In-situ FTIR Spectroelectrochemical Study of Dopamine at a Glassy Carbon Electrode in a Neutral Solution

Xiayan WANG,* Baokang JIN,** and Xiangqin LIN**†

*Department of Chemistry, University of Science and Technology of China, Hefei 230026, China
**Department of Chemistry, Anhui University, Hefei 230039, China

(Received March 15, 2002; Accepted June 6, 2002)

Introduction

Dopamine (DA) serves as a neurotransmitter in the central and sympathetic nervous systems, or as a hormone in vesicles of the adrenal medulla for regulating the heart rate and blood pressure.1 A loss of DA-containing neurons may result in some serious disease, such as Parkinson’s disease. Therefore, detailed information regarding its reaction at the molecular level and a determination of the concentration of DA are important.

The fact that DA and other catecholamines are easily oxidizable compounds makes their detection possible by electrochemical methods based on anodic oxidation. Several studies of electrochemical redox processes of DA have been carried out.2,3 However, the redox process of DA is very complicated due to the formation of a series of intermediates, and the mechanism is still uncertain.

In situ Fourier transform infrared (FTIR) spectroelectrochemistry is one of the useful methods to characterize the intermediates in redox processes. To our knowledge, a study of the redox pathway of DA using the in situ FTIR spectroelectrochemical method has not been reported previously. In this work the electrochemical redox processes of DA were studied by thin-layer cyclic voltammetry and an in situ FTIR technique. It is our goal to identify the absorbance characteristics of any intermediates in the electrochemical oxidation of DA and to clearly understand the reaction pathway of DA in detail.

Experimental

Reagents

Dopamine hydrochloride was obtained from Sigma Chemical Company (USA). KCl, K₂HPO₄ and KH₂PO₄ were purchased from Shanghai Chemical Company (Shanghai), Hongxing Chemical Company (Beijing), and Xilong Chemical Company (Guangdong), respectively. All chemicals were of analytical reagent grade. All solutions were prepared in D₂O and oxygen was removed by purging high-purity nitrogen.

Instruments and in-situ FTIR spectroelectrochemical measurements

The in-situ FTIR experiments were carried out on a Nicolet Nexus 870 spectrometer equipped with a variable-angle specular reflectance accessory (VeeMax II) and an MCT-A detector cooled with liquid nitrogen. The electrochemical equipment used was an EG&G PAR Model 283 potentiostat/galvanostat. The in situ FTIR and voltammetric measurements were performed in a spectroelectrochemical cell. The working, counter and reference electrodes were a glassy carbon electrode (EG&G), a Pt wire and an Ag/AgCl electrode, respectively. The IR transparent window was a disk of calcium fluoride, and the angle of incidence on the CaF₂ window was 50°. A total of 50 interferometric scans with a resolution of 4 cm⁻¹ were accumulated for the spectrum, and the current was recorded simultaneously. The spectra were successively taken while the electrode potential was scanned at a rate of 2 mV s⁻¹. All of the IR spectra obtained are represented as ∆R/R in the normalized form according to the formula

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

where R(Eₜ) and R(Eₚ) are the reflected intensities measured at the sample and base potentials, respectively.

Results and Discussion

Thin-layer cyclic voltammogram

The thin-layer cyclic voltammogram of 4 mmol l⁻¹ dopamine in a pH 7.0 phosphate buffer solution (PBS) is shown in Fig. 1. A peak (A) on the first positive scan was observed at 0.184 V (vs. Ag/AgCl). Upon reversal of the potential scan from 0.7 V, a weak peak (B) and another cathodic peak (C) were observed at 0.135 and –0.256 V, respectively. However, from the second cycle on, two new anodic peaks (D and E) appeared; thus, there were three oxidation peaks at –0.198, 0.09 and 0.253 V. Peak A corresponds to the oxidation of dopamine to the open-chain quinone, and peak B to the reduction of quinone to dopamine:

From the cyclic voltammogram, it can be concluded that the redox of DA is an irreversible process and that peaks D and E can be attributed to the oxidation of the intermediates produced in the first cycle. Peaks C and D can be ascribed to the redox of...
The contribution of peak E is the oxidation of an unknown compound formed during the first cycle. It was clearly observed that the initially colorless solution turned yellow, then red, and through brown to black on the surface of the electrode during voltammetry. The red material was dopaminechrome, and the black was the polymeric material, melanin.5

**In-situ FTIR spectroscopy**

The potential dependence spectra on a glassy carbon electrode (GCE) with a reference potential at −0.10 V (versus Ag/AgCl) in a solution 0.1 mol l−1 PBS + 0.5 mol l−1 KCl are shown in Fig. 2. In the subtractively normalized spectra, the upward peak indicates the disappearance of a certain group, while downward indicates its appearance.

The most intense bands were observed in the spectral range 1200 – 1700 cm−1. The in-plane-skeleton vibration and the carbonyl group vibration should fall within this region. The peaks observed downward at 1674 and 1662 cm−1 are attributable to carbonyl stretching. The bands are in the quinone carbonyl region.6,10 The coupling of vibrations of the two-carbonyl results in a split of the absorptions in the ortho-position structure.7 It is therefore an important evidence supporting that DA is oxidized to dopaminequinone. The band intensities of 1674 and 1662 cm−1 increase with positive potentials until about 0.15 V, and then decrease. This indicates that, after 0.15 V, the formed o-quinone (dopaminequinone) begins to disappear. This is due to the loss of o-quinone in the thin-layer solution, resulting from a sequence of follow-up chemical reactions. Another evidence for o-quinone formation is the upward band at ca. 1289 cm−1 assigned to C-O stretching, which illuminates that the characteristic of C-O stretching disappears during the oxidation process.

A weak peak at about 1624 cm−1 appeared from 0.29 V, and the intensity increased with an increase of the positive potential. This band is in the C=C stretching region of indole.8 Because a part of the open-chain quinone can be cyclized to dopaminechrome during the oxidation process, we assigned the band to the C=C stretching of dopaminechrome. The bands in the 1530 – 1600 cm−1 region seem to be an overlapping of several peaks, and are difficult to assign one by one, though we can conclude that one of the contributions results from the C=C stretching of dopaminequinone.7 The positive band at 1522 cm−1 is assigned to the C=C stretching of dopamine, and shifts to a higher frequency of about 1564 cm−1, which is due to the C=C stretching of dopaminequinone during the oxidation process.

The upward band at 1437 cm−1 is assigned to the C-N stretching of dopamine.8 It is clear that the characteristic of the C-N single bond is reduced during the oxidation process. This is because the formation of a cyclized product results in a loss of strength in the C-N bond and the appearance of two downward bands at 1546 and 1418 cm−1. The two bands begin at potentials of around 0.29 V. Morris performed resonance Raman studies of aminochrome generated through excess triiodide oxidation of the dopamine molecule.6 He assigned these two bands to a C≡N or C≡N-C stretching. A part of dopaminechrome formulate as the o-quinone (I), and others as the p-quinonemine (II). In aqueous solutions at neutral pH, the predominant chrome form would be the dipolar ion (III) in acid-base equilibrium.9

Thus, the appearance of downward bands at 1456 and 1418 cm−1 is due to the formation of the p-quinonemine-dopaminechrome and dipolar ion dopaminechrome. The downward peak at 1328 cm−1 is the contribution of a C=C single bond stretching of a six-member ring;2 its intensity increases with a positive potential until 0.29 V, and then decreases. The characteristic dependence on the potential is similar to that of 1564 cm−1. The downward peak at 1339 cm−1 begins at 0.29 V, and is the v(CC) contribution from the pyrrole ring,4 which further confirms the formation of dopaminechrome. These bands show no isotopic change upon deuteration and are comparable with other reported results.8

**Conclusions**

The present results suggest that dopamine is oxidized to the open-chain quinone, and forms an unknown compound simultaneously. The dopaminequinone is rapidly cyclized to dopaminechrome. In a neutral solution, dopaminechrome is
transformed to its tautomer, $p$-quinonemine-dopaminechrome, which is polymered to form melanin. A further investigation of the unknown compound and other intermediates is now underway.

Acknowledgements

We are thankful for financial support by the National Natural Science Foundation of China.

References