. Chem.* 33 (1994) 5065–5072.
- [55] W. Nam, M. Lim, S.Y. Oh, *Angew. Chem. Int. Ed.* 39 (2000) 3646–3649.
- [56] J. Kaizer, M. Costas, L. Que Jr., *Angew. Chem. Int. Ed.* 42 (2003) 3671–3673.
- [57] M. Kang, W.J. Song, A. Han, Y.S. Choi, H.G. Jang, W. Nam, *J. Org. Chem.* 72 (2007) 6301–6304.
- [58] S.P. Visser, K. Oh, A. Han, W. Nam, *Inorg. Chem.* 46 (2007) 4632–4641.
- [59] S.I. Joschek, H.I. Miller, *J. Am. Chem. Soc.* 88 (1966) 3273–3281.
- [60] C.V. Sastri, J. Lee, K. Oh, Y.J. Lee, T.A. Jackson, W. Nam, *Proc. Natl. Acad. Sci. U.S.A.* 104 (2007) 19181–19186.
- [61] H. Tang, Y. Ren, B. Yue, S. Yan, H. He, *J. Mol. Catal. A: Chem.* 260 (2006) 121–127.
- [62] J. Choi, S. Yoon, S. Jang, W. Ahn, *Catal. Today* 111 (2006) 280–287.
- [63] P.A. MacFaul, K.U. Ingold, J. Lusztyk, *J. Org. Chem.* 61 (1996) 1316–1321.