

## Studies on in situ FTIR Spectra of Pentafluorobenzoic acid During Electrochemical Reaction Process

Fen Wang<sup>1,2</sup>, Lini Zhu<sup>1</sup>, Fang Wang<sup>3</sup>, Pu Yang<sup>1,a,\*</sup>, Yelin Jiang<sup>1,2</sup>,  
Guanjun Hou<sup>1,2</sup> and Suofei Ji<sup>1,2</sup>

<sup>1</sup>Anhui academy of agricultural sciences, Hefei 230031, China;

<sup>2</sup>Anhui Engineering Research Center for turtle Farming Technology, Bengbu 233701, China;

<sup>3</sup>Huzhou Center for Disease Control and Prevention, Huzhou 313000, China.

<sup>a</sup>kycyp@126.com

### Abstract

Cyclic voltammetry (CV) and in situ FTIR spectrometry were used to study the electrooxidation decarboxylation reaction of Pentafluorobenzoic acid (PFBA) in NaOH solution. The bond dissociation energy of C-COO and C4-F were employed to supply theoretical guidance. The results showed that the Pt electrode exhibited a high electrochemical activity for the electrooxidation reaction of PFBA in NaOH solution. PFBA radical was generated firstly after losing an electron, decarboxylation was occurred with HO· and COO was taken away from benzene ring in the form of CO<sub>2</sub>. Because of the strong electronegativity of F atom, the benzene ring didn't occur.

### Keywords

Pentafluorobenzoic acid, Electrochemical, In situ FTIR spectrometry, Bond Dissociation Energy.

### 1. Introduction

Pentafluorobenzoic acid (PFBA) has been extensively used for the synthesis of medicines and crucial catalyst during the manufacturing processes [1]. In alkali media, -COOH of PFBA is in the form of COO<sup>-</sup>, which is a stable functional group because of strong conjugation effect, and could remove from benzene ring as CO<sub>2</sub> [2], which means that PFBA could undertake decarboxylation reaction. There are five F atoms on the benzene ring of PFBA, which could be a representative mode to study the effect of the strong electron-withdrawing group on decarboxylation reaction. Electrochemical decarboxylation reaction has the advantages of little chemical reagents used and almost no environmental pollution generated. *In situ* FTIR spectroscopy is a useful technology, which could monitor the intermediates or products generated on the electrode surface [3,4]. In this manuscript, *In situ* FTIR spectroscopy was used to study the electrochemical decarboxylation reaction of PFBA.

### 2. Experimental section

#### 2.1 Materials

Pentafluorobenzoic acid (PFBA) (99% purity) from Aldrich Chemical Company was used without further purification. The pH of the solutions was adjusted using NaOH.

#### 2.2 Cyclic voltammetry and in situ FTIR experiments

All voltammetric measurements were tested with a standard three-electrode cell using a model 263 Potentiostat/Galvanostat (EG&G, USA). The platinum sheet (1.5 cm×2.0 cm) and a saturated calomel electrode (SCE) were used as the counter electrode and the reference one, respectively. All potentials were relative to that of SCE.

The electrochemical measurements were performed on a EG&G potentiostat/galvanostat 263A and the in situ FTIR spectra were obtained with a Nicolet 670 FTIR spectrometer equipped with MCT-A

detector cooled with liquid nitrogen. A spectroelectrochemical cell coupled to a  $\text{CaF}_2$  disk window ( $32 \text{ mm} \times 2 \text{ mm}$ ) was used for the in situ FTIR electro spectroscopic measurements. All normalized IR spectra obtained were calculated according to the formula:

$$\frac{\Delta R}{R} = \frac{[R(E_S) - R(E_R)]}{R(E_R)} \quad (1)$$

$R(E_S)$  and  $R(E_R)$  were the single-beam spectra of reflection measured at sample potential  $E_S$  and reference potential  $E_R$ , respectively [3,4]. According to Eq. (1), the negative-going bands indicated the gain of the intermediates or products in the thin layer solution, and positive-going bands indicated the consumption of reactants. Each spectrum corresponded to 200 interferometer scans taken at  $8 \text{ cm}^{-1}$  resolution and the polarization time was about 90 s.

### 2.3 Bond dissociation energy

DFT/B3LYP/6-31G(d) was carried out to calculate the energy and geometry optimization, which was confirmed by frequency calculations to ensure that each of the geometries corresponded to a minimum on the potential energy surface. Bond dissociation energy (BDE) was an important parameter in the study of reaction mechanism. The BDE values of C-COO and C4-F were calculated according to the expression (2) [5]. All the calculations were performed with the Gaussian03 package program.

$$\Delta H_{298}(A-B) = \Delta_f H_{298}(A\cdot) + \Delta_f H_{298}(B\cdot) - \Delta_f H_{298}(A-B) \quad (2)$$

$\Delta H$  represented the heats of formation of the respective species in the ideal gas state at 1Atm.

## 3. Results and discussion

### 3.1 cyclic voltammetry studies

Fig. 1 shows the cyclic voltammograms for the electrochemical reaction of 0.5 M PFBA on Pt electrode between 0 and 1.8 V with the scan rate of  $50 \text{ mV}\cdot\text{s}^{-1}$ . Except oxygen peak, no other peaks were observed in the blank solution. Oxygen reaction occurred at about 1.5 V, and the curve became unsmooth. It could be observed that there was a oxygen peak on Ag electrode at the potential more positive than 0.8 V, indicating that Pt possessed good electrocatalytic properties toward the electrochemical reaction of PFBA. There were no corresponding oxidation peaks of PFBA on the positive sweep, and the electrochemical reaction of PFBA was irreversible.

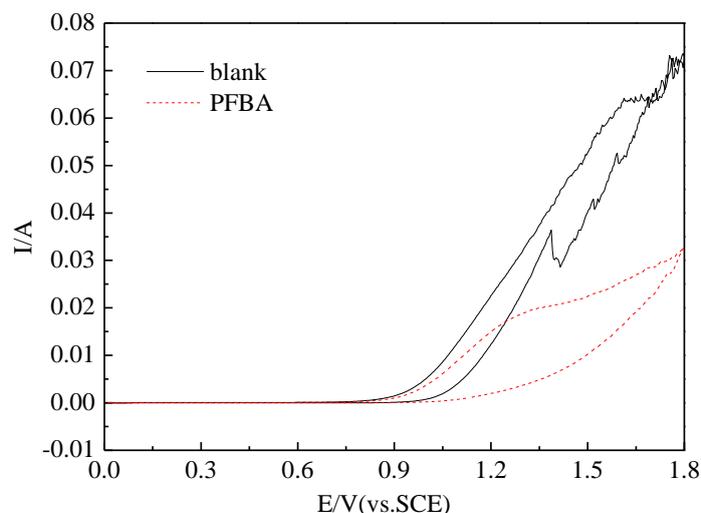


Fig.1 Cyclic voltammograms for the electrochemical reaction of PFBA on Pt electrode.

### 3.2 In situ FTIR studies

Fig. 2 shows *in situ* FTIR spectra obtained during electrochemical reaction of PFBA on Pt electrode. The reference potential was 0 mV, and the polarization time at each potential was about 90 s. As shown in Fig.1, no obvious peak was observed in Fig.1, so the Pt cathode was polarized from 700 to 2700 mV.

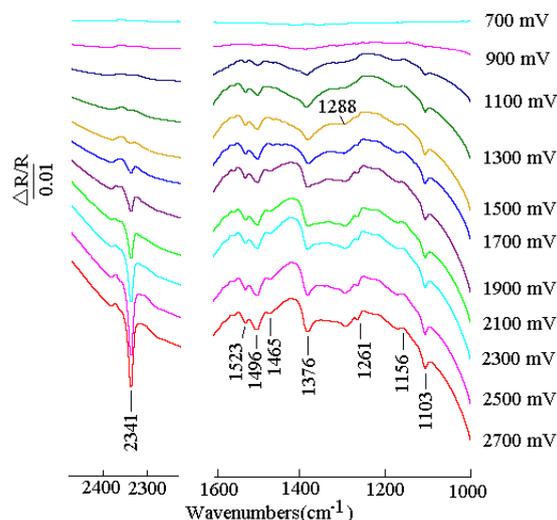


Fig.2 In situ FTIR spectra collected during electrooxidation reaction of BCBA on Pt electrode.

At approximately 1100 mV, the spectra were dominated by three characteristic negative-going bands at 1523, 1496, 1465, 1376 and 1103  $\text{cm}^{-1}$ , which were respectively attributed to stretching vibration of benzene ring, symmetric stretching vibration of carboxylate anion ( $\nu_s(\text{COO}^-)$ ) and ring breathing of PFBA [6,7,8]. As described in section 1.2, negative-going bands meant the gain of the intermediates or products in the thin layer solution, and the conclusion could be obtained that PFBA radical was got after an electron lost.

When the potential stepped to 1300 mV, the negative-going band located at 2341  $\text{cm}^{-1}$  was observed clearly, and was attributed to asymmetric stretching vibration of  $\text{CO}_2$ , which meant that C-COO was broken and COO was removed from the benzene ring in the form of  $\text{CO}_2$ . The presence of -COO substituting group has great effect on the bonding intensity between  $\alpha$ -C of benzene ring and carboxyl group. In addition, PFBA was in the form of negative ion in alkali media, which increase the increase the stability of carboxyl group. The above analysis could lead to the conclusion that electrochemical decarboxylation reaction of PFBA occurred at 1500 mV. An important positive-going band at 1288 and 1261  $\text{cm}^{-1}$  was observed at 1500 mV, which was assigned to stretching vibration of C-O, generated from C-O bond [6,9]. There are two possible paths of decarboxylation: (1) the electrochemical decarboxylation reaction occurred directly, and PFBA radical was gotten after C-COO band broken, which was reacted with  $\text{HO}\cdot$  immediately, new C-O band was generated. (2) the electrochemical decarboxylation reaction occurred by  $\text{HO}\cdot$  attacked.

In addition, with the potential shifting to more positive values, no new band was observed and no peak intensities increased but  $\text{CO}_2$ . The result showed that the electrochemical decarboxylation reaction was the main reaction, and the intermediates and products were absorbed on the electrode without diffusion in the thin layer [6].

Time-resolved FTIR (TR-FTIR) spectra collected as a function of time during electrochemical decarboxylation reaction of PFBA at 1500 mV are shown in Fig.3. The band related to  $\text{CO}_2$  appeared and the intensity increased with the time. This fact indicated that electrochemical decarboxylation reaction occurred at 1500 mV. It's worthy to mention that the band assigned to C-O stretching at 45 s, while the band related to  $\text{CO}_2$  appeared at 135 s. The observation suggested that the electrochemical decarboxylation reaction occurred by  $\text{OH}\cdot$  attacked (the path 2).

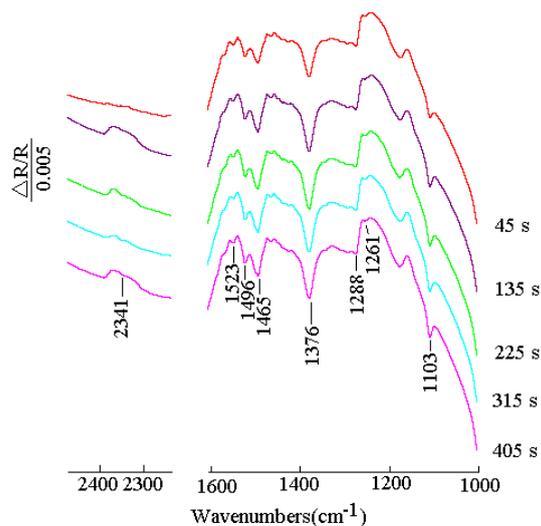


Fig.3 TR-FTIR spectra collected during electrochemical decarboxylation reaction of PFBA on Pt at 1500 mV.

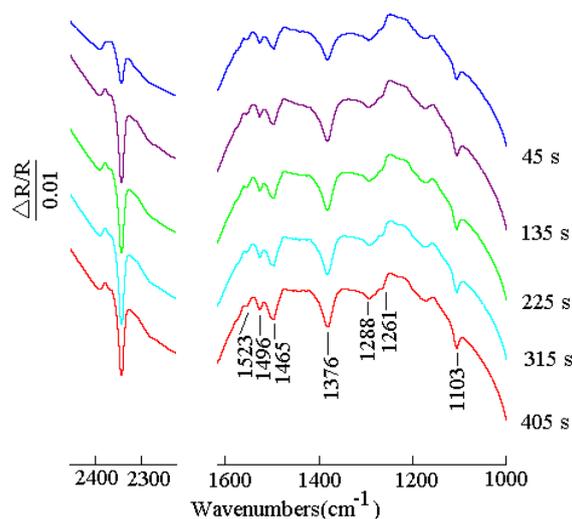


Fig.4 TR-FTIR spectra collected during electrochemical reaction of PFBA on Pt at 2700 mV.

Fig. 4 displayed TR-FTIR spectra collected during electrochemical reaction of PFBA on Pt at 2700 mV. The intensity of the band related to  $\text{CO}_2$  first increased then decreased with increase of the time. Decarboxylation reaction was fierce at 2700 mV with high  $\text{CO}_2$  generation. Then the amount of PFBA in the thin layer between Pt disk electrode and  $\text{CaF}_2$  decreased with time, so the intensity of the band related to  $\text{CO}_2$  decreased. The electrooxidation reaction of 3-bromobenzoic acid on Pt electrode was studied by Ma *et al* [10]. As compared with debromination reaction, the occurrence of decarboxylation in the first place during electrochemical degradation, that  $-\text{COO}$  were removed directly. At the end, some organic carboxylic acids generated after ring cleavage reaction occurred. But the similar bands related to organic carboxylic acids weren't observed in Fig.2, Fig.3 and Fig.4, which meant that the benzene ring cleavage reaction didn't occurred. In addition, the bands related to C-F weren't observed in the Figs, so the electrochemical defluorination reaction didn't occur.

### 3.3 Theoretical calculate

To verify the result of *in situ* FTIR, BDE values of C-COO and C4-F were calculated, which could predict the breaking sequence of bond [11]. According to the expression (2), the BDE values of C-COO and C-F ( $\text{X}=\text{Cl}, \text{Br}$ ) were got. As compared with C-COO bond, the BDE value of C-F was higher and the bond length was shorter. It's well known that the bigger BDE value, the more difficult the corresponding bond was to break, and C-COO ( $233.5 \text{ kJ mol}^{-1}$ ) was much easier to be eliminated than C-F ( $470.8 \text{ kJ mol}^{-1}$ ). The decarboxylation reaction is easier to carry out and the carboxyl group

is prior to remove from the benzene ring in the form of  $\text{CO}_2$ . This result coincided well with the results of *in situ* FTIR.

On the basis of *in situ* FTIR data and theoretical calculation, the pathway for electrochemical decarboxylation reaction of PFBA on Pt electrode is illustrated in Fig.5. One electron was removed from PFBA anion and the corresponding free radical was generated. The electrochemical decarboxylation reaction occurred by  $\text{HO}\cdot$ -attracted, and  $\text{COO}$  was removed from PFBA as  $\text{CO}_2$ , and pentafluorophenol were obtained.

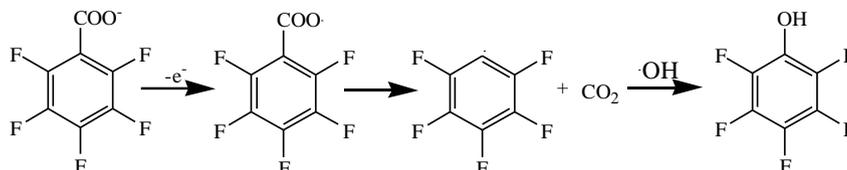


Fig.5 Mechanism of electrochemical decarboxylation reaction of PFBA on Pt electrode

#### 4. Conclusion

*In situ* FTIR spectroscopy is a critically important tool in monitoring the intermediate or product generated on the electrode surface, while BDE was an important parameter in the study of reaction mechanism. Pt electrode possessed electrocatalytic activity toward PFBA, but the benzene ring didn't cleave because of the strong electron-withdrawing effect of F. First of all, PFBA generated after an electron lost, then the electrochemical decarboxylation reaction occurred directly and  $\text{CO}_2$  was removed from PFBA, and pentafluorobenzene radical was got. At the end, pentafluorophenol was obtained after  $\text{HO}\cdot$  attracted. The electrochemical reaction of PFBA on Pt electrode couldn't be continue because of the strong electron-withdrawing effect of F.

#### Acknowledgements

This work is supported by Science and Technology Major Project of Anhui Province (16030701065); the International Science and Technology Cooperation Project of Anhui Province (1604b0602019); Academician Workstation (KR[2014]12); Achievement Demonstration Project of State Administration of Foreign Experts Affairs (Y20153400009) and National Spark Plan (2014GA 710011).

#### References

- [1] L. Ravichandran, K. Selvam, M. Swaminathan: Photo-Fenton Defluoridation of Pentafluorobenzoic Acid with UV-C Light, *Journal of Photochemistry and Photobiology A: Chemistry*. Vol. 188 (2007) NO.2, P.392-398.
- [2] J. Fu: Studies on Decarboxylation Reactions in High Temperature in Liquid Water. College of Chemical and Biological Engineering, Zhejiang University, (2011) (In Chinese)
- [3] G.A. Camara, R.B. de Lima, T. Iwasita: The Influence of PtRu Atomic Composition on the Yields of Ethanol Oxidation: A study by *in situ* FTIR Spectroscopy. *Journal of Electroanalytical Chemistry*, Vol. 585 (2005) No.1, p. 128-131.
- [4] Q. Wang, G.Q. Sun, L.H. Jiang, *et al*: Adsorption and Oxidation of Ethanol on Colloid-based Pt/C PtRu/C and Pt<sub>3</sub>Sn/C Catalysts: *in situ* FTIR Spectroscopy and on-line DEMS Studies. *Physical Chemistry Chemical Physics*, Vol.9 (2007) No.21, p. 2686-2696.
- [5] R. Walsh: Bond Dissociation Energy Values in Silicon-containing Compounds and Some of Their Implications. *Accounts of Chemical Research*, Vol. 14, (1981) p. 246-252.
- [6] R. Chetty, P.A. Christensen, B.T. Golding, *et al*: Fundamental and Applied Studies on the Electrochemical Hydrodehalogenation of Halogenated Phenols at a Palladised Titanium Electrode. *Applied Catalysis A: General*, Vol. 271 (2004) No. 1-2, p. 185-194.
- [7] R.D. Webster: *In situ* Electrochemical-ATR-FTIR Spectroscopic Studies on Solution Phase 2,4,6-tri-substituted Phenoxyl Radicals. *Electrochemistry Communications*, Vol.5 (2003) No.1, p. 6-11.

- 
- [8] N. Kumar, S. Thomas, R.B. Tokas, *et al*: Investigation on the adsorption characteristics of sodium benzoate and taurine on gold nanoparticle film by ATR-FTIR spectroscopy. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, Vol.118 (2014) p. 614-618.
- [9] R. Chetty, P.A. Christensen, B.T. Golding: In situ FTIR Studies on The Electrochemical Reduction of Halogenated Phenols. *Chemical Communication*, No.8 (2003) p. 984-985.
- [10] Y.W. Ye, X. Wang, W.F. Zheng *et al*: Electrooxidation Reaction of 3-Bromobenzoic Acid on Pt Electrode. *Acta Physico-Chimica Sinica*, Vol. 29 (2013) No.3, p. 553-558. (In Chinese)
- [11] J. Suegara, B.D. Lee, M.P. Espino *et al*: Photodegradation of Pentachlorophenol and its Degradation Pathways Predicted Using Density Functional Theory, *Chemosphere*, Vol. 61 (2005) p. 341-346.