Fixation of CO$_2$ along with bromopyridines on a silver electrode

Yingtian Zhang$^1$, Shuxian Yu$^1$, Peipei Luo$^1$, Shisong Xu$^1$, Xianxi Zhang$^1$, Huawei Zhou$^1$, Jiyuan Du$^1$, Jie Yang$^1$, Nana Xin$^1$, Yuxia Kong$^1$, Junhai Liu$^1$, Baoli Chen$^1$ and Jiaxing Lu$^2$

$^1$Shandong Provincial Key Laboratory of Chemical Energy Storage and Novel Cell Technology, School of Chemistry and Chemical Engineering, Liaocheng University, Liaocheng 252059, People’s Republic of China

$^2$Shanghai Key Laboratory of Green Chemistry and Chemical Processes, School of Chemistry and Molecular Engineering, East China Normal University, Shanghai 200062, People’s Republic of China

HZ, 0000-0002-9428-5400; BC, 0000-0001-7462-5845

Resulting from the drastic increase of atmospheric CO$_2$ concentration day by day, global warming has become a serious environmental issue nowadays. The fixation of CO$_2$ to obtain desirable, economically competitive chemicals has recently received considerable attention. This work investigates the fixation of CO$_2$ along with three bromopyridines via a facile electrochemical method using a silver cathode to synthesize picolinic acids, which are important industrial and fine chemicals. Cyclic voltammetry is employed to investigate the cyclic voltammetric behaviour of bromopyridines. In addition, systematic study is conducted to study the relationships between the picolinic acids’ yield and the electrolysis conditions and intrinsic parameters. The results show that the target picolinic acids’ yields are strongly dependent on various conditions such as solvent, supporting electrolyte, current density, cathode material, charge passed, temperature and the nature of the substrates. Moreover, in the studied electrode materials such as Ag, Ni, Ti, Pt and GC, electrolysis and cyclic voltammetry show that Ag has a good electrocatalytic effect on the reduction and carboxylation of bromopyridine. This facile electrochemical route for fixation of CO$_2$ provides an indispensable reference for the conversion and utilization of CO$_2$ under mild conditions.

1. Introduction

Nowadays, the sustainable development of society and its related ecological environment, resources and economy have become the...
focus of the international community. But, global warming has been becoming a serious environmental problem due to the increasing concentration of atmospheric CO$_2$, and hence how to effectively convert CO$_2$ has become an urgent problem for chemists [1–5].

In contrast to toxic carbon monoxide and phosgene, CO$_2$ is a renewable and environmentally friendly C1-organic building block [6–9]. However, owing to the intrinsic high thermodynamic stability of CO$_2$, the facile reduction of CO$_2$ has always been a challenge. Fortunately, electrochemical technology can reduce CO$_2$ at normal temperature and atmospheric pressure [10–13]. So far, a lot of attention has been drawn to the study of the fixation of CO$_2$ along with various substrates including epoxides [14], alcohols [15], imines [16–19], ketones [16–19], alkenes [20,21], dienes [22–24], alkynes [25] and halides [26–29]. In addition, electroreduction of organic halides is an extremely facile method to generate active anions which can readily activate CO$_2$ to ensure that a carboxylic functional group is introduced into the organic centre while leaving intact the original carbon skeleton. That is why much attention is drawn to the study of the electrocarboxylation of organic halides [30–33]. Furthermore, some of these reaction pathways are particularly important for producing fine chemicals such as anti-inflammatory drugs. Catalytic systems based on transition-metal complexes, such as nickel [34], palladium [35] and cobalt complexes [36], have been proposed to increase the yield of the corresponding carboxylic acid. Electrode material with excellent catalytic properties can effectively improve the reaction, so mercury was once the preferred electrode material. However, it is now abandoned for being unfriendly to the environment. At present, the silver (Ag) electrode has been recognized as a useful catalyst for the electroreduction of organic halides [27,28,37–39]. Moreover, although electrocarboxylation with regard to organic halides has gained popularity in recent times, only a small number of reports involve the electrochemical reduction of heterocyclic halides along with CO$_2$ [40]. Electrochemical carboxylation of heterocyclic halides is one of the most useful methods for obtaining heterocyclic carboxylic acids, which are a class of important compounds, and some of them are of meaning to the industry of fine chemicals such as anti-inflammatory drugs [41–43]. From the perspective of applications, high yields will greatly reduce production costs. To make the electrolysis of heterocyclic carboxylic acid industrially and commercially feasible, it is necessary to develop a low-cost, environmentally friendly, high-yield synthetic route.

In this paper, we study the electrosynthesis of picolinic acids (2) from three bromopyridines (1a, 1b, 1c) and CO$_2$ on Ag electrodes (scheme 1). To optimize the yield of 2, on the one hand, the influence of a series of synthesis conditions on the electrocarboxylation of 1a is investigated; on the other hand, the influence of the position of C–Br bond on the pyridine ring on the electrocarboxylation of 1, which has not been reported previously, is the other major focus of our research. This study is to establish a facile electrochemical method for introducing CO$_2$ into 1 using Ag as a cathode to yield 2 under mild conditions, providing a more effective and environmentally friendly method for the fixation of CO$_2$.  

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**Scheme 1.** The Schematic diagram of electrocarboxylation of bromopyridines.
2. Experimental

2.1. Chemicals

Ortho-bromopyridine (1a) and meta-bromopyridine (1b) are commercially obtained from J&K. para-bromopyridine (1c) is commercially available from Shanghai Lanke Medical Technology. Acetonitrile (MeCN) and N,N-dimethylformamide (DMF), which are kept over 4 Å molecular sieves, are commercially obtained from Sinopharm Chemical. All other reagents are used without extra processing.

2.2. Product measurement

Cyclic voltammograms are recorded using a CHI 760E. Galvanostatic electrolysis is carried out using a DC-regulated power supply HY5003M equipped with a one-compartment electrochemical cell. The electrocarboxylation product yields based on the starting substrate are determined by high-performance liquid chromatography (HPLC) (Waters 505 pump) connected to a UV detector (Waters 2489) and a CenturySIL C18-EPS column.

2.3. Typical electroanalytical procedure

A typical electroanalytical experiment is carried out in 10 ml DMF with 0.1 M tetraethylammonium tetrafluoroborate (TEABF₄) at 25°C in a one-compartment three-electrode electrochemical cell, along with glassy carbon (GC, diameter = 2 mm) or Ag (diameter = 2 mm) as a working electrode, Ag/AgI/0.1 M TBAI in DMF as a reference electrode and platinum spiral as an auxiliary electrode. All experiments are carried out at atmospheric pressure.

2.4. Typical electrosynthesis procedure

A typical galvanostatic electrolysis is performed in 10 ml of MeCN or DMF solution with 0.1 M supporting electrolyte and 0.1 M 1 in a one-compartment electrochemical cell, along with a sacrificial magnesium rod (Mg) anode and one of these cathodes: Ag (8 cm²) or Pt (4 cm²), Ni (8 cm²), GC (4 cm²), Ti (8 cm²). The system is always saturated with CO₂ during the electrolysis process. After a certain amount of charge is passed through the cell, the current is switched off. At the end of the electrolysis, the solvent is distilled off in vacuo. The residue is hydrolysed in a mixture (24/76, v/v) of MeCN and a NaH₂PO₄/Na₂HPO₄ buffer at pH 6. Then the yields of 2 are determined by HPLC after appropriate dilution with the detection wavelength of 265 nm, and the eluent is a mixture (12/88, v/v) of MeCN and a NaH₂PO₄/Na₂HPO₄ buffer at pH 6.

3. Results and discussion

3.1. Electroanalytical measurements of ortho-bromopyridine

Cyclic voltammograms for reduction of ortho-bromopyridine (1a) on a GC electrode in DMF with 0.1 M TEABF₄ are depicted in figure 1. As shown in curve a of Figure 1, electroreduction of 1a causes a single irreversible cathodic peak at −1.55 V in the region of −0.5 to −2.0 V under a N₂ atmosphere with a scan rate of 0.1 V s⁻¹, which corresponds to a two-electron reduction of the C–Br bond. The synthesis of pyridine, which is detected by gas chromatography–mass spectrometry (GC–MS), via potentiostatic electrolysis at −1.55 V under a N₂ atmosphere, also confirms the result. In addition, the reduction peak currents are proportional to v¹/₂ (electronic supplementary material, figure S1), indicating that the electroreduction process is diffusion-controlled. When the CO₂ is piped into the system (0.2 M) [44], different behaviour is observed (figure 1, curve b). The reduction peak potential moves more positively and the current increases, indicating that there is a rapid chemical reaction between the electroreduced intermediate and CO₂.

3.2. Preparative scale electrolysis

1a as a model molecule is first chosen to study the electrocarboxylation of 1 with a one-compartment electrochemical cell (scheme 2). A series of electrolytic reactions have been carried out to study the
3.2.1. Effect of solvent, supporting electrolyte and current density

Electrosynthesis is often influenced by the solvents [45]. In this paper, we investigate the electrosynthesis of \( \text{1a} \) in a solvent of MeCN or DMF in order to study the effect of the solvents. As shown in table 1 (entries 1–4), \( \text{2a} \)'s yield in DMF is much higher than that in MeCN, despite the higher solubility of CO\(_2\) in MeCN [44]. Generally speaking, the electroreduction of aromatic bromides in protic media is likely to go through a reductive hydrogenation pathway [46]. The result that pyridine is detected by GC–MS via potentiostatic electrolysis at \(-1.55\) V under a N\(_2\) atmosphere (in §3.1) indicates that the intermediate that resulted from two-electron reduction of \( \text{1a} \) would go through a hydrogenation step described in scheme 3 in the process of the reduction of \( \text{1a} \) just as the electroreduction of aromatic bromides in protic solvent, and yet scheme 3 is the competitive reaction of the carboxylation reaction described in scheme 2. When compared with DMF, MeCN is a more powerful proton donor [18,41], so it is more beneficial to the formation of the corresponding hydrogenated product than DMF during the reaction according to scheme 3. Besides, to further investigate the effect of a proton donor on the electrocarboxylation reaction, a certain amount of water is deliberately added into the system (entry 5). As shown in table 1 (entry 2 and entry 5), \( \text{2a} \)'s yield decreases from 55.0% to 20.6% when 0.1 M water is added into the system, which indicates that a proton donor has a greater impact on the reaction. In addition, DMF is a better solvent than acetonitrile, and it facilitates the dissolution of the products. In the electrolysis process, we observe that the DMF electrolyte is generally a transparent and clear liquid, while the MeCN electrolyte is turbid. In general, turbid electrolytes can affect the mass transfer process of the system, and then affect the electrocarboxylation reaction here. Moreover, we also observe that some undissolved substances are attached to the electrode surface in the electrolysis process and the electrolysis voltage is higher when MeCN is used as a solvent in the experiment, and these two phenomena are either detrimental to the reaction or are detrimental to energy use. Therefore, combining the electrolysis results and the solubility limit of reagent or product, the most suitable solvent in this study is DMF.

Next, we study the effect of the supporting electrolyte on the reaction. The results are summarized in table 1 (entries 2, 4, 6–10). The best supporting electrolyte is tetrabutylammonium bromide (TBA\( \text{Br} \)) with 55.0% electrocarboxylation yield. It is notable that with the same anion of Cl\(^{-}\), Br\(^{-}\), I\(^{-}\), respectively,
the electrolysis concerning the TBA$^+$ cation gives higher carboxylation yield than that involved with TEA$^+$ (table 1, entries 2, 4, 6–9), showing that the cations may impact the synthesis. It is known that protonation of $\text{o}$-bromopyridine described in scheme 3 is the competitive reaction of the carboxylation of $\text{o}$-bromopyridine described in scheme 2. In fact, the tetraalkylammonium cation (TRA$^+$) can act as a proton donor strongly depending on the length of the alkyl chain via Hoffman elimination [47,48], and the TEA$^+$ cation is a much better proton donor than the TBA$^+$ cation [49]. So, when tetraethylammonium (TEA$^+$) salt acts as a supporting electrolyte, it is more beneficial to the formation of the corresponding hydrogenated product than tetrabutylammonium (TBA$^+$) salt during the reaction. For that reason, the electrocarboxylation process reported here gives higher picolinic acid yields in the presence of the TBA$^+$ cation than the TEA$^+$ cation (table 1, entries 2, 4, 6–9). In addition, in the same TRA$^+$ cases, the carboxylation yield decreases in the following sequence: \( \text{Br}^- > \text{I}^- > \text{Cl}^- \) (table 1, entries 2, 4, 6–9).

The current density affects the reaction. Higher or lower current densities lead to lower electrocarboxylation yield owing to the significant contribution from the undesired Faradaic process. As shown from the results summarized in entry 2 and entries 11–16 of table 1, with the increase of current density from 4 to 9 mA cm$^{-2}$, the yield is increased from 49.0% to 59.0%; but the electrocarboxylation yield declines when the current density is raised over 9 mA cm$^{-2}$.

### 3.2.2. Effect of cathode material, charge passed and temperature

The nature of cathode material also strongly affects the reaction. As shown from the results in table 2 (entries 1–5), the best cathode material is Ag with 59.0% electrocarboxylation yield (table 2, entry 1). Table 2 (entries 1–5) also shows that the yields decrease according to the cathode materials in the

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**Scheme 3.** Electroreduction of $\text{o}$-bromopyridine with a hydrogen source.

**Table 1.** Effect of solvent, supporting electrolyte and current density on the fixation of CO$_2$ along with $\text{o}$-bromopyridine.$^a$

| entry | solvent | supporting electrolyte | current density (mA cm$^{-2}$) | yield$^c$ of 2a (%) |
|-------|---------|------------------------|---------------------------------|--------------------|
| 1     | MeCN    | TBABr                  | 8                              | 16.4               |
| 2     | DMF     | TBABr                  | 8                              | 55.0               |
| 3     | MeCN    | TEABr                  | 8                              | 13.6               |
| 4     | DMF     | TEABr                  | 8                              | 46.2               |
| 5     | DMF$^b$ | TBABr                  | 8                              | 20.6               |
| 6     | DMF     | TBACI                  | 8                              | 49.6               |
| 7     | DMF     | TBAI                   | 8                              | 50.8               |
| 8     | DMF     | TEACl                  | 8                              | 36.6               |
| 9     | DMF     | TEAI                   | 8                              | 38.6               |
| 10    | DMF     | TEABF$_4$              | 8                              | 41.4               |
| 11    | DMF     | TBABr                  | 4                              | 49.0               |
| 12    | DMF     | TBABr                  | 6                              | 50.6               |
| 13    | DMF     | TBABr                  | 9                              | 59.0               |
| 14    | DMF     | TBABr                  | 10                             | 55.6               |
| 15    | DMF     | TBABr                  | 12                             | 48.2               |
| 16    | DMF     | TBABr                  | 16                             | 42.6               |

$^a$Electrolytic conditions: 10 ml of solvent, 0.1 M supporting electrolyte concentration, 0.1 M $\text{o}$-bromopyridine, Ag cathode, Mg anode, 0°C, 2 F mol$^{-1}$ charge passed, 1 atm CO$_2$.

$^b$0.1 M water is added to the system.

$^c$The yield calculated with respect to the starting substrate is determined by HPLC.
following sequence: Ag (59.0%) > Pt (36.2%) > Ni (30.4%) > GC (18.6%) > Ti (10.2%). The yields are related to the reduction potentials of 1a on the electrodes used: Ag (−1.19 V, curve a of figure 2) > Pt (−1.29 V, curve b of figure 2) > Ni (−1.45 V, curve c of figure 2) > GC (−1.55 V, curve d of figure 2) > Ti (−1.84 V, curve e of figure 2). Both electrolysis and cyclic voltammetry indicate that Ag displays outstanding electrocatalytic activities with regard to the reduction and carboxylation of 1a.

Then the effect of the charge passed is discussed. The results are presented in table 2 (entries 1, 6–9). When the charge passed is increased from 1.0 to 2.0 F mol$^{-1}$, the electrocarboxylation yield increases linearly; however, the yield decreases when the charge passed is raised over 2.0 F mol$^{-1}$. Therefore, the best choice is 2.0 F mol$^{-1}$ of 1a.

The influence of the temperature is also complicated. In general, the temperature affects the solubility of CO$_2$ in the solvent, as well as the nature of the thermodynamics and kinetics of carboxylation. On the one hand, decreasing the temperature will increase the solubility of CO$_2$ in the solvent [44]; on the other hand, decreasing the temperature may decrease the activity of the reactants. To study the influence of temperature, electrolysis is performed at diverse temperatures. The results are given in table 2 (entries 1, 10–12). When the temperature is raised from −5°C to 0°C, the yield increases (table 2, entries 1, 10), but the yield reduces when the temperature is further raised (table 2, entries 1, 11, 12). So, 0°C is the optimal temperature.

Table 2. Effect of cathode material, charge passed and temperature on the fixation of CO$_2$ along with o-bromopyridine.

| entry | cathode material | charge passed (F mol$^{-1}$) | temperature (°C) | yield$^b$ of 2a (%) |
|-------|-----------------|-----------------------------|------------------|------------------|
| 1     | Ag              | 2.0                         | 0                | 59.0             |
| 2     | Ni              | 2.0                         | 0                | 30.4             |
| 3     | Ti              | 2.0                         | 0                | 10.2             |
| 4     | Pt              | 2.0                         | 0                | 36.2             |
| 5     | GC              | 2.0                         | 0                | 18.6             |
| 6     | Ag              | 1.0                         | 0                | 15.6             |
| 7     | Ag              | 1.5                         | 0                | 31.4             |
| 8     | Ag              | 2.5                         | 0                | 44.2             |
| 9     | Ag              | 3.5                         | 0                | 35.8             |
| 10    | Ag              | 2.0                         | −5               | 35.8             |
| 11    | Ag              | 2.0                         | 5                | 32.0             |
| 12    | Ag              | 2.0                         | 25               | 21.6             |

$^a$Electrolytic conditions: 10 ml DMF, 0.1 M TBABr, 0.1 M o-bromopyridine, Mg anode, 9 mA cm$^{-2}$ current density, 1 atm CO$_2$.

$^b$The yield calculated with respect to the starting substrate is determined by HPLC.

Figure 2. Cyclic voltammograms of 10 mM o-bromopyridine obtained in DMF + 0.1 M TEABF$_4$ with the scan rate of 0.1 V s$^{-1}$ on different electrodes: (a) Ag; (b) Pt; (c) Ni; (d) GC; (e) Ti.
3.2.3. Influence of the nature of substrates

To test the validity and universality of the provided electrochemical route for fixation of CO$_2$ and investigate the influence of the position of the C−Br bond on the pyridine ring on the reaction, the investigation is expanded to $m$-bromopyridine (1b) and $p$-bromopyridine (1c) under the optimized electrolytic conditions (table 2, entry 1). As shown from the results in table 3, CO$_2$ incorporation into 1b obtaining the corresponding carboxylation product 2 with good electrocarboxylation yields is successfully completed in all cases and the yield of 2 increases from 59.0% to 65.8% in the following sequence: o-picolinic acid, m-picolinic acid, p-picolinic acid.

In addition, the cyclic voltammograms are also extended to $m$-bromopyridine and $p$-bromopyridine. As revealed in figure 3, an irreversible reduction peak for the two-electron transfer process of the C−Br bond is obtained for all the three bromopyridines on the Ag electrode. The reaction peak potential of $p$-bromopyridine is significantly more positive than that of $o$-bromopyridine and $m$-bromopyridine, showing that $p$-bromopyridine is more easily reduced than $o$-bromopyridine and $m$-bromopyridine. In addition, the peak potentials of $o$-bromopyridine and $m$-bromopyridine are very close, except that the peak current of $m$-bromopyridine is higher than that of $o$-bromopyridine, and this may be due to the fact that the diffusion coefficient of $m$-bromopyridine in the system is larger than that of $o$-bromopyridine. In combination with the previous electrolysis results (table 3) we can know that the electrochemical route for the fixation of CO$_2$ works well for all the 1, and $p$-bromopyridine with the most positive reduction potential achieves optimal performance in CO$_2$ fixation.

4. Conclusion

In conclusion, the important pharmaceutical intermediate picolinic acids (2) are synthesized by electrocarboxylation from three bromopyridines (1) and CO$_2$ using a Ag electrode. The electrolysis experiment is conducted under mild conditions with a one-compartment electrochemical cell. The effect of various electrolysis conditions and intrinsic properties on the fixation of CO$_2$ along with 1 has been investigated.
to improve the yield. After optimizing the synthetic parameters, the target 2 with good yields (59.0–65.8%) is achieved in the DMP-TBABr electrolyte with a current density of 9 mA cm\(^{-2}\) and an electric charge of 2 F mol\(^{-1}\) on a Ag electrode at 0°C. In addition, among the five materials of Ag, Ni, Ti, Pt and GC, both electrolysis and cyclic voltammograms show that Ag has the best electrocatalytic performance for the reduction and carboxylation of 1. Moreover, the position of the C–Br bond on the pyridine ring would affect the electrocarboxylation reaction. Among the 1 investigated, both cyclic voltammetry and preparative electrolysis indicate para-bromopyridine achieves optimal performance in CO\(_2\) fixation. This research is of significance for fundamental research and practical applications of CO\(_2\) fixation and synthesis of pharmaceutical intermediates by a simple and efficient means.

Data accessibility. All data used in this article are present in the article and its electronic supplementary material.
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