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Investigation on redox mechanism of p-aminophenol in non-aqueous media by FT-IR spectroelectrochemistry

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ABSTRACT

The electrochemical character of p-aminophenol in non-aqueous media was investigated by cyclic voltammetry (CV). Two couples of redox peaks and two shoulder peaks are observed in cyclic voltammogram. By in situ FT-IR spectroelectrochemistry, several IR absorption peaks, 1518, 1256, 1210; 1610, 1503, 1272; 1664, 1649, 1595, 1287 cm^{-1}, corresponding to $OHC_6H_4NH_2$; $(OHC_6H_4NH_2)^{+\bullet}$ and dimer; $(OHC_6H_4NH_2)^{2+}$ and C_6H_4ONH, are observed. Based on cyclic voltabsorptometry (CVA) and derivative cyclic voltabsorptometry (DCVA) techniques, we can track the changes of each species during electrochemical process. The results indicate that p-AP is oxidized in two-step one-electron transfer, and moreover, amino group is first oxidized than the hydroxyl group. The final oxidized product is quinonimine, and meanwhile the formation of dimer is detected. The dimer can be oxidized at more positive potential to form the final oxidation product (quinonimine) and reduced at more negative potential to form a new reduction product. By calculating relative energy, three possible structures of the dimer are proposed.

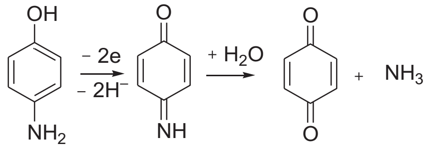
1. Introduction

Aminophenols are different from aniline [1] and other substituted anilines [2], they have two groups ($-NH_2$ and $-OH$), which could be oxidized. Generally hydroxyl group is oxidized to carbonyl group and amino group is oxidized to imino group.

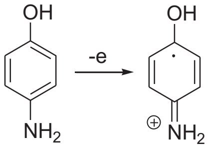
The electrochemical oxidation of p-AP was studied in different media (acid [3–7], aqueous [8–12], organic [12–14], neutral media [15,16], etc.) and electrodes (gold [10,12,17], platinum [14,18], mercury [4], glassy carbon [4,19], SnO_2 electrode [20], etc.). Up to now, many techniques have been used to investigate the electron transfer mechanism, such as voltammetry [21–23], FT-IR [5,10,24], UV–Vis spectrochemistry [12], time-resolved resonance Raman [25] and ESR spectroscopy [26].

In the previous work, Wang et al. [27] have proposed that the intermediate of the oxidation of p-AP is p-benzoquinoneimine in acid media, then a coupled hydrolysis occurs to form the final product (p-benzoquinone). The following hydrolytic reaction of the p-benzoquinoneimine is studied by various methods, such as cycling chronopotentiometry [28], chronopotentiometry [29], cyclic voltammetry and potential step.

In the later work, Salavagione et al. [5] have studied the oxidation of aminophenols (para-, meta-, ortho-aminophenols) in acid medium on platinum electrode. The electrochemical result of p-AP shows that a quasi-reversible redox couple is observed without detecting polymeric material. By spectroscopy study, the author further demonstrated that oxidized p-AP suffers hydrolysis to form p-benzoquinone.



In organic media, Taj et al. [14] have reported the electropolymerization of the p-AP to yield a new soluble and electroactive polymer on a platinum electrode. Then Schwarz et al. [12] have studied of p-AP in acetate buffer solution and acetonitrile solution at gold electrode by voltammetry and UV–Vis spectrochemistry. The results show that p-AP is oxidized to produce an intermediate of a radical cation.



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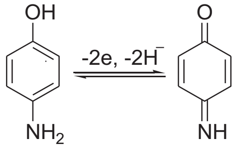
Yin et al. [19] have discussed that the electrochemical oxidation of p-AP based on modified glassy carbon electrode is 2e, $2H^+$ process in 0.1 M pH 6.3 phosphate buffer solution.



In aqueous media, Menezes and Maia [10] have found that a film is formed upon the oxidation of p-AP in the pH values from 2 to 12. The film generated is thinker at pH 6 or 8, and film formed at pH 4 is greater charge retention. The main factor that affects film formation is charge-transfer complex precipitation.

In this paper, CV, in situ FT-IR spectroelectrochemistry, IR CVA, DCVA were used to study the electron transfer of p-AP electrochemical oxidation in non-aqueous media. The results indicate that the oxidation of p-AP is two-step one-electron transfer. The final oxidized product is quinonimine, and meanwhile the formation of dimer is detected. The results of CVA, DCVA not only make us understand the redox mechanism of p-AP, but also draw an entire map of the electrochemical oxidation of p-AP in acetonitrile media.

2. Experiment

2.1. Chemicals

p-Aminophenol (≥99%, HPLC) and acetonitrile (anhydrous, 99.8%) were purchased respectively from Sigma–Aldrich. Tetrabutylammonium perchlorate was synthesized and recrystallized from ethanol, then dried overnight under reduced pressure at 100 °C before use. Other reagents were ethanol (analytical reagent) and second-distilled water.

2.2. Electrochemistry

The electrochemical experiments were tested with an electrochemical analyzer CHI630C potentiostat. A homemade thin-layer spectroelectrochemical cell [30] was used. 4 mm gold disk electrode as the working electrode, a platinum wire as auxiliary electrode and Ag/AgCl as reference electrode. The gold disk electrode was polished with alumina slurry on a polishing cloth and cleaned under bath sonication for 10 min in the mixture of deionized water and ethanol. All solutions were purged with pure N_2 for 15 min before the experiments.

2.3. FT-IR spectroelectrochemistry

FT-IR spectroscopic experiments were carried out on a Nicolet Nexus 870 spectrometer equipped with a specular reflectance accessory (SMART iTR) and a HgCdTe/A (MCT/A) detector cooled with liquid-nitrogen. 30–40 interferograms were added to each spectrum for rapid-scan time-resolved spectroscopic measurements. The sampling interval is 0.7–0.8 s and spectral resolution is 16 cm^{-1}. The spectra result was listed as following:

$$\frac{\Delta R}{R}=\frac{R(E_S)-R(E_R)}{R(E_R)}$$

$R(E_R)$, $R(E_S)$ represent reference potential and sampling potential spectrum respectively. The resulting spectra were determined with Grams/3D software.

3. Results and discussion

3.1. FT-IR spectroelectrochemistry: scan range from −0.2 to 1.0 V

A typical CV of p-AP recorded in CH_3CN solution on Au disk electrode is shown in Fig. 1(A). Two couples of prominent anodic and cathodic peaks at 0.300 V (A_1) and 0.167 V (C_1), 0.686 V (A_2) and 0.540 V (C_2) are observed, respectively. Besides, two shoulder peaks at A_2' and C_3 are also apparent in the voltammogram. The experimental results show that p-AP is oxidized resulting likely in the formation of a radical cation intermediate $(OHC_6H_4NH_2)^{+\bullet}$ at A_1 and the divalent cations $(OHC_6H_4NH_2)^{2+}$ at A_2 and attributed to the two electrons p-AP redox process.

In Schwarz's work [12], a peak at +0.58 V is seen in acetonitrile at gold electrode using spectroelectrochemical cell. It dues to the oxidation of p-AP to an intermediate oxidation product $(OHC_6H_4NH_2)^{+\bullet}$. However, little information discusses the followed reacting mechanism in detail. Salavagione et al. [5] have observed a quasi-reversible peak in $HClO_4$ solution. An anodic peak at 0.8 V and cathodic peak at 0.75 V are shown in voltammogram. They propose the oxidation of p-AP is 2e, $2H^+$ process and the final oxidation product is quinonimine. Then quinonimine suffers hydrolytic reaction to form the final product benzoquinone. And they observe that on the electrode surface no polymeric product is formed. In our work, we observe not only two couples of redox peaks but also the peaks at A_2' and C_3 which have not been reported in previous works. In acetonitrile solution, hydrolytic reaction will not happen to form benzoquinone because the first step redox potential of benzoquinone [31] is reported at about −0.35/−0.23 V. Thus we can not ascribe the shoulder peaks at A_2' and C_3 to the redox peaks of the hydrolytic product (benzoquinone).

Cyclic voltammogram of consecutive scan was conducted and the result is shown in Fig. 1(B). From Fig. 1(B) (the black line), a new anodic peak at A_3 corresponding to C_3 is observed and the peak current at A_1 decreases in the second and third cycle. The current of other peaks is nearly invariable.

The electrode is immersed in CH_3CN solution containing 20 mM p-aminophenol and 0.2 M TBAP to scan for continuous three cycles, pulled out and washed with ethanol, then put it into the blank solution (without p-aminophenol) for cyclic voltammogram. The result is shown in Fig. 1(B) (the red line). It is found that no obvious redox peaks emerge. Thus we can exclude that the anodic at A_2' and cathodic peak at C_3 are due to adsorption current. We guess it may be the formation of dimer which can be oxidated at A_2' to form the final oxidation product (quinonimine) and reduced at C_3 to form a new reduction product.

In order to further explore the mechanism, FT-IR spectroelectrochemical experiment was conducted to track the changes of species during the electrochemical process. The rapid-scan IR spectra recorded in situ during the electrochemical process in the scan range from −0.2 to 1.0 V are shown in Fig. 2(A). The reference spectrum is recorded at −0.2 V.

In the 3D spectra, ten clear IR absorption peaks at 1664, 1649, 1595, 1287; 1610, 1503, 1272; 1518, 1256, 1210 cm^{-1} can be observed. The three negative-going bands at 1518, 1256, 1210 cm^{-1} which are due to the absorption of p-AP, indicate that the concentration of p-AP decreases in the oxidation process while p-AP increases in reduction process. Four positive-going bands at 1664, 1649, 1595, 1287 cm^{-1} which are due to the absorption of divalent cations $(OHC_6H_4NH_2)^{2+}$ and C_6H_4ONH, indicate that the concentration of $(OHC_6H_4NH_2)^{2+}$ and C_6H_4ONH increases in the positive potential scan while they decrease in the negative potential scan. The two positive-going bands at 1610 and 1272 cm^{-1} which are due to the intermediate $(OHC_6H_4NH_2)^{+\bullet}$ appear and disappear during both the oxidation and reduction processes. Interestingly, the positive-going band at 1503 cm^{-1} appears and disappears during

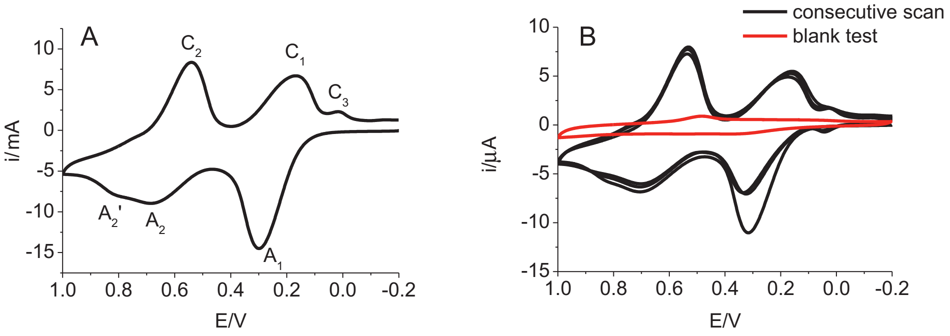


Fig. 1. (A) Cyclic voltammogram in CH_3CN solution containing 20 mM p-aminophenol and 0.2 M TBAP as the supporting electrolyte and (B) black line: consecutive scan; red line: cyclic voltammogram in the solution without p-aminophenol. Au disk electrode as the working electrode. Scan rate was 5 mV s^{-1}. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

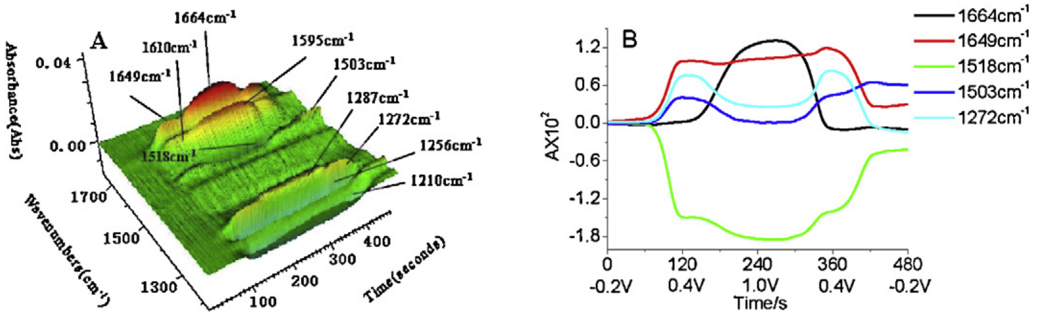


Fig. 2. (A) The corresponding 3D spectra to the cyclic voltammogram and (B) CVAs for the p-AP electrochemical reaction at the five IR absorption peaks.

the oxidation process while it continues to produce during the reduction process. The assignment of IR absorption peaks observed is listed in Table 1.

To observe the behavior of the absorption at different wavenumbers clearly, the cyclic voltabsorptometry responses (CVAs) at 1664, 1649, 1518, 1503, 1272 cm^{-1} IR absorption peaks are shown in Fig. 2(B).

From Fig. 2(B), we can observe that in the oxidation process, the absorbance at 1518 cm^{-1} starts to decrease gradually at about 60 s (0.1 V) and completely vanishes at about 220 s (0.9 V). When it disappears gradually, the absorbance at 1649, 1503, 1272 cm^{-1} starts to increase at about 60 s (0.1 V) and reaches their maximum absorbance at about 120 s (0.4 V). Then the absorbance value at 1503, 1272 cm^{-1} begins to decline gradually at about 150 s (0.55 V) and completely vanishes at about 220 s (0.9 V). At the same time, the absorbance at 1664 cm^{-1} starts to increase at about 150 s (0.55 V) and reaches the maximum value at about 220 s (0.9 V). A reversed phenomenon can be found in the reduction process for the absorbance at 1664, 1649, 1518 cm^{-1}, but not for 1503, 1272 cm^{-1}. It can be found that the absorbance at 1272 cm^{-1} produces again at about 290 s (0.75 V) in the reduction and reaches the maximum at about 350 s (0.45 V). Then it starts to decrease again at about 360 s (0.4 V) and completely vanishes at about 420 s (0.1 V).

Table 1
The assignment of FT-IR absorption peaks in acetonitrile solution.

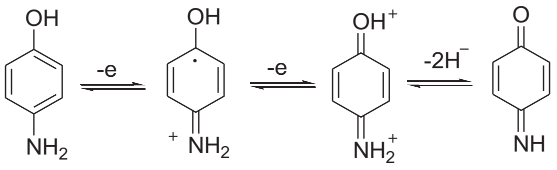
Peak position (cm^{-1})	Assignment
1664	$\nu_{C=O}$ from $(OHC_6H_4NH_2)^{2+}$ and C_6H_4ONH
1649	$\nu_{C=N}$ from $(OHC_6H_4NH_2)^{+\bullet}$ and $(OHC_6H_4NH_2)^{2+}$ and C_6H_4ONH
1610	$\nu_{C=C}$ from $(OHC_6H_4NH_2)^{+\bullet}$
1595	$\nu_{C=C}$ from $(OHC_6H_4NH_2)^{2+}$ and C_6H_4ONH
1518 [5]	$\nu_{C=C}$ from p-AP
1503	$\nu_{C=C}$ from $(OHC_6H_4NH_2)^{+\bullet}$ and dimer
1287	δ_{O-H} from $(OHC_6H_4NH_2)^{2+}$
1272	ν_{C-O} from $(OHC_6H_4NH_2)^{+\bullet}$
1256 [5]	ν_{C-O} or δ_{O-H} from p-AP
1210	ν_{C-N} from p-AP

Thus, we can suggest that the oxidation of p-AP produces quinonimine as is presented in Scheme 1.

The absorbance at 1503 cm^{-1} is interesting. In oxidation process, it increases gradually then vanishes. But in reduction process, it continues to increase. To explain the phenomenon and investigate the cathodic peak at C$_3$ in detail, we limited the potential scan range from −0.2 to 0.5 V.

3.2. FT-IR spectroelectrochemistry: scan range from −0.2 to 0.5 V

The typical cyclic voltammogram and the corresponding 3D in the scan range from −0.2 to 0.5 V are shown in Fig. 3(A) and (B). Again, the cathodic peak at C$_3$ is observed. It may be considered that a chemical reaction occurs between the reactant p-AP and the radical cation intermediate $(OHC_6H_4NH_2)^{+\bullet}$ to form dimer. Then the dimer can be reduced at C$_3$. From Fig. 3(B), three negative-going bands at 1518, 1256, 1210 cm^{-1} and four positive-going bands at 1649, 1610, 1503, 1272 cm^{-1} are observable, but the absorbance at 1664, 1595, 1287 cm^{-1} are unobservable. The result suggests that the first step oxidation (A$_1$) of p-AP forms the C=N bond not C=O bond and a radical cation intermediate $(OHC_6H_4NH_2)^{+\bullet}$ is produced as illustrated in Scheme 1.



Scheme 1. The redox mechanism of p-aminophenol in non-aqueous media.

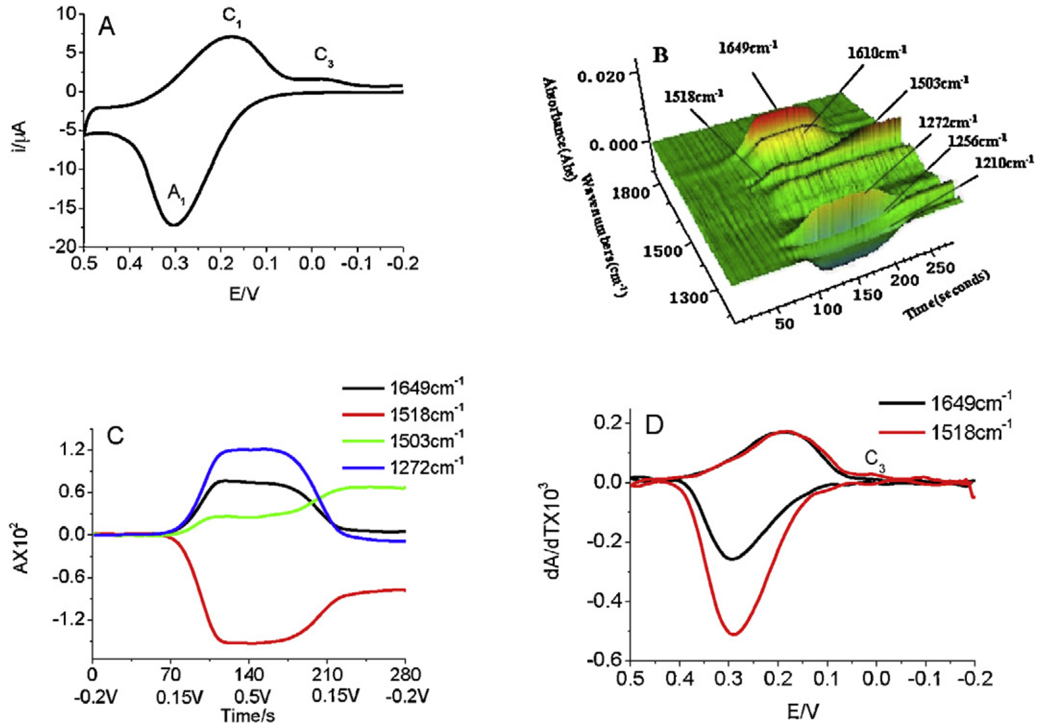


Fig. 3. (A) Cyclic voltammogram, (B) the corresponding 3D spectra, (C) the corresponding CVAs and (D) selected DCVAs in CH_3CN solution containing 20 mM p-aminophenol and 0.2 M TBAP as the supporting electrolyte. Au disk electrode as the working electrode. Scan rate was 5 mV s^{-1}. The DCVA date at 1649 cm^{-1} was multiplied by −1 to make the DCVA date readily compared to CV.

Similarly, the cyclic voltabsorptometry responses (CVAs) at the 1649, 1518, 1503, 1272 cm^{-1} absorption peaks are shown in Fig. 3(C). In oxidation process, the absorbance at 1518 cm^{-1} starts to decrease gradually at about 60 s (0.1 V) and completely vanishes at about 120 s (0.4 V). The absorbance at 1649, 1272 cm^{-1} starts to increase at about 60 s (0.1 V) and reaches their maximum value at about 120 s (0.4 V). In reduction process, the absorbance at 1518 cm^{-1} starts to increase gradually at about 160 s (0.4 V) and reaches the stable value at about 220 s (0.1 V). But it does not reach its initial value. The result suggests that a chemical reaction of 4-AP occurs. The absorbance at 1649, 1272 cm^{-1} starts to decrease at about 160 s (0.4 V) and reaches the stable value at about 220 s (0.1 V).

The absorbance at 1503 cm^{-1} shows different behavior. In the oxidation process, it first starts to increase at about 60 s (0.1 V) and reaches the stable value at about 120 s (0.4 V), then continues to increase at about 160 s (0.4 V) in the reduction process. At last, it reaches the final stable value at about 220 s (0.1 V). In other words, the absorbance at 1503 cm^{-1} is continuous to increase both in oxidation and reduction process. The phenomenon can be explained as follow. In oxidation process, the absorbance increases gradually because of the formation of the radical cation intermediate $(OHC_6H_4NH_2)^{+\bullet}$ and dimer which is formed by a reaction between the radical cation intermediate and the reactant. In the reduction process, the radical cation intermediate $(OHC_6H_4NH_2)^{+\bullet}$ can be reduced to the reactant p-AP, then the p-AP and the radical cation intermediate $(OHC_6H_4NH_2)^{+\bullet}$ which has not been reduced react to form dimer. So the absorbance at 1503 cm^{-1} continues to increase in reduction process.

The result of the derivative cyclic voltabsorptometric (DCVA) at 1649, 1518 cm^{-1} is shown in Fig. 3(D). A couple of redox peaks and a small cathodic peak (C_3) are observed. The result is similar to the obtained CV in Fig. 3(A).

To observe the anodic peak at A_3 (Fig. 1B) which is related to the cathode peak at C_3, continuous three circles of CV and the corresponding 3D spectra were conducted.

From Fig. 4(A), the anodic peak at A_3 corresponding to C_3 is also observed and the current at A_1 decreases in the second cycle. The

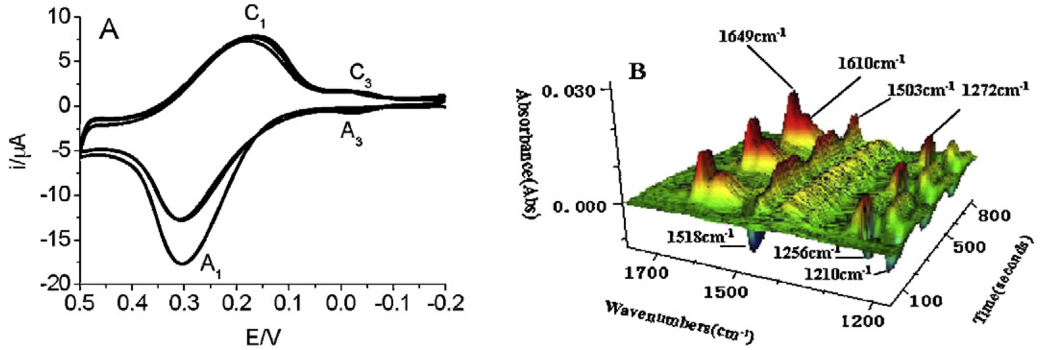


Fig. 4. (A) Cyclic voltammogram of continuous three cycles and (B) the corresponding 3D spectra in CH_3CN solution containing 20 mM p-aminophenol and 0.2 M TBAP as the supporting electrolyte. Au disk electrode as the working electrode. Scan rate was 5 mV s^{-1}.

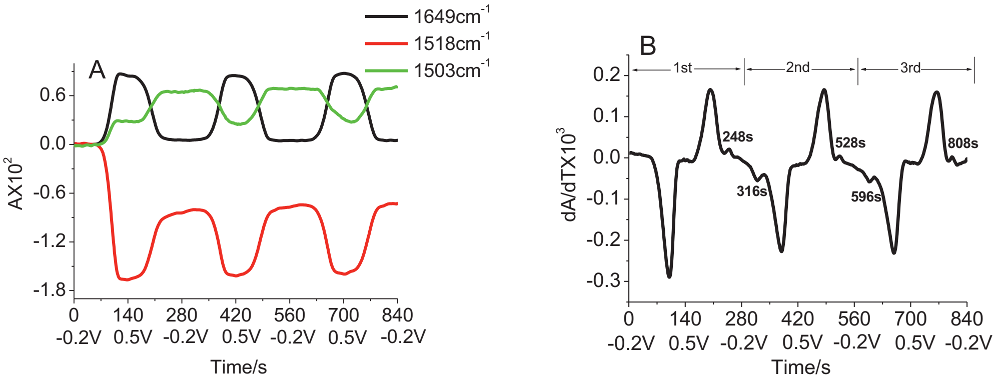
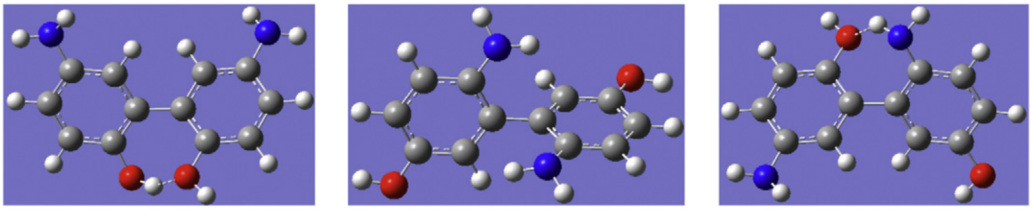
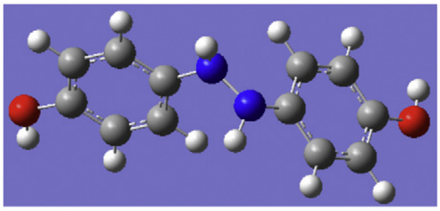


Fig. 5. (A) The CVAs at 1649, 1518, 1503 cm^{-1} and (B) the DCVAs at 1210 cm^{-1} during the continuous three cycles potential scans.



Dimer1 (0.00 eV) Dimer2 (0.07 eV) Dimer3 (0.09 eV)



Dimer4 (1.31 eV)

Fig. 6. The low-energy isomers for dimer at B3LYP/6-311++G** level, enclosed are relative energies in eV to the first isomer.

current of other peaks is nearly invariable. Three negative-going bands at 1518, 1256, 1210 cm^{-1} and four positive-going bands at 1649, 1610, 1503, 1272 cm^{-1} are also observable in Fig. 4(B). Similarly, the cyclic voltabsorptometry responses (CVAs) at the 1649, 1518, 1503 cm^{-1} IR absorption peaks are shown in Fig. 5(A).

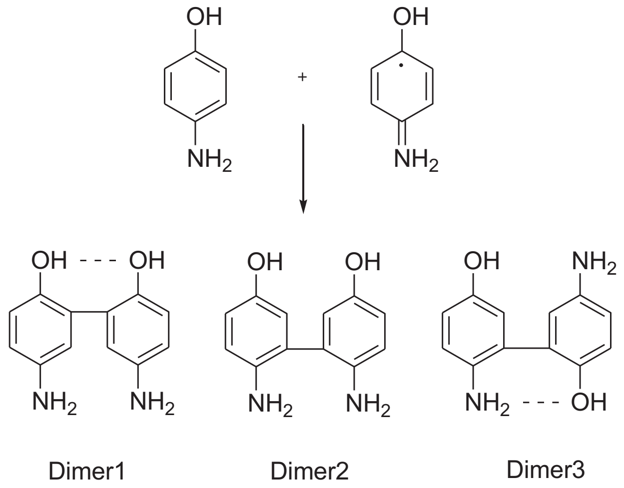
In Fig. 5(A), in the first circle, the absorbance at 1649, 1503 cm^{-1} starts to increase with the absorbance at 1518 cm^{-1} decreasing gradually in the oxidation process. Then in the reduction process, the absorbance at 1518 cm^{-1} starts to increase with the absorbance at 1649 cm^{-1} starting to decrease. But the absorbance at 1503 cm^{-1} continues to increase. In the second and third circle, the changes of the absorbance at 1649, 1518 cm^{-1} are similar to the first circle. However, the change of the absorbance at 1503 cm^{-1} is the same as that at 1518 cm^{-1} in the second and third cycle.

The selected DCVAs at 1210 cm^{-1} is showed in Fig. 5(B). In the first cycle, a small peak observed at 248 s is corresponded to the cathode peak at C_3 which is shown in Fig. 5(A). Then in the second circle, at 316 s also appears a small peak which is corresponded to the anode peak at A_3. At 528 s the cathode peak at C_3 similarly appears. In the third circle, the anode peak at A_3 and the cathode peak at C_3 are observed respectively at 596 s and 808 s. So the absorbance at 1210 cm^{-1} is related to the redox couple at A_3/C_3. This also shows that the dimer is reduced without forming new functional group.

By analyzing all of the above results, we ensure that p-AP is oxidated to form quinonimine. At the same time, a chemical reaction can happen between p-AP and the radical cation intermediate.

To explore the structure of dimer, the relative energy of possible dimer structure was calculated at B3LYP/6-311++G** level. The calculation was carried out by the Gaussian 09 package [32] and the main structures are listed in Fig. 6. The value in the brackets is relative energy in eV.

From Fig. 6, four possible structures of dimer are shown (the relative energy of monomer is 2.64 eV). Generally, we think that



Scheme 2. Possible structures of dimer.

ortho-substituted p-aminophenol easily takes place, but the energy of meta-substituting p-aminophenol is the lowest due to intermolecular hydrogen bond. Compared with relative energy of dimer, three main possible structures (dimer1, dimer2, dimer3) are proposed and the most stable state is dimer1.

So we can suggest that the formation of dimer as is presented in Scheme 2.

4. Conclusion

In the article, the oxidation of p-AP in acetonitrile solution is studied. The result shows that the oxidation of p-AP is two-step one-electron process and meanwhile the p-AP and the radical cation intermediate can react to form the dimer which can be oxidized at more positive potential and reduced at more negative potential. Four dimer structures are simulated and the relative energy was calculated at B3LYP/6-311++G** level using Gaussian 09. Compared with relative energy of dimer, three possible structures are proposed.

Acknowledgments

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