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In-situ FTIR Spectroelectrochemical and Electrochemical Studies of Ferrocene and Derivatives at a Platinum Electrode

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Abstract: Redox mechanism of ferrocene, acetylferrocene, ferrocenyl cinnamenyl ketone at a platinum electrode was studied with cyclic voltammetry (CV) and *in-situ* Fourier transform infrared (FTIR) spectroelectrochemistry. The IR bands in the range of 2000-1000 cm^{-1} attributed to the stretching and ring vibrations of these materials show the main spectral changes in the processes.

Keywords: *in-situ* FTIR spectroelectrochemistry, ferrocene(FcH), acetylferrocene(AFc), ferrocenyl cinnamenyl ketone(FcCK).

In recent years many groups have focused their research interests on the synthesis and electrochemical investigation of redox active compounds useful for electrochemical applications. For example, ferrocenyl and multiferrocenyl systems have been used as redox sensors for molecular recognition[1], as mediators in amperometric biosensors[2], as building blocks in polymersas[3] or as coatings to modify electrode surfaces[4]. *In-situ* FTIR spectroelectrochemistry is one of the useful methods to characterize the intermediates in redox processes and the mechanism of electron transfer. In our group, the mechanism of electron transfer of a metal bridged biferrocene trinuclear complex was studied by *in-situ* spectroelectrochemistry technique[5-8]. However, to our knowledge there were no studies on the redox of ferrocene and its derivatives reported yet by using *in-situ* FTIR spectroelectrochemistry. In this work, the redox mechanism of ferrocene(FcH), acetylferrocene(AFc), ferrocenyl cinnamenyl ketone(FcCK) at the Pt electrode surface has been investigated by CV and *in-situ* FTIR spectroelectrochemistry.

Experimental

Acetylferrocene(AFc) was synthesized according to the method in the literature[9]. Using an EtOH solution of the benzaldehyde and AFc (molar ratio 1:1), ferrocenyl cinnamenyl ketone(FcCK) formed after stirred for 8 h was collected by filtration, washed with EtOH and dried under vacuum. The structures of AFc and FcCK were confirmed by IR and NMR. Solutions of FcH, AFc, and FcCK were prepared by dissolving them

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in CH_3CN solution respectively. As the supporting electrolyte, 0.1 mol/L Bu_4NClO_4 was used. Other inorganic and organic reagents were of analytical grade and used without further purification. Electrochemistry was carried out on a model 283 Potentiostat/Galvanostat (EG&G, U.S.A). FTIR experiments were performed on a Nexus 870 spectrometer (Nicolet, U.S.A) equipped with a MCT/A detector cooled with experiment, 0.6 ml of the analyte solution is inserted into the cell with a 1 mL syringe. Spectra are recorded at a resolution of 8 cm^{-1} with 50 interferograms collected for eliquid nitrogen. A homemade thin-layer electrochemical cell[5] was used which consists of a platinum working electrode, a Ag/AgCl reference electrode, a platinum wire auxiliary electrode. For a spectroelectrochemicalach spectrum, 20 s after each change of potential. The resulting spectra were normalized as:

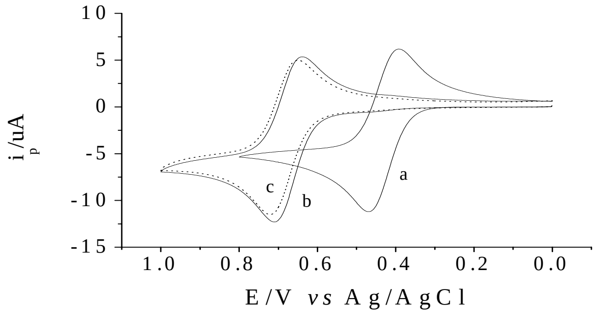
$$\Delta R/R = [R(E_S)-R(E_R)]/R(E_R)$$

By subtracting the reflection spectrum at sample potential E_S, $R(E_S)$, from the reflection spectrum at reference potential E_R, $R(E_R)$, the background due to the absorption of the solvent system is eliminated.

Results and Discussion

The cyclic voltammograms of 1 mmol/L FcH, AFc, and FcCK on a Pt electrode in CH_3CN solution containing 0.1 mol/L Bu_4NClO_4 as a supporting electrolyte are shown in **Figure 1.**

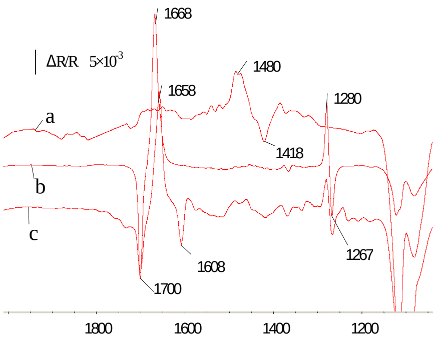
Figure 1 Cyclic voltammetric response of FcH, AFc, FcCK solutions



(a) FcH; (b) AFc; and (c) FcCK in 0.1 mol/L Bu_4NClO_4/CH_3CN (*vs*. Ag/AgCl). Scan rate, 50 mV/s.

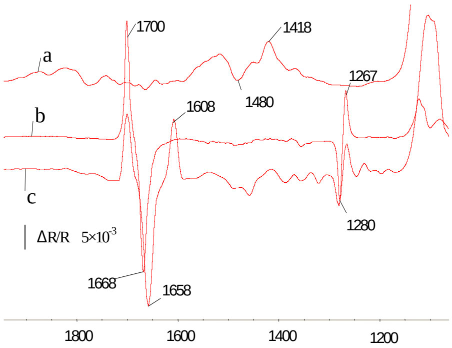
For AFc, a quasi-reversible one-electron redox process has been observed at $E_{1/2} = 0.675$ V with the separation of peak potentials $\triangle E_p = 0.071$ V. The potential value is considerably more positive than that of FcH ($E_{1/2} = 0.430$ V). This is due to the strong electron-withdrawing effect of the acetyl substituent which bound directly to the cyclopentadienyl ring, making oxidation of the ferrocene unit in FcMK thermodynamically more difficult, than that of unsubstituted ferrocene. In comparison to AFc, the respective redox response of FcCK almost has the same $E_{1/2}$(0.685 V) and $\triangle E_p$ (0.072 V). The reason of that the $E_{1/2}$ becomes a little positive maybe for that the large π-conjugation system of cinnamenyl makes the electro-withdrawing effect larger.

Figure 2 *In-situ* FTIR spectra of 5 mmol/L solutions



(a) FcH (E_S=0.5 V); (b) AFc (E_S=0.7 V); (c) FcCK(E_S=0.7 V) in 0.1 mol/L Bu_4NClO_4 /CH_3CN during oxidation process. (E_R=0V)

Figure 3 *In-situ* FTIR spectra of 5 mmol/L solutions



(a) FcH (E_R=0.5 V); (b) AFc (E_R=0.7 V); (c)FcCK (E_R=0.7 V) in 0.1 mol/L Bu_4NClO_4 /CH_3CN during reduction process. (E_S=0V)

In order to study the differences of redox pathways of FcH, AFc, FcCK, *in-situ* FTIR was used to confirm the interactions of the electrochemical process. Different FTIR spectra of FcH, AFc, and FcCK recorded during oxidation process in the spectral range of 2000–1000 cm^{-1} are shown in **Figure 2**. In the measurement of the FTIR spectra, E_R was set at 0V, where no oxidation of FcH, AFc, and FcCK had occurred. For FcH, the formations of two distinct peaks are observed at 1480 and 1418 cm^{-1} which can be ascribed to C-H stretching modes[10]. And these two peaks disappeared for AFc and FcCK because the C=O group affects the changes of C-H bond strength caused by oxidation of ferrocenyl. For AFc, the band of 1668 cm^{-1} is assigned to the C=O vibration[11], and it seems to have a dipolar character. Oxidation of AFc shifts the C=O bands from 1668 to 1700 cm^{-1}. And the FcCK spectrum shows three peaks at 1700,1658, 1608 cm^{-1}, which can be assigned to C=O vibration. The formation of these bands may be resulted from the extensive electron delocalization of cinnamenyl. Lastly, a pair of dipolar bands at around 1267 and 1280 cm^{-1} is clearly shown in the spectra of AFc and FcCK and these peaks can be assigned to C-H or O-H vibration[10].

From **Figure 3**, difference FTIR spectra of FcH, AFc, and FcCK recorded during the reduction process in the spectral range of 2000–1000 cm^{-1}, we can find the same position of peaks in **Figure 2** just with inversion. The spectra of the reduction process are consistent with that of the oxidation process which further confirms that the redox of these compounds is reversible process, and that agree with the results of electrochemical experiments.

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