

# Phenol hydroxylation by iron(II) phenanthroline: The reaction mechanism

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## Abstract

Phenol hydroxylation catalyzed by iron(II)-1,10-phenanthroline is investigated through kinetics, ESR, UV–Vis as well as cyclic voltammogram studies. The optimum reaction conditions are obtained for diphenols production. Radical substitution mechanism is first proposed to explain the effects of pH, reaction medium and other factors on the phenol hydroxylation with  $\text{H}_2\text{O}_2$  as oxidant, and found that the coexisting of iron(II)-1,10-phenanthroline and iron(III)-1,10-phenanthroline is the key for phenol hydroxylation to occur with  $\text{H}_2\text{O}_2$  as oxygen donor.

*Keywords:* Phenol hydroxylation; Iron(II)-1,10-phenanthroline; Radical substitution

## 1. Introduction

Diphenols production through phenol hydroxylation has been studied a lot since 1970s. Water soluble metal salts and their complexes have been used to catalyze phenol hydroxylation with  $\text{H}_2\text{O}_2$  and other oxidants as oxygen donors. For example,  $\text{Cu}^{2+}$ ,  $\text{Au}^{3+}$ ,  $\text{Co}^{2+}$  [1],  $\text{Fe}^{3+}$  [2,3],  $\text{Fe}^{2+}$  [4–6], etc. have been investigated on their catalysis in hydroxylation of phenol. Although these simple metal ions have some activity to catalyze the phenol hydroxylation, their selectivity to diphenols, conversion of phenol, as well as the distribution of catechol and hydroquinone are not good enough to satisfy real needs. Thus, scientists started to study

the catalysis of metal complexes. Some complexes, such as,  $\text{M}-\text{Pc}$  [7] ( $\text{M} = \text{Sb}, \text{Bi}, \text{V}, \text{Mo}, \text{Sn}, \text{Sn}-\text{Mo}, \text{and Sn}-\text{Sb}$ ),  $\text{Fe(III)-bi-pyridine}$  [8],  $\text{Co(I, II, III)-Schiff base}$  [9],  $\text{Co(II)bis[3(salicylideneconine)propyl methylamine]}$  [10], as well as the porphyrin complexes of IA–VIA group, IVB–VIII and VIII group metal cations [11], have been investigated about their catalysis in hydroxylation of phenol with  $\text{H}_2\text{O}_2$  and other oxidants as the oxygen donors, and found they all have some catalytic activity to phenol hydroxylation and better selectivity to certain product than that of the simple metal ions. While many investigations have been done on phenol hydroxylation to produce diphenols, no satisfied mechanism was given to explain this reaction.

The catalysis of  $\text{Fe(II)-porphyrin}$  [12] and  $\text{Fe(II)-Pc}$  [13] have been studied, these two complexes have planar structure and poor cat-

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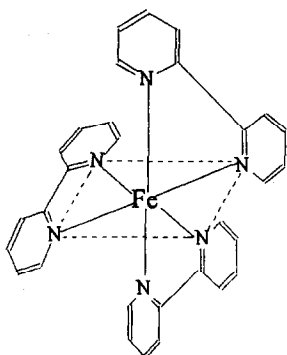


Fig. 1. Octahedral structure of iron(II)-phenanthroline.

alytic activity to phenol hydroxylation. However, Fe(II)-1,10-phenanthroline is an octahedral complex (shown in Fig. 1) which may have good activity to hydroxylation of phenol. This paper first studies the catalysis of iron(II)-1,10-phenanthroline in the phenol hydroxylation with  $\text{H}_2\text{O}_2$  as the oxygen donor under different reaction conditions and found that the complex has better activity than that of the simple ion  $\text{Fe}^{2+}$  in water medium when pH is equal to 7.0. Meanwhile, the mechanism of phenol hydroxylation is also given with the help of the UV–Vis, ESR spectra and kinetic studies.

## 2. Experimental

### 2.1. Hydroxylation of phenol

Catalyst and solvent were added successively into a glass reactor of 25 mL capacity equipped with a stirring machine and a thermostat. The

reaction was initiated by adding  $\text{H}_2\text{O}_2$  (30 mass%) at the set temperature. Products were analyzed with a gas chromatograph equipped with a flexible glass capillary column coated with XE-60. Programmed temperature was adopted for product analyses. The initial temperature was  $100^\circ\text{C}$ , the final temperature was  $190^\circ\text{C}$ .

The UV–Vis studies were carried on with Specord UV–Vis (Zeiss, Jena). ESR study was carried on with JES-FE3AX ESR spectrometer (Japan). The cyclic voltammetry was carried out with a Model 500 A.C. impedance analyzer (CH Instrument, USA) equipped with a cell stand, an Ag/AgCl reference electrode and a platinum wire counter electrode was used for cyclic voltammetric measurements. The working electrode used was glassy carbon disk electrode.

## 3. Results

The catalysis of iron(II) ion and iron(II)-1,10-phenanthroline is studied in the phenol hydroxylation, the results are shown as Table 1.

In Table 1, it is shown that  $\text{Fe}(\text{phen})_3^{2+}$  has better catalytic activity than that of  $\text{Fe}^{2+}$ . Meanwhile, the amount of by-products of benzoquinone and oxygen is less for catalyst  $\text{Fe}(\text{phen})_3^{2+}$ . Table 1 also shows that the phenol hydroxylation can not occur between phenol and  $\text{H}_2\text{O}_2$  without the participation of catalyst under the above mentioned experimental conditions.

Table 1  
Catalytic activity comparison of iron(II) ion and iron(II)-1,10-phenanthroline to phenol hydroxylation<sup>a</sup>

Catalyst	Observed phenol conversion (%)	Observed product distribution (%)			Efficiency of $\text{H}_2\text{O}_2$ (%)
		CAT	HQ	PBQ	
No catalyst	0.0	—	—	—	—
$\text{Fe}^{2+}$	24.5	69.4	22.2	8.4	40
$\text{Fe}(\text{phen})_3^{2+}$	29.5	70.0	28.2	1.8	65

<sup>a</sup> CAT = catechol; HQ = hydroquinone; PBQ = *p*-benzoquinone. Reaction medium: water pH = 7.0; reaction temperature:  $40^\circ\text{C}$ . Reaction time: 3 h. Volume of reaction mixture: 15 ml. Phenol =  $5 \times 10^{-3}$  mol, molar ratio: phenol/ $\text{H}_2\text{O}_2$ /catalyst = 1000/1000/1. Efficiency of  $\text{H}_2\text{O}_2$  =  $[\text{H}_2\text{O}_2]_{\text{a}} / [\text{H}_2\text{O}_2]_{\text{b}} \times 100\%$ .  $[\text{H}_2\text{O}_2]_{\text{a}}$  refers to the quantity of  $\text{H}_2\text{O}_2$  used for observed phenol conversion.  $[\text{H}_2\text{O}_2]_{\text{b}}$  refers to the difference of the quantity of  $\text{H}_2\text{O}_2$  initially added and that of the left after reaction.

Table 2  
Effect of solvent on phenol hydroxylation with iron(II)-1,10-phenanthroline as the catalyst <sup>a</sup>

Solvent	Observed phenol conversion (%)	Observed product distribution (%)			Efficiency of H <sub>2</sub> O <sub>2</sub> (%)
		CAT	HQ	PBQ	
Cyclohexane	0.0	—	—	—	—
Aetone	2.0	70.0	8.2	21.8	60
Acetonitrile	18.9	67.2	15.4	17.4	60
Water	29.5	70.0	28.2	1.8	65

<sup>a</sup> CAT = catechol; HQ = hydroquinone; PBQ = *p*-benzoquinone. Reaction medium: pH = 7.0 (water); reaction temperature: 40°C. Reaction time: 3 h. Volume of reaction mixture: 15 ml. Phenol =  $5 \times 10^{-3}$  mol, molar ratio: phenol/H<sub>2</sub>O<sub>2</sub>/catalyst = 1000/1000/1.

Table 3  
Effect of pH on the phenol hydroxylation when Fe(phen)<sub>3</sub><sup>2+</sup> is used as the initial catalyst <sup>a</sup>

pH	Observed phenol conversion (%)	Observed product distribution (%)			Efficiency of H <sub>2</sub> O <sub>2</sub> (%)
		CAT	HQ	PBQ	
2	36.5	67.3	10.2	22.5	45
4	34.5	68.0	13.0	19.0	55
7	29.5	70.0	28.2	1.8	65
9	8.5	70.0	30.0	0.0	50
12	0.0	—	—	—	—

<sup>a</sup> CAT = catechol; HQ = hydroquinone; PBQ = *p*-benzoquinone. Reaction medium: water; reaction temperature: 40°C. Reaction time: 3 h. Volume of reaction mixture: 15 ml. Phenol =  $5 \times 10^{-3}$  mol, molar ratio: phenol/H<sub>2</sub>O<sub>2</sub>/catalyst = 1000/1000/1.

Table 4  
Effect of molar ratio (phenol/H<sub>2</sub>O<sub>2</sub>) on the phenol hydroxylation <sup>a</sup>

Molar ratio (phenol/H <sub>2</sub> O <sub>2</sub> )	Observed phenol conversion (%)	Observed product distribution (%)			Efficiency of H <sub>2</sub> O <sub>2</sub> (%)
		CAT	HQ	PBQ	
0.2	50.6	69.3	10.6	20.1	51
0.5	34.5	69.2	20.2	10.6	60
1	29.5	70.0	28.2	1.8	65
2	12.0	70.2	29.1	0.7	70
5	8.2	70.0	30.0	0.0	80
10	4.0	70.0	30.0	0.0	90

<sup>a</sup> CAT = catechol; HQ = hydroquinone; PBQ = *p*-benzoquinone. Reaction medium: water; reaction temperature: 40°C. Reaction time: 3 h. Volume of reaction mixture: 15 ml. Phenol =  $5 \times 10^{-3}$  mol, molar ratio: phenol/H<sub>2</sub>O<sub>2</sub>/catalyst = 1000/1000/1.

Table 5  
Activity comparison of iron(II)-1,10-phenanthroline and TS-1 in phenol hydroxylation <sup>a</sup>

Catalyst	Observed phenol conversion (%)	Observed product distribution (%)			Efficiency of H <sub>2</sub> O <sub>2</sub> (%)
		CAT	HQ	PBQ	
TS-1	27	53.0	47.0	0.0	70
Fe(phen) <sub>3</sub> <sup>2+</sup>	20	70.0	29.0	1.0	72

<sup>a</sup> CAT = catechol; HQ = hydroquinone; PBQ = *p*-benzoquinone. Reaction medium: water pH = 7.0; reaction temperature: 55°C. Reaction time: 6 h. Volume of reaction mixture: 15 ml. Phenol =  $5 \times 10^{-3}$  mol, phenol/H<sub>2</sub>O<sub>2</sub>(molar) = 3. For Fe(phen)<sub>3</sub><sup>2+</sup>: molar ratio: phenol/catalyst = 1000/1. For TS-1 [Ti/(Ti + Si) = 0.021]: phenol/catalyst (g/g) = 10.

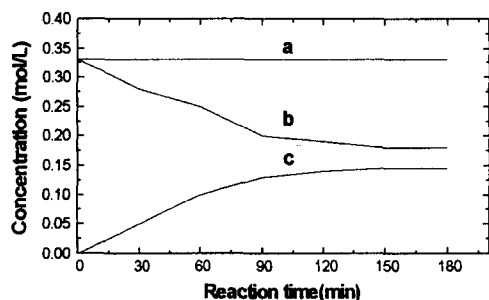


Fig. 2. Concentration change of catechol (a), hydroquinone (b) and benzoquinone (c).

Table 2 shows the result of the phenol hydroxylation carried out in different solvent media.

$\text{Fe(phen)}_3^{2+}$  was used as the initial catalyst, the effect of pH on phenol hydroxylation is shown in Table 3.

The effect of molar ratio(phenol/ $\text{H}_2\text{O}_2$ ) on activity is also investigated in phenol hydroxylation, which is shown in Table 4

In order to compare the activity of TS-1 and iron(II)-1,10-phenanthroline, their catalysis is studied in phenol hydroxylation, the results are shown in Table 5.

In the phenol +  $\text{Fe(phen)}_3^{2+}$  +  $\text{H}_2\text{O}_2$  +  $\text{H}_2\text{O}$  reaction system, at the beginning of the reaction, phenol is replaced with catechol and hydroquinone. The concentration change of some substances is shown in Fig. 2.

The redox properties of  $\text{Fe(phen)}_3^{2+}$  are studied with the cyclic voltammetric measurement. The typical voltammogram is shown in Fig. 3. From Fig. 3, we know that  $E_{pc} = 0.945$  V and  $E_{pa} = 0.873$  V. Based on the potential difference

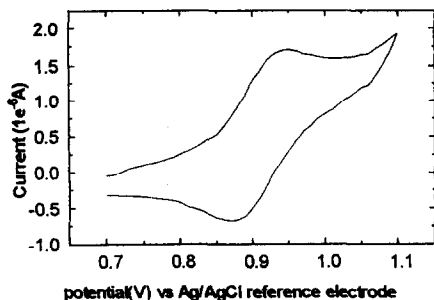


Fig. 3. Cyclic voltammogram of  $\text{Fe(phen)}_3^{2+}$ .

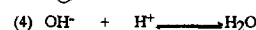
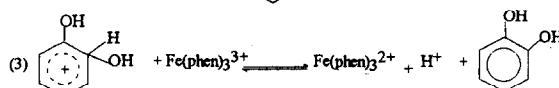
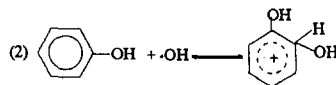
$\Delta E$  (72 mV), this redox reaction was considered as reversible, and the potential of redox couple  $\text{Fe(phen)}_3^{3+/2+}$   $E^\circ = 1/2(0.945 + 0.873) = 0.91$  (V), which is similar to the reported value [14]. We also know that the potential of redox couple  $\text{H}_2\text{O}_2/\text{H}_2\text{O}$  is 1.77 V [15], the large potential difference can lead to redox reaction between  $\text{H}_2\text{O}_2$  and  $\text{Fe(phen)}_3^{2+}$  easily, a certain active species produced during this reaction can react with phenol to produce diphenols.

## 4. Discussion

### 4.1. Mechanism of phenol hydroxylation catalyzed by $\text{Fe(phen)}_3^{2+}$

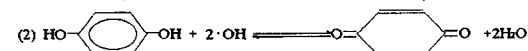
Based on above mentioned kinetics and cyclic voltammetry studies, a radical substitution mechanism could be proposed as follows:

Main reactions:



The production of hydroquinone is similar to that of catechol.

Side reactions [16]:



With this mechanism, many experimental results could be demonstrated clearly.

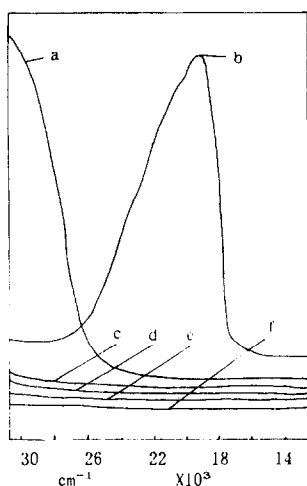


Fig. 4. UV-Vis spectra of  $\text{Fe}(\text{phen})_3^{2+}$  (a),  $\text{Fe}(\text{phen})_3^{3+}$  (b), phenol (c),  $\text{H}_2\text{O}_2$  (d), catechol (e) and hydroquinone (f).

The UV-Vis spectra of  $\text{Fe}(\text{phen})_3^{2+}$ ,  $\text{Fe}(\text{phen})_3^{3+}$ , phenol,  $\text{H}_2\text{O}_2$ , catechol and hydroquinone are shown in Fig. 4.

$\text{H}_2\text{O}_2$  was added to  $\text{Fe}(\text{phen})_3^{2+}$  aqueous solution, the change of  $\text{Fe}(\text{phen})_3^{2+}$  into  $\text{Fe}(\text{phen})_3^{3+}$  is shown evidently in Fig. 5. From change of peak height of  $\text{Fe}(\text{phen})_3^{2+}$  as well as that of  $\text{Fe}(\text{phen})_3^{3+}$ , the change of the concentration of redox components could be confidently evaluated.

The change of concentration of  $\text{Fe}(\text{phen})_3^{2+}$  and  $\text{Fe}(\text{phen})_3^{3+}$  is expressed in percent by the ratio of  $H_t/H_0 \times 100\%$ , making  $H = H_t/H_0 \times$

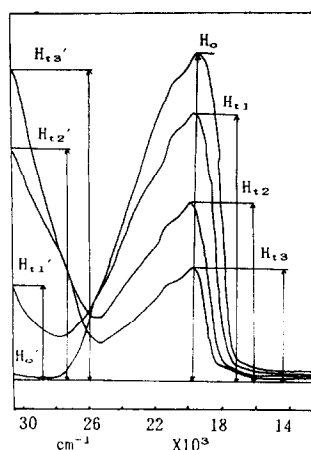


Fig. 5. Peak change of  $\text{Fe}(\text{phen})_3^{2+}$  in  $\text{H}_2\text{O}_2$  solution.

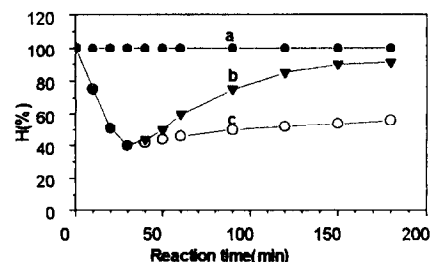


Fig. 6. Peak change of  $\text{Fe}(\text{phen})_3^{2+}$  with the appearance and disappearance of  $\text{H}_2\text{O}_2$ .

100%,  $H_t$  stands for the peak height at the time  $t$ , and  $H_0$  stands for the peak height at time zero. The peak height change in Fig. 5 could be expressed as Fig. 6, which indicates that the concentration of  $\text{Fe}(\text{phen})_3^{2+}$  decreases with the increase of  $\text{Fe}(\text{phen})_3^{3+}$ 's concentration, when  $\text{H}_2\text{O}_2$  was added in the  $\text{Fe}(\text{phen})_3^{2+}$  aqueous solution, at a certain time (about 30 min), there is only a little change for their peak height, due to the reaching of the balance between  $\text{Fe}(\text{phen})_3^{2+}$  and  $\text{Fe}(\text{phen})_3^{3+}$  (as shown in Fig. 6c), this change of peak height could be attributed to the side reaction (1a). At this moment, if phenol was added into this system, the peak height of  $\text{Fe}(\text{phen})_3^{2+}$  can approach the original faster than that without addition of phenol (shown in Fig. 6b), which shows that the hydroxylation of phenol (main reaction (2)) takes place and runs more faster than the side reaction (1a).

Nevertheless, when the phenol is added first into the  $\text{Fe}(\text{phen})_3^{2+}$  solution, there is no change of the peak height of  $\text{Fe}(\text{phen})_3^{2+}$  (shown in Fig.

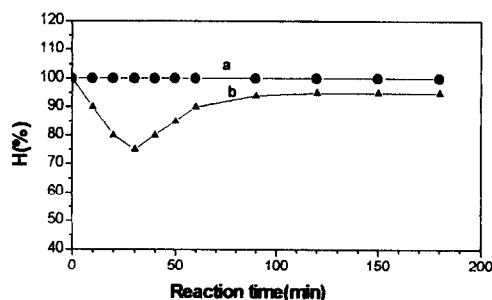


Fig. 7. Peak change of  $\text{Fe}(\text{phen})_3^{2+}$  + phenol system without (a) and with (b) addition of  $\text{H}_2\text{O}_2$ .

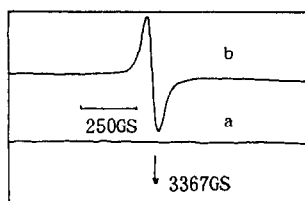


Fig. 8. ESR spectra of  $\text{Fe}(\text{phen})_3^{2+}$  and  $\text{Fe}(\text{phen})_3^{3+}$ .

7a), thereafter, when  $\text{H}_2\text{O}_2$  was added, the peak height of  $\text{Fe}(\text{phen})_3^{2+}$  will decrease slowly to the lowest point and then come back to the original height quickly (shown in Fig. 7b). Evidently, both the change of peak position and the appearance of new peak do not happen during this period, illustrating that  $\text{H}_2\text{O}_2$  first produce the active species  $\cdot\text{OH}$ , which goes on to react with phenol to produce diphenols without formation of new intermediate complex.

The transformation of  $\text{Fe}(\text{phen})_3^{2+}$  to  $\text{Fe}(\text{phen})_3^{3+}$  in  $\text{Fe}(\text{phen})_3^{2+} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$  system is also confirmed with ESR study. The ESR spectra of the samples were obtained through liquid method. Water solution of  $\text{Fe}(\text{phen})_3^{2+}$ ,  $\text{Fe}(\text{phen})_3^{3+}$  and  $\text{Fe}(\text{phen})_3^{2+} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$  system are individually transferred into capillary tubes and then used for ESR studies. The ESR spectra of  $\text{Fe}(\text{phen})_3^{2+}$  and  $\text{Fe}(\text{phen})_3^{3+}$  are shown in Fig. 8. From Fig. 8, we know that  $\text{Fe}(\text{phen})_3^{2+}$  has no ESR signal, but  $\text{Fe}(\text{phen})_3^{3+}$  does, which is in accordance with the report of

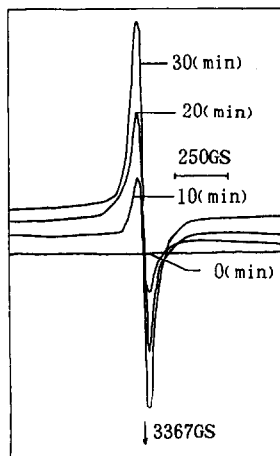


Fig. 9. ESR spectra of  $\text{Fe}(\text{phen})_3^{2+} + \text{H}_2\text{O}_2 + \text{H}_2\text{O}$  system.

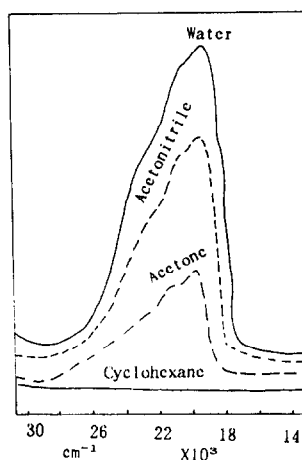


Fig. 10. UV-Vis spectra of  $\text{Fe}(\text{phen})_3^{2+}$  in different solvents.

Kuznetsova [17]. Evidently, when  $\text{H}_2\text{O}_2$  was added to the  $\text{Fe}(\text{phen})_3^{2+}$  solution, an ESR spectrum of  $\text{Fe}(\text{phen})_3^{3+}$  appears (shown in Fig. 9), and the peak height also increases with time, which is similar to the results of UV-Vis studies, this shows that a part of the  $\text{Fe}(\text{phen})_3^{2+}$  in the  $\text{Fe}(\text{phen})_3^{2+} + \text{H}_2\text{O}_2$  system has been oxidized to  $\text{Fe}(\text{phen})_3^{3+}$  successively.

It has been shown in Table 2 that the reaction in water medium is better than that in acetonitrile, acetone and cyclohexane. The UV-Vis spectra of  $\text{Fe}(\text{phen})_3^{2+}$  in these solvent are shown in Fig. 10. There are no spectrum of  $\text{Fe}(\text{phen})_3^{2+}$  in cyclohexane due to non-dispersion of  $\text{Fe}(\text{phen})_3^{2+}$  in this solvent. When  $\text{H}_2\text{O}_2$  was added into these four systems, the change of the peak height of  $\text{Fe}(\text{phen})_3^{2+}$  in different solvents are displayed in Fig. 11, which shows that the

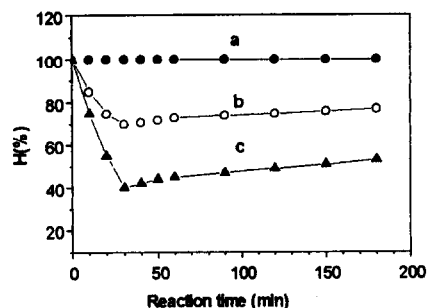


Fig. 11. Peak change of  $\text{Fe}(\text{phen})_3^{2+}$  in different solvents with the addition of  $\text{H}_2\text{O}_2$ .

peak change in water is faster than that in acetonitrile and there is no change for that in acetone and cyclohexane, this means that the first reaction is difficult to happen in weak polar organic solvent for the production of  $\cdot\text{OH}$  and  $\text{OH}^-$  in these solvents.

From these results, a conclusion that the active species  $\cdot\text{OH}$  and  $\text{OH}^-$  in reaction system are easily produced and dispersed in water than that in the other three organic solvents could be thus drawn, moreover, the reactant phenol,  $\text{H}_2\text{O}_2$  and the catalyst  $\text{Fe}(\text{phen})_3^{2+}$  can form a better homogeneous system in water than that in the organic solvent. As shown in Table 2, in the solvent cyclohexane, even no reaction can occur, this may be due to the fact that no  $\text{H}_2\text{O}_2$  and catalyst could be dissolved, which makes the first reaction very difficult to produce  $\cdot\text{OH}$  for the further hydroxylation. In acetonitrile and acetone, not only the first reaction takes place more slowly than in water, but also the difficultly dispersed  $\cdot\text{OH}$  can easily contact with and get  $\text{H}$  from hydroquinone to produce benzoquinone, the condensation of benzoquinone can also lead to tarry by-products. This is the reason for high selectivity to benzoquinone and low efficiency of  $\text{H}_2\text{O}_2$  in these reactions systems. Fig. 2 also shows that the hydroquinone can be further oxidized into benzoquinone, even if being together with catechol, this means that hydroquinone is easier to be reoxidized than catechol.

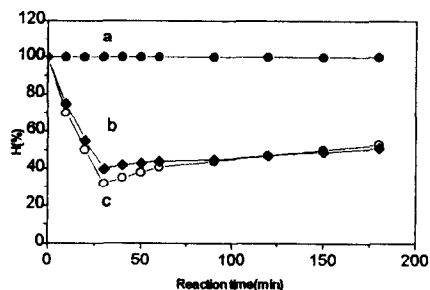


Fig. 12. Peak height change of  $\text{Fe}(\text{phen})_3^{2+}$  in solution of different pH.

The pH of the reaction medium has great effect on the phenol hydroxylation. When the reaction is carried in acidic medium, phenol conversion is higher than that in neutral and basic medium (shown in Table 3). The change of UV-Vis spectra peak height of  $\text{Fe}(\text{phen})_3^{2+}$  in water system of different pH is shown in Fig. 12, showing that there is no peak height change for  $\text{Fe}(\text{phen})_3^{2+}$  into basic medium (Fig. 12a), and the peak height change of  $\text{Fe}(\text{phen})_3^{2+}$  in acidic medium (Fig. 12c) is faster than that of  $\text{Fe}(\text{phen})_3^{2+}$  in neutral medium (Fig. 12b). So we conclude that, in acidic reaction system,  $\text{H}^+$  can accelerate the first reaction, more  $\cdot\text{OH}$  could be thus produced easily and quickly than that of neutral and basic reaction system, moreover, the lower the pH, the faster production of  $\cdot\text{OH}$ . More  $\cdot\text{OH}$  not only increases the phenol conversion, but also raises the selectivity to benzoquinone and reduces that of hydroquinone, meanwhile, some tarry by-products may be produced from condensation of benzoquinone (side reaction (3)). When the reaction occurs in basic medium, the first reaction is perhaps inhibited by two reasons, the one is, more  $\text{OH}^-$  is not in favor of production of  $\cdot\text{OH}$ , and the other is, in basic medium, it is very hard for  $\text{H}_2\text{O}_2$  to produce  $\cdot\text{OH}$  and  $\text{OH}^-$ , so there is no reaction occurring in basic medium of large pH value.

## 5. Conclusion

In conclusion,  $\text{Fe}(\text{phen})_3^{2+}$  has better catalytic activity than that of  $\text{Fe}^{2+}$ . Kinetics and spectra studies help to establish the mechanism of phenol hydroxylation. The mechanism not only gives a good understanding of this reaction and points out the suitable conditions for the production of diphenols, but also be useful for further study of its industrial application. Like the heterogeneous catalysts TS-1 [18,19] and TS-2 [20,21], the results shown in Table 5 show that this catalyst system may be used for phenol hydroxylation in the future.

## References

- [1] I.Y. Litvintsev, Y.V. Mitnik and A.I. Mikhailyuk, *Kinet. Katal.* 34(1) (1993) 68.
- [2] A.V. Eliseev, *React. Kinet. Catal. Lett.* 43(2) (1992) 419 (in English).
- [3] M.B. Hocking, *J. Chem. Tech. Biotechnol. Chem. Technol. A* 35(7) (1985) 365.
- [4] P. Maggioni, *Chim. Ind. (Milan)* 59(4) (1977) 239.
- [5] A.I. Brodskii, *Zh. Obshch. Khim.* 32 (1962) 2273.
- [6] A.P. Ereemeev, *Zh. Prikl. Khim.* 53(2) (1980) 386.
- [7] Y. Masri and M. Hronec, *Dioxygen Activation and Homogeneous Catalytic Oxidation*, L.I. Simandico (ed.) (Elsevier Science Publishers B.V., Amsterdam, 1991) pp. 455–460.
- [8] P.V.S. Rao, K.V. Subbaiah, P.S.N. Murty and R.V.S. Murty, *Indian J. Chem. Sect. A* 19(3) (1980) 257.
- [9] W. Du, G.X. Wang and Z.W. Xi, *Fenzi Cuihua* 4(4) (1990) 306.
- [10] A. Zombeck, R.S. Drago, B.B. Gorden and J.H. Gaul, *J. Am. Chem. Soc.* 103(25) (1981) 7580.
- [11] T. Shinji, S. Manabu and K. Motomasu, *Jp.* 02,250,883 [90, 250, 883] (1990).
- [12] Z.Y. Zhang, H.J. Zhang, M.M. Ma and Y. Wu, *J. Molec. Catal.* 17 (1982) 65.
- [13] X.Y. Qi, X.K. Ye and Y. Wu, *Chem. J. Chin. Univ.* 5 (1995) 791.
- [14] Y. Ohsaw, Y. Shimazaki and S. Aoyagui, *J. Electroanal. Chem. Interfacial Electrochem.* 114(2) (1980) 235.
- [15] M.M. Jones, *Ligand Reactivity and Catalysis* (Academic Press, 1968) p. 99.
- [16] A.R. Sheldon and J.K. Kochi, *Metal-Catalyzed Oxidation of Organic Compounds* (Academic Press, New York, 1981) p. 35.
- [17] N.I. Kuznetsova, L.B. Okhlopakova, E.P. Talzi and V.A. Likholobov, *Koord. Khim.* 16(7) (1990) 950.
- [18] M.G. Clerici, *Appl. Catal.* 68 (1991) 249.
- [19] M.G. Clerici, G. Bellussi and U. Romano, *J. Catal.* 129 (1991) 159.
- [20] J.S. Reddy, R. Kumar and P. Ratnasamy, *Appl. Catal.* 58 (1990) L1.
- [21] J.S. Reddy and S. Sivasanker, *Catal. Lett.* 11 (1991) 241.