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In situ FTIR studies on the electrochemical hydrodechlorination of 3,4,5,6-tetrachloropicolinic acid on Ag cathode

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ABSTRACT

The electrochemical hydrodechlorination reaction from starting material 3,4,5,6-tetrachloropicolinic acid (3,4,5,6-TCP) to the end product 3,6-dichloropicolinic acid (3,6-DCP) was investigated by cyclic voltammetry and in situ Fourier transform infrared spectroscopy (in situ FTIR). Compared with copper and glassy carbon, Ag cathode showed a high electrocatalytic activity for the irreversible reduction process of 3,4,5,6-TCP in NaOH aqueous solution. In situ FTIR results suggested that electrochemical hydrodechlorination took place in the 4- or 5-position of 3,4,5,6-TCP on Ag cathode after receiving an electron to get mixed trichloropicolinic acid free radical, which could receive another electron and give 3,5,6-trichloropicolinic acid (3,5,6-TCP) and 3,4,6-trichloropicolinic acid (3,4,6-TCP) at the potential more positive than −1000 mV afterwards. Finally, 3,5,6-TCP and 3,4,6-TCP were further dechlorinated to produce 3,6-dichloropicolinic acid (3,6-DCP) at the potential more negative than −1000 mV. Further studies of preparative electrolysis experiments by constant current electrolysis were carried out. The results were in good agreement with those from in situ FTIR investigations.

1. Introduction

With high biological activity and low toxicity, heteroaromatic compounds containing nitrogen atoms often play important roles as the scaffolds of bioactive substances [1–3]. Pyridine-monocarboxylic acids are one of the most popular intermediates for the synthesis of pharmaceutical and agrochemical products [4,5]. Among them, 3,6-dichloropicolinic acid (3,6-DCP) is proved to be a highly active plant growth regulator and selective herbicide. Not only has the 3,6-DCP a low toxicity to mammals, fish and birds, but it is relatively short lived in soil [6,7].

The common methods to prepare 3,6-DCP are acid hydrolysis with the starting material 3,6-dichloro-2-(trichloromethyl)pyridine in sulfuric acid or nitric acid [8], and chemical dechlorination reduction with starting material 3,5,6-trichloro-4-hydrazino picolinic acid by excess hydrazine hydrate in alkaline aqueous solution [9]. However, the process cost of the former is relatively high, and the latter shows low yield and poor quality. Due to low cost, high yield, good quality and low environmental contamination, the preparation method from 3,4,5,6-tetrachloropicolinic acid (3,4,5,6-TCP) to 3,6-DCP by electrochemical hydrodechlorination has attracted more and more attentions recently [10–12]. However, to the best of our knowledge, there are only a few reports about the electrochemical hydrodechlorination mechanism of 3,4,5,6-TCP to 3,6-DCP so far.

The present contribution aims to investigate the electrochemical hydrodechlorination reaction mechanism of 3,4,5,6-TCP in NaOH aqueous solution at the molecular level by means of a powerful technique such as in situ FTIR spectroscopy [13,14]. In addition, preparative electrolysis experiments using constant current electrolysis have been carried out, and high performance liquid chromatography method is applied to detect the intermediates during electrochemical hydrodechlorination reaction.

2. Experimental

All reagents were of analytical reagent grade and used as received. All solutions were prepared using Millipore-Q water. The experiments were carried out at room temperature.

Cyclic voltammetry measurements were performed using EG&G potentiostat/galvanostat Model 263A. The electrochemical hydrodechlorination reaction from 3,4,5,6-TCP to 3,6-DCP was carried out in 0.1 M NaOH solution containing 0.05 M 3,4,5,6-TCP by cyclic voltammetry between −0.6 and −1.4 V at a scan rate of 50 mV s^{-1}. Ag plate, copper plate and glassy carbon (GC) with the geometric area of 0.2 cm^2 were used as the working electrodes respectively. A saturated calomel electrode (SCE) was used as the

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reference electrode, and a platinum sheet (1 cm × 1 cm) as the counter electrode.

In situ FTIR spectroscopic experiments were performed on a Nicolet 670 FTIR spectrometer equipped with a MCT-A detector cooled with liquid nitrogen. The spectroelectrochemical cell was provided with CaF_2 disk window (diameter 32 mm and thickness 2 mm). The interferograms were acquired with the working electrode surface pressed against the CaF_2 disk window. The resulting spectra recorded were defined as the potential-difference spectra, and were calculated by the following formula [14]:

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

In the formula, $R(E_R)$ represents single-beam spectrum collected at the reference potential and $R(E_S)$ at the sample potential. Two hundred interferograms were collected and co-added into a single-beam spectrum. The spectral resolution was set at 8 cm^{-1}.

Preparative electrolysis experiments were performed in a two-compartment cell, divided by a Nafion membrane, assembled with magnetic stirring bar. The cathode was a Ag plate (2 cm × 3 cm × 0.05 cm) and a platinum sheet (2 cm × 3 cm × 0.05 cm) was used as the anode to provide a harmless count reaction. The electrolysis experiments were performed on Model 263A potentiostat/galvanostat in 0.5 M NaOH solution containing 0.05 M 3,4,5,6-tetrachloropiclinic acid by galvanostatic mode with the constant current 0.5 mA. The composition variation of the electrolytic processes was monitored by Waters high performance liquid chromatography (HPLC) system equipped with a symmetry column and a Waters 2996 Photodiode Array Detector.

3. Results and discussion

3.1. Cyclic voltammetry behavior of 3,4,5,6-TCP

Since the electrode material can affect electrochemical reactions, the electrochemical hydrodechlorination reaction has been carried out on three different electrodes. Cyclic voltammograms for the electrochemical reduction of 3,4,5,6-TCP in NaOH solution on Ag, Cu and GC electrodes respectively are shown in Fig. 1. On Ag cathode, a characteristic irreversible reduction current peak for 3,4,5,6-TCP reduction at about −1.1 V (*vs* SCE) can be obviously observed from Fig. 1, which shows that the electrochemical reduction of 3,4,5,6-TCP took place on Ag cathode. However, under the similar conditions, no corresponding current peaks for the cathodic process of 3,4,5,6-TCP are observed on Cu or GC electrode, though Cu and GC electrodes are common cathodes for electroreduction reaction. The electrocatalytic activity of Ag for electrocatalytic reduction of 3,4,5,6-TCP in NaOH solution is highest as compared with Cu and GC electrodes, and thus is chose as the cathode for electrochemical hydrodechlorination reaction of 3,4,5,6-TCP in the following investigations.

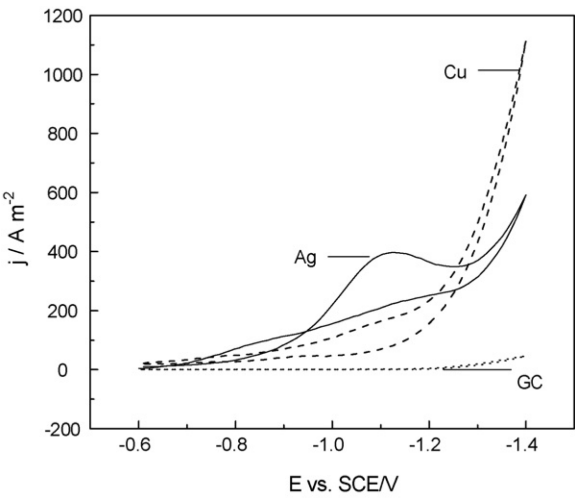


Fig. 1. Cyclic voltammograms for the electrochemical hydrodechlorination reaction of 0.05 M 3,4,5,6-TCP in 0.1 M NaOH at Ag, Cu and GC electrodes at the scan rate of 50 mV s^{-1}.

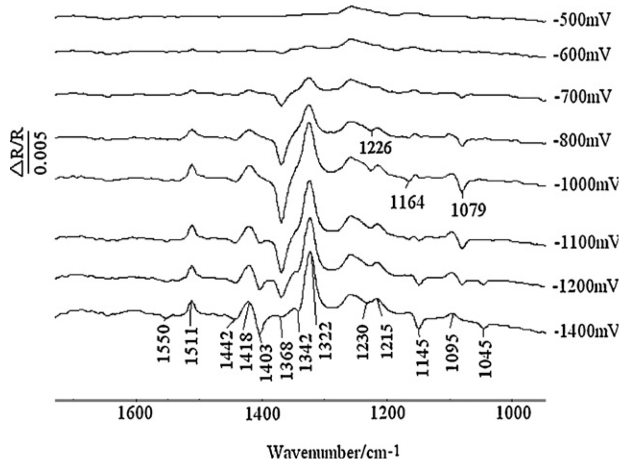


Fig. 2. In situ FTIR spectra collected during electrochemical hydrodechlorination reaction of 3,4,5,6-TCP on Ag cathode. The sample potential was stepped from −500 to −1400 mV and the reference potential was 0 V. The spectral resolution was set at 8 cm^{-1}.

3.2. In situ FTIR spectroscopic study

In alkaline solution, 3,4,5,6-TCP exists in the form of its corresponding base salt and adsorbed on the surface of Ag cathode. Fig. 2 shows a set of in situ FTIR spectra obtained during electrochemical hydrodechlorination reaction of 3,4,5,6-TCP on Ag cathode in alkaline solution. Firstly the reference spectrum is acquired at 0 mV, then the Ag cathode is polarized from −500 to −1400 mV and the sample spectra are collected. The polarization time at each potential is about 90 s. The spectra in Fig. 2 display three characteristic positive-going bands at 1511, 1418 and 1322 cm^{-1}, which are assigned to the C=C stretching vibration and C–N stretching vibration of 3,4,5,6-TCP [13,15,16]. Another important positive-going band at about 1095 cm^{-1} is related to the C–Cl stretching vibration of 3,4,5,6-TCP [17,18]. Table 1 summarizes the assignments of the peak frequencies observed for all the positive-going and negative-going bands. When the sample potentials are more positive than

Table 1
Assignments of all the positive-going and negative-going bands.

Band	Frequency/cm^{-1}	Assignments
Positive-going	1511, 1418	C=C stretching of 3,4,5,6-TCP
	1322	C–N stretching of 3,4,5,6-TCP
	1215	C–O stretching of 3,4,5,6-TCP
	1095	C–Cl stretching of 3,4,5,6-TCP
Negative-going	1368	C–N stretching of 3,5,6-TCP or 3,4,6-TCP
	1079	C–Cl stretching of 3,5,6-TCP or 3,4,6-TCP
	1226	C–O stretching of 3,5,6-TCP or 3,4,6-TCP
	1164	C–H in plane bending of 3,5,6-TCP or 3,4,6-TCP
	1403	C–N stretching of 3,6-DCP
	1045	C–Cl stretching of 3,6-DCP
	1550, 1442	C=C stretching of 3,6-DCP
	1230	C–O stretching of 3,6-DCP
	1145	C–H in plane bending of 3,6-DCP

−600 mV, no obvious changes can be observed on the FTIR spectra. It indicates that the electrochemical hydrodechlorination of 3,4,5,6-TCP on Ag cathode is quite slow. When it steps to more negative potential, the intensities of all the bands increase, thus showing the consume of 3,4,5,6-TCP and the progress of electrochemical hydrodehalogenation with the applied potentials.

During the reduction of 3,4,5,6-TCP at potentials of −500 and −1000 mV, two negative-going bands are observed. Bands at 1164 and 1079 cm^{-1} are related to C–H in plane bending and C–Cl stretching of 3,4,6- or 3,5,6-TCP [18,19], and the peak intensities increase with the potential shifting to more negative values. With the dechlorination of picolinic acid, the wavenumber of C–O the stretching vibration shifts slightly from 1215 to 1226 cm^{-1}, and thus a positive-going band at 1215 cm^{-1} and a negative-going band at 1226 cm^{-1} are observed. Heterocyclic aromatic ring is easier to receive electron to form radical-anion on the ring rather than on the chlorine atom [20]. In addition, on the basis of the inductive effect of the adjacent electronegative nitrogen atom, chloride in 4- or 5-position of 3,4,5,6-TCP is more active and easier to be reduced than those in 3- and 6-position [21]. Therefore, the chlorine atom in 4- or 5-position on carbon atom drops out selectively and is replaced with the hydrogen to give 3,5,6-trichloropicolinic acid (3,5,6-TCP) or 3,4,6-trichloropicolinic acid (3,4,6-TCP). At the same time, there are no other positive-going bands at 1615–1545 and 1420–1300 cm^{-1}, which suggest that no decarboxylation reaction occurs to 3,4,5,6-TCP [13,22].

However, at potentials more negative than −1000 mV, the two peak intensities at 1164 and 1079 cm^{-1} decrease and two negative-going bands at about 1403 and 1230 cm^{-1} emerges, which are assigned to the C–N and C–O stretching vibration of 3,6-DCP. In addition, three characteristic negative-going bands at about 1550, 1145 and 1045 cm^{-1} can be observed, which are assigned to C=C stretching vibration, C–H in plane bending and C–Cl stretching of 3,6-DCP [17]. Their intensities increase with the potential shifting to more negative values. It shows that both the 4- and 5-position of 3,4,5,6-TCP are replaced with a hydrogen to generate the end product 3,6-DCP.

In order to observe the reaction more carefully, time-resolved FTIR (TR-FTIR) spectra are collected during electroreduction of 3,4,5,6-TCP on Ag cathode. Fig. 3 shows plots of the intensities of the various features observed at −700 mV as a function of time. From the Fig. 3, one can see that the positive-going bands at 1151, 1418, 1322 and 1095 cm^{-1} related to 3,4,5,6-TCP increase with the time. The negative-going bands at 1442, 1368, 1164 and 1079 cm^{-1} related to 3,5,6- or 3,4,6-trichloropicolinic acid increase with the time too. It indicated that at −700 mV, the main electrochemical hydrodehalogenation reaction is from 3,4,5,6-TCP to form 3,5,6- or 3,4,6-trichloropicolinic acid.

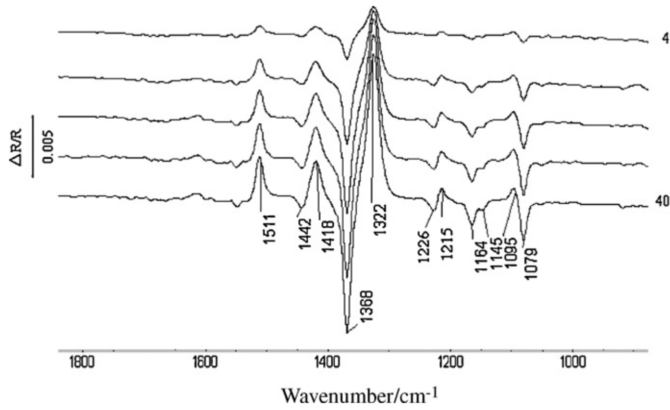


Fig. 3. TR-FTIR spectra collected during electrochemical hydrodehalogenation reaction of 3,4,5,6-TCP on Ag cathode at −700 mV. The reference potential was 0 V. The spectral resolution was set at 8 cm^{-1}.

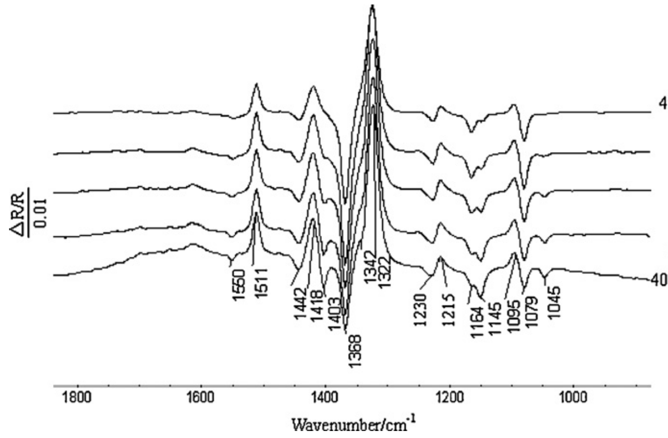
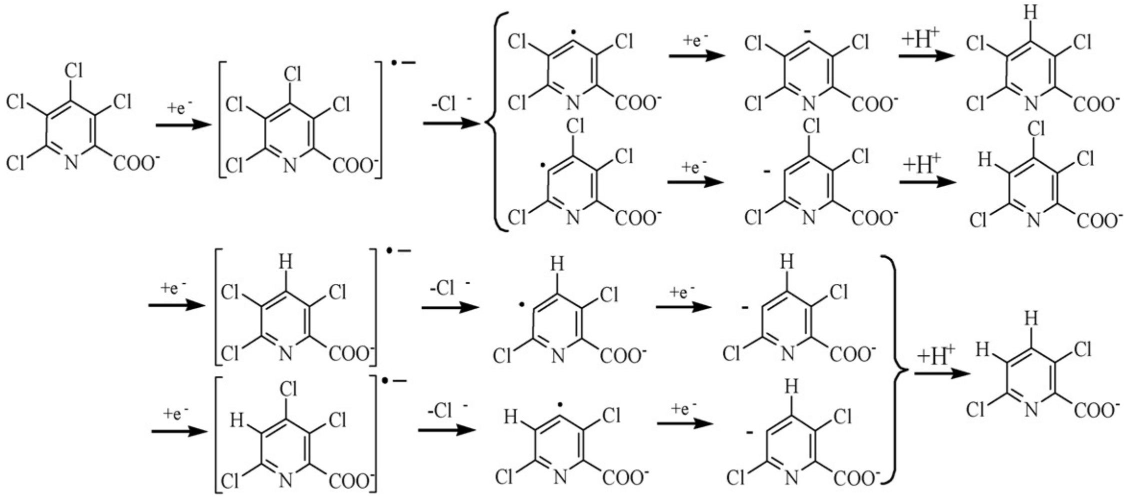


Fig. 4. TR-FTIR spectra collected during electrochemical hydrodehalogenation reaction of 3,4,5,6-TCP on Ag cathode at −1100 mV. The reference potential was 0 V. The spectral resolution was set at 8 cm^{-1}.

Fig. 4 displays time-resolved FTIR spectra collected during electroreduction of 3,4,5,6-TCP on Ag cathode at −1100 mV. In Fig. 4, the negative-going bands at 1550, 1403, 1342 and 1045 cm^{-1} can



Scheme 1. Electrochemical hydrodechlorination reaction mechanism of 3,4,5,6-TCP on Ag cathode.

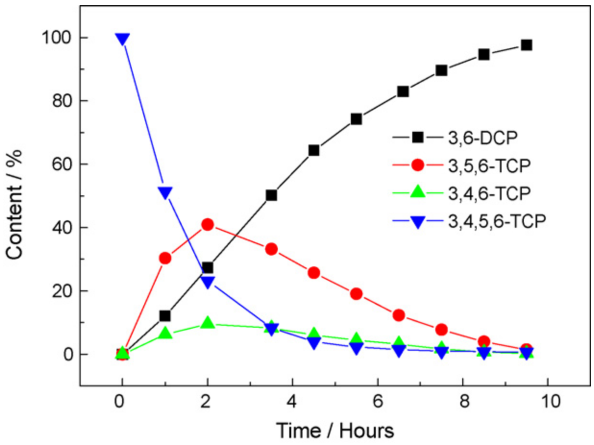


Fig. 5. Constant current electrolysis of 3,4,5,6-TCP on the silver electrode, electrolyte: 300 mL 0.5 M NaOH solution containing 0.05 M 3,4,5,6-tetrachloropiclinic acid, electrolyte temperature: 298 K, current efficiency: 0.83 A/m^2.

be seen clearly. Their intensities increase with time. It indicates that 3,4,5,6-TCP is electroreduced to 3,6-DCP at −1100 mV by electrochemical hydrodechlorination.

From the above integrating analysis, the possible electroreduction mechanism of 3,4,5,6-TCP on Ag cathode is shown in Scheme 1. Firstly 3,4,5,6-TCP receives an electron to form 3,4,5,6-TCP radical-anion, which can lose a chlorine ion in the 4- or 5-position respectively to form trichloropicolinic acid free radical. Then the free radical receives a proton to give 3,5,6-TCP and 3,4,6-TCP. Finally, with the potential shifting to more negative values, 3,5,6-TCP and 3,4,6-TCP were further dechlorinated to generate the end product 3,6-DCP.

3.3. Preparative electrolysis experiments

In order to demonstrate the electrochemical hydrodechlorination reaction mechanism of 3,4,5,6-TCP, preparative electrolysis experiments are carried out in NaOH solution containing 3,4,5,6-tetrachloropiclinic acid at the room temperature with the constant current 0.5 mA. The reaction is monitored and analyzed by high performance liquid chromatography. It is found that the main intermediate product is 3,5,6-TCP with a small amount of 3,4,6-TCP, and the end product is 3,6-DCP. The products distribution with time is shown in Fig. 5. These results from preparative electrolysis experiments are accordant with those from in situ FTIR study.

4. Conclusions

The in situ FTIR characterization method allows to obtain vibrational information from very small amounts of material, and then to obtain the direct spectroscopic information of the intermediates and monitor the species of intermediate or product generated on the electrode surface. It was used to analyse the electrochemical hydrodechlorination reaction mechanism of 3,4,5,6-TCP in 0.1 M NaOH aqueous solution on Ag cathode for the first time.

Firstly electrochemical hydrodechlorination reaction took place in the 4- or 5-position of 3,4,5,6-TCP on Ag cathode to get mixed trichloropicolinic acid free radical. Then the mixed trichloropicolinic acid free radical received another electron and gave 3,5,6-TCP and 3,4,6-TCP at the potential more positive than −1000 mV. Finally, with the potential shifting to more negative values, 3,5,6-TCP and 3,4,6-TCP took off another chlorine ion to achieve 3,6-DCP as the end product. The results were in good agreement between the in situ FTIR measurements and constant current electrolysis.

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