

# Electrocarboxylation of Alkynes with Carbon Dioxide in the Presence of Metal Salt Catalysts<sup>†</sup>

Li, Chuanhua(李传华) Yuan, Gaoqing(袁高清) Jiang, Huanfeng\*(江焕峰)

School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, Guangdong 510640, China

With some common metal salts (CuI, FeCl<sub>3</sub>) as catalysts, alkynes can be effectively electrocarboxylated with CO<sub>2</sub> (4 MPa) in an undivided cell with Ni cathode and Al sacrificial anode containing *n*-Bu<sub>4</sub>NBr-DMF as supporting electrolyte with a constant current at room temperature. The saturated tricarboxylic acids besides the dicarboxylic acids were obtained in good yields. The yields of the tricarboxylic acids were strongly influenced by various metal salt catalysts, cathode materials and the property of substituted groups. Finally, the possible electrochemical mechanism was discussed.

**Keywords** electro-synthesis, alkynes, carbon dioxide, electrocarboxylation, metal salt catalyst

## Introduction

Carbon dioxide (CO<sub>2</sub>) as C<sub>1</sub> building block has aroused considerable attention because it is a naturally abundant, low-cost, and non-toxic carbon source that can sometimes substitute toxic chemicals such as isocyanates, phosgene or carbon monoxide.<sup>1</sup> From the ecological and economic points of view, the chemical fixation of CO<sub>2</sub> becomes more and more important. In spite of the intrinsic thermodynamic stability of CO<sub>2</sub>, it can be readily reduced at the cathode<sup>2</sup> or indirectly activated by using transition metal complexes (Pd, Ni-, and Co).<sup>3-5</sup> In the last 50 years, many research groups have been devoted to study the fixation and conversion of CO<sub>2</sub> with various substrates involving alkenes,<sup>6-10</sup> alkynes,<sup>5,11-13</sup> ketones,<sup>14-16</sup> halides,<sup>17-23</sup> epoxides<sup>24-25</sup> and imines.<sup>26</sup>

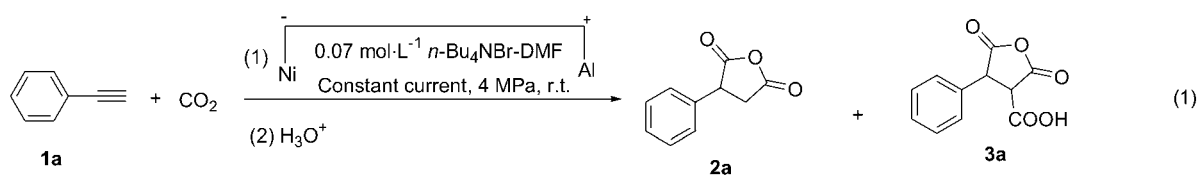
The electrochemical fixation of CO<sub>2</sub> into the unsaturated hydrocarbons to form new carbon-carbon bonds is an interesting topic because it could afford valuable fine chemicals. By now, the electrocarboxylation of nonactivated and unsaturated hydrocarbons with CO<sub>2</sub> have been reported in the presence of catalysts<sup>5,12</sup> or only depending on the nature of the cathode material used.<sup>13</sup> In particular, Duñach and co-workers<sup>12</sup> have successfully synthesized the  $\alpha,\beta$ -unsaturated acids via

nickel-bipyridine complexes catalyzing the alkynes and CO<sub>2</sub> under electrochemical conditions. Our previous works have shown that an efficient electrochemical method for the dicarboxylation of arylacetylenes and CO<sub>2</sub> with Ni as cathode in the absence of additional catalysts. The corresponding aryl-maleic anhydrides and 2-arylsuccinic acids were obtained in excellent yields.<sup>28</sup> In this paper, we found that, the electrolysis of phenylacetylene with CO<sub>2</sub> in the presence of some common metal salts, the saturated tricarboxylic acid (**3a**) besides dicarboxylic acid (**2a**) were obtained, which were apparently different from that of the previous works (Eq. 1).<sup>12,28</sup> It may be that the electrochemical reaction catalyzed by some common metal salts passes through different reaction mechanism.

## Experimental

### General procedure

The electrolytic cell and the pretreatment of electrodes referenced the literatures.<sup>27,28</sup> In a typical experimental procedure, dried DMF (35 mL), *n*-Bu<sub>4</sub>NBr (2.5 mmol), and solid metal salt catalyst (0.1 equiv.) were added to the cell in turn. The mixture solution was stirred by a magnetic stirrer at room temperature until



\* E-mail: jianghf@scut.edu.cn; Tel.: 0086-020-22236518; Fax: 0086-020-87112906

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metal salt was completely dissolved in DMF. After the cell was assembled, CO<sub>2</sub> was charged into the cell at the desired pressure. The reaction was carried out at suitable constant current. When the charge (4 F·mol<sup>-1</sup> of substrate) passed through the cell, the reaction was stopped. After the electrolyte was distilled at reduced pressure, the residue was acidified with hydrochloric acid (1.0 mol·L<sup>-1</sup>) and continuously stirred for 3 h. The acidic solution was extracted with diethyl ether (25 mL × 4). The ether phase was washed two times with distilled water and dried over anhydrous MgSO<sub>4</sub>. After evaporation of ether, the obtained crude products were separated by re-crystallization or thin layer chromatography and column chromatography, with the suitable ratio of petroleum ether-ethyl acetate as eluent, and then dried at 60 °C in a vacuum oven.

### Characterizations of products

Mass spectra analyses were done on a Shimadzu QP5050A spectrometer. FTIR spectra were measured by a TENSOR27 spectrometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR were determined on a Bruker DRX-400 spectrometer with DMSO-*d*<sub>6</sub> as the solvent in the presence of SiMe<sub>4</sub> as an internal standard. Spectroscopic data of the prepared compounds were given as follows.

**Dihydro-3-phenylfuran-2,5-dione (2a)** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) δ: 7.25–7.35 (m, 5H), 3.90 (dd, *J*=5.6, 11.6 Hz, 1H), 2.95 (dd, *J*=10, 16.8 Hz, 1H), 2.53 (dd, *J*=5.2, 16.8 Hz, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz) δ: 173.0, 169.0, 135.9, 128.3, 127.7, 127.0, 46.8, 37.4; IR (KBr) *v*: 1763, 1695 cm<sup>-1</sup>; MS *m/z*: 176 (M<sup>+</sup>).

**Tetrahydro-2,5-dioxo-4-phenylfuran-3-carboxylic acid (3a)** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) δ: 12.3 (s, 1H), 7.26–7.33 (m, 5H), 4.01 (d, *J*=7.6 Hz, 1H), 3.90 (d, *J*=5.6 Hz, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz) δ: 174.0, 172.6, 168.4, 138.7, 128.6, 127.7, 127.2, 55.3, 50.5; IR (KBr) *v*: 1765, 1700 cm<sup>-1</sup>; MS *m/z*: 220 (M<sup>+</sup>).

**Dihydro-3-*p*-tolylphenylfuran-2,5-dione (2b)** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) δ: 7.10–7.15 (m, 4H), 3.83 (dd, *J*=2.4, 7.6 Hz, 1H), 2.1 (dd, *J*=10.0, 16.8 Hz, 1H), 2.51 (dd, *J*=5.6, 11.2 Hz, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz) δ: 173.1, 169.2, 136.3, 132.8, 129.1, 127.6, 46.4, 37.4, 20.6; IR (KBr) *v*: 1772, 1680 cm<sup>-1</sup>; MS *m/z*: 190 (M<sup>+</sup>).

**Tetrahydro-2,5-dioxo-4-*p*-tolylfuran-3-carboxylic acid (3b)** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) δ: 12.6 (s, 1H), 7.12–7.16 (m, 4H), 3.94 (d, *J*=11.6 Hz, 1H), 3.85 (d, *J*=9.6 Hz, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz) δ: 174.1, 172.6, 168.4, 136.9, 135.6, 129.1, 128.2, 55.3, 50.1, 20.6; IR (KBr) *v*: 1768, 1702 cm<sup>-1</sup>; MS *m/z*: 234 (M<sup>+</sup>).

**Dihydro-3,4-diphenylfuran-2,5-dione (2c)** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) δ: 7.28–7.46 (m, 10H), 4.23 (s, 2H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz) δ: 172.4, 137.3, 128.6, 128.0, 127.0, 53.4; IR (KBr) *v*: 1763, 1675 cm<sup>-1</sup>; MS *m/z*: 252 (M<sup>+</sup>).

**Tetrahydro-2,5-dioxo-3,4-diphenylfuran-3-carb-**

**oxylic acid (3c)** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) δ: 12.4 (s, 1H), 7.28–7.46 (m, 10H), 4.35 (s, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz) δ: 174.1, 172.4, 169.2, 136.0, 135.7, 128.9, 128.7, 128.3, 128.0, 127.7, 127.0, 65.2, 54.3; IR (KBr) *v*: 1760, 1689 cm<sup>-1</sup>; MS *m/z*: 296 (M<sup>+</sup>).

**Dihydro-3-(4-nitrophenyl)furan-2,5-dione (2d)** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) δ: 7.25–7.35 (m, 4H), 3.86 (dd, *J*=5.2, 11.2 Hz, 1H), 2.95 (dd, *J*=9.6, 16.4 Hz, 1H), 2.53 (dd, *J*=5.6, 17.2 Hz, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz) δ: 173.3, 169.3, 136.8, 135.5, 128.1, 127.8, 46.7, 37.2; IR (KBr) *v*: 1753, 1685 cm<sup>-1</sup>; MS *m/z*: 221 (M<sup>+</sup>).

**Tetrahydro-4-(4-nitrophenyl)-2,5-dioxofuran-3-carboxylic acid (3d)** <sup>1</sup>H NMR (DMSO-*d*<sub>6</sub>, 400 MHz) δ: 12.3 (s, 1H), 8.11–8.39 (m, 4H), 3.95 (d, *J*=4 Hz, 1H), 3.53 (d, *J*=4.4 Hz, 1H); <sup>13</sup>C NMR (DMSO-*d*<sub>6</sub>, 100 MHz) δ: 173.2, 165.9, 163.6, 139.5, 136.9, 129.0, 122.6, 47.6, 42.8; IR (KBr) *v*: 1766, 1700 cm<sup>-1</sup>; MS *m/z*: 265 (M<sup>+</sup>).

## Results and discussion

### Effect of metal salt catalysts

The experimental results have shown that the formation of the tricarboxylic acid **3a** depended on the influence of metal salts to some extent. Hence, we selected phenylacetylene (model molecule) to investigate the influence of metal salts. As shown in Table 1. Among these metal salts (CuI, FeCl<sub>3</sub>, CuCl<sub>2</sub>, FeCl<sub>2</sub> and Pd(OAc)<sub>2</sub>), CuI exhibited good catalytic activation, the yield of **3a** could reach 70% (Table 1, Entry 1). With FeCl<sub>3</sub>, CuCl<sub>2</sub> and FeCl<sub>2</sub>, the yields of **3a** were 61%, 52% and 50%, respectively (Table 1, Entries 2–4). In contrast, with Pd(OAc)<sub>2</sub> as catalyst, low yield **3a** was obtained in 31% (Table 1, Entry 5) because there was black substances clung to the surface of the cathode due to the reduction of Pd<sup>2+</sup> so that the voltage between the anode and cathode increased dramatically leading to the

**Table 1** Effect of various metal salt catalysts on the electrocarboxylation of phenylacetylene with CO<sub>2</sub><sup>a</sup>

Entry	Catalyst <sup>b</sup>	Yield of <b>2a</b> <sup>c</sup> /%	Yield of <b>3a</b> <sup>c</sup> /%	η <sup>d</sup> /%
1	CuI	27	70	73
2	FeCl <sub>3</sub>	30	61	68
3	CuCl <sub>2</sub>	26	52	59
4	FeCl <sub>2</sub>	27	50	58
5	Pd(OAc) <sub>2</sub>	5	31	27

<sup>a</sup> Experimental conditions: phenylacetylene (2 mmol), DMF (35 mL), CO<sub>2</sub> 4 MPa, room temperature, *n*-Bu<sub>4</sub>NBr (2.5 mmol), electricity (4 F·mol<sup>-1</sup>), current density 10 mA·cm<sup>-2</sup>, Ni cathode and Al anode; <sup>b</sup> Metal salt catalyst (0.1 equiv.); <sup>c</sup> Total isolated yield based on phenylacetylene and the yield of **2a** and **3a** were determined by GC-MS; <sup>d</sup> η = Q<sub>1</sub>/Q<sub>2</sub> (η: Current efficiency; Q<sub>1</sub>: Quantity of electricity consumed in forming product; Q<sub>2</sub>: Total electricity quantity in the electrolysis).

reaction difficult to proceed. It is worth noting that the product **2a** was always generated in different metal salts conditions (Table 1, Entries 1–5). In addition, some addition protons are involved in the products (**2a** and **3a**). As reported in the literatures,<sup>12,28</sup> the protons may mainly originate from the residual water.

### Effect of cathode materials

CuI as metal salt catalyst can effectively catalyze the electrocarboxylation reaction. Can different cathode materials influence the yield of **3a**? With the question, various cathode materials were investigated. The experimental results are presented in Table 2. Different cathode materials can influence the yield of **3a** but have

**Table 2** Influence of various electrodes on the electrocarboxylation of phenylacetylene with CO<sub>2</sub><sup>a</sup>

Entry	Electrode	Yield of <b>2a</b> <sup>b</sup> /%	Yield of <b>3a</b> <sup>b</sup> /%	$\eta^c$ /%
1	Zn	14	26	30
2	Ag	18	47	49
3	Cu	22	50	54
4	Pt	28	60	66
5	Stainless steel	29	67	72
6	Ni	27	70	73

<sup>a</sup> Experimental conditions: phenylacetylene (2 mmol), DMF (35 mL), CO<sub>2</sub> 4 MPa, room temperature, *n*-Bu<sub>4</sub>NBr (2.5 mmol), electricity (4 F•mol<sup>-1</sup>), current density 10 mA•cm<sup>-2</sup>, Al as sacrificial anode, CuI (0.1 equiv.); <sup>b</sup> Total isolated yield based on phenyl-acetylene and the yields of **2a** and **3a** were determined by GC-MS; <sup>c</sup> Current efficiency.

not apparently changed the selectivity. In comparison, Ni as cathode can more effectively favor the formation of **3a**, conversely, Zn shows the worst one (Table 2, Entries 2 and 6).

### Electrocarboxylation of alkynes with CO<sub>2</sub>

With CuI as metal salt catalyst, we continued to investigate the electrocarboxylation of other alkynes with CO<sub>2</sub>. The obtained results are listed in Table 3. The electrolysis of 4-methyl-phenylacetylene, 1,2-diphenylacetylene, 1-ethynyl-4-nitrobenzene with CO<sub>2</sub> were very similar to that of phenylacetylene, affording the corresponding tricarboxylic acids in good yields (Table 3, Entries 1–4). It was also found that the property of substituted groups could influence the yield of **3a**. With electron-donating substituted groups, relative high yields **3a** were obtained than that of electron-withdrawing groups (Table 3, Entries 2 and 4).

### Electrochemical reaction mechanism

To further understand the electrochemical mechanism, the CV behavior of phenylacetylene (model compound) and CO<sub>2</sub> was carried out at an Auto LAB (PGSTAT 30) electrochemical workstation with Ni as a working electrode and a saturated calomel electrode (SCE) as a reference electrode. The working electrode and counter-electrode (Al) were built with the same size (2 mm × 2 cm). The CV results are shown in Figure 1. The reduction current of CO<sub>2</sub> is almost zero at -2.0 V (vs. SCE) in the absence of metal catalyst (Figure 1a). However, in the presence of metal salt catalyst (such as CuI), the reduction current of CO<sub>2</sub> becomes very obvi-

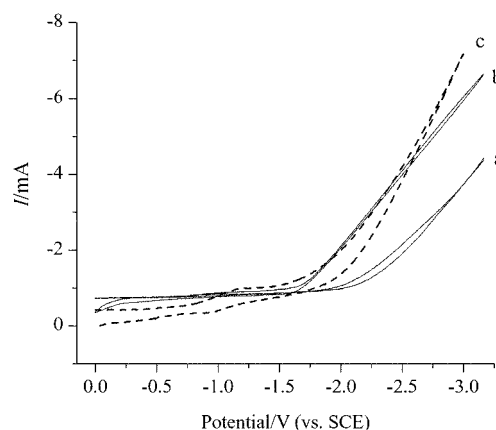
**Table 3** Electrocarboxylation of alkynes with CO<sub>2</sub><sup>a</sup>

Entry	Substrate	Product	$\eta^c$ /%
1			73
2			74
3			60
4			53

<sup>a</sup> Experimental conditions: alkyne (2 mmol), DMF (35 mL), CO<sub>2</sub> 4 MPa, room temperature, *n*-Bu<sub>4</sub>NBr (2.5 mmol), electricity (4 F•mol<sup>-1</sup>), current density 10 mA•cm<sup>-2</sup>, Ni cathode and Al anode, CuI (0.1 equiv.); <sup>b</sup> Total isolated yield based on alkyne (2 mmol); <sup>c</sup> Current efficiency.

ous at  $-2.0$  V versus SCE (Figure 1b), indicating that  $\text{CO}_2$  could be activated by metal salt catalyst. Based on the literatures,<sup>24,29,30</sup> it could be inferred that  $\text{CuI}$  could be coordinated to  $\text{CO}_2$ . For the reduction of phenylacetylene in the presence of metal salt catalyst, the reduction current of phenylacetylene is obviously observed at  $-2.0$  V (vs. SCE, Figure 1c). The CV experimental results indicate that the electrochemical reductions of  $\text{CO}_2$  and phenylacetylene could almost occur at the same time in the presence of the catalyst.

According to the experimental results and the references,<sup>5,12,13,28</sup> the plausible mechanism of phenylacetylene with  $\text{CO}_2$  is proposed in Scheme 1. At the anode,  $\text{Al}^{3+}$  ions are generated from metal Al. At the cathode, phenylacetylene or  $\text{CO}_2$  gets electrons to form radical anions on the surface of the nickel cathode almost at the same time. Then, the intermediate **A** is produced by the reaction of phenylacetylene radical anions with  $\text{CO}_2$  or the attack of  $\text{CO}_2$  radical anions to phenylacetylene. Further reaction of **A** with  $\text{CO}_2$  after **A** getting one electron, or with  $\text{CO}_2$  radical anions, gives intermediate **B**. On the one hand, in the presence of water, **B** is reduced to intermediate **C**. The product **2a** is formed via acidification and dehydration. On the other hand, in the presence of the metal catalyst ( $\text{CuI}$ ),  $\text{CuI}$  can be coordinated to  $\text{CO}_2$ , which enables  $\text{CO}_2$  to be easily reduced into the radical anion. In addition,  $\text{CuI}$  is probably coordinated with **B** to give **D**, followed by the attack of the  $\text{CO}_2$  radical anions to produce **E**. Further, **E** is reduced to **F**. After being acidified and dehydrated, the product **3a** is obtained.



**Figure 1** Cyclic voltammograms of a  $0.07 \text{ mol}\cdot\text{L}^{-1}$   $n\text{-Bu}_4\text{NBr}\text{-DMF}$  solution (35 mL) at room temperature at the scan rate  $50 \text{ mV}\cdot\text{s}^{-1}$  on a Ni working electrode: (a) only in the presence of saturated  $\text{CO}_2$  (0.1 MPa); (b) only in the presence of saturated  $\text{CO}_2$  (0.1 MPa) with metal salt catalyst ( $\text{CuI}$ ); (c) only addition of phenylacetylene with metal salt catalyst ( $\text{CuI}$ ).

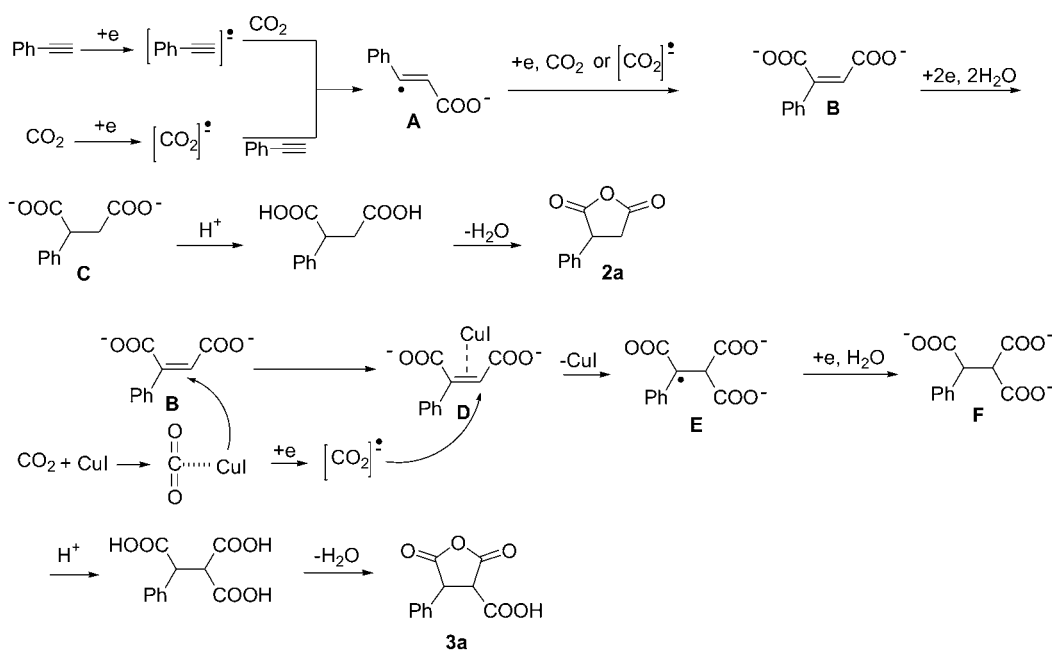
## Conclusions

In conclusion, in the presence of some metal salts, the electrocarboxylation of alkynes with  $\text{CO}_2$  has been described. Compared with the previous works,<sup>5,12,13,28</sup> the electrochemical reaction has apparently a different mechanism. The electrochemical reaction can be activated by some common metal salt catalysts. It has obvious significance for the theoretical study and practical applications because it may be helpful for the conver-

### Scheme 1 Electrochemical reaction mechanism of phenylacetylene with $\text{CO}_2$

At the anode:  $\text{Al} \longrightarrow \text{Al}^{3+} + 3\text{e}$

At the cathode in the solution:



sion and utilization of CO<sub>2</sub>.

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