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Efficient electrochemical dicarboxylations of arylacetylenes with carbon dioxide using nickel as the cathode

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ABSTRACT

The electrochemical dicarboxylation of arylacetylenes with carbon dioxide could be smoothly achieved in an undivided cell using Ni as the cathode and Al as the anode with *n*-Bu_4NBr–DMF as the supporting electrolyte, at a constant current under CO_2 pressure of 3 MPa and room temperature in the absence of additional catalysts. The corresponding aryl-maleic anhydrides and 2-arylsuccinic acids were afforded in excellent total yields (82–94%). Under anhydrous conditions, an unsaturated aryl-maleic anhydride as the main product was obtained, while the presence of H_2O would lead to the formation of saturated 2-arylsuccinic acids. The results of cyclic voltammetric experiments show that a nickel cathode itself plays the catalytic role in the reduction reaction of arylacetylenes with CO_2.

1. Introduction

In the recent decades, the continuously increasing carbon dioxide content in the atmosphere has aroused an extensive attention in the whole world because it might lead to global climate warming. Hence, the utilization of CO_2 is one of the important problems to be solved for the mankind. On the other hand, carbon dioxide is an abundant, non-toxic, and recyclable carbon source. It should be significant to convert carbon dioxide into valuable organic chemicals. Although CO_2 is very stable under normal conditions, its activation could be easily achieved via an electrochemical reaction at mild conditions. An electrochemical method has become one of the efficient routes for the conversion of CO_2. As reported in the literatures,[1–5] the direct electrochemical reduction of carbon dioxide could give some useful small molecules, such as CO, CH_4, C_2H_4, CH_3OH, HCOOH, oxalic acid, etc. In addition, the electrochemical reaction of CO_2 with various organic compounds, including benzyl chlorides,[6–10] allylic halides,[11] vinyl bromides,[12] vinyl triflates,[13] carbonyl compounds,[14] benzoyl bromides,[15] ketones,[16–19] amines,[20] heterocyclic compounds,[21,22] and epoxides,[23–25] could also afford valuable carboxylic acids, carbamates, or cyclic carbonates.

The electrochemical fixation of CO_2 into unsaturated hydrocarbons, such as alkenes[26–32] and alkynes,[33,34] is also an interesting topic. The obtained carboxylic acids are used as synthetic intermediates in organic synthesis and in the production of polymeric materials or pharmaceuticals. Duñach and co-workers' study has shown that zero-valence nickel complexes could effectively activate CO_2 and the unsaturated hydrocarbons toward C–C bond formation.[28,33] Based on the idea of Ni(0) complex catalysis, we recently reported the electrochemical route with nickel as the cathode as well as the catalyst for the electrocarboxylation of CO_2 with styrene derivatives in an undivided cell at room temperature, which could afford the corresponding 2-arylsuccinic acids in moderate to high yields.[35] Without additional catalysts, an electrochemical reaction system becomes much simple and more efficient. In this paper, our purpose is to extend this method for the electrocarboxylation of arylacetylenes with CO_2. To our knowledge, no systematic investigation on the electrochemical dicarboxylation of phenylacetylene derivatives with CO_2, using Ni as the cathode in the absence of additional catalysts, has been reported.

2. Results and discussion

In order to optimize the electrochemical reaction conditions, we first chose phenylacetylene as a model compound to be investigated, and examined the effect of various parameters (such as electrode materials, conducting salts and solvents, water, CO_2 pressure and electricity, temperature, etc.) on the result of electrosynthesis. Then, under the optimized conditions, we further studied the electrocarboxylation of phenylacetylene derivatives with CO_2.

In our experiments, all the electrosyntheses were carried out in the high-pressure stainless-steel undivided cell with a constant current at room temperature. To ensure that the electrosyntheses were conducted under anhydrous conditions, the chemicals used in the electrosyntheses were dried further. DMF was distilled under

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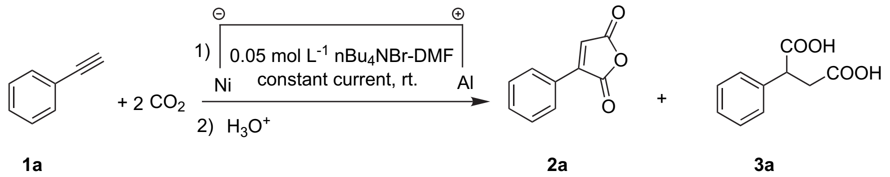


Scheme 1. Electrochemical dicarboxylation of phenylacetylene with CO_2.

reduced pressure and dried by 4 Å molecular sieves. Carbon dioxide was dried by passing through a 4 Å molecular sieves column before charging it to the cell. The conducting salts were dried in a vacuum oven at 50 °C. The electrochemical dicarboxylation of phenylacetylene with CO_2 follows the principle as shown in Scheme 1.

2.1. Influence of electrode materials

During electrolysis, the reduction of phenylacetylene or CO_2 takes place on the surface of cathodes. Thus, the property of cathode materials is of importance for the reduction activity of substrates. For comparison, the electrocarboxylation of phenylacetylene with CO_2 was investigated by using different cathodes (Ni, Pt, Ag, Cu, Zn, stainless steel, and Cu–Sn alloy) and anodes (Al or Mg) without any additional catalysts. The results of the electrocarboxylation are presented in Table 1. With Ni as the cathode and Al or Mg as the anode, as we expected, it could be smoothly realized that two CO_2 molecules were selectively incorporated into the triple bond of phenylacetylene to afford the corresponding phenylmaleic anhydride (**2a**) in excellent isolated yields (88% and 83%, respectively, Table 1, entries 1 and 7). Under the same experimental conditions, the use of Cu or Cu–Sn alloy and stainless-steel cathodes could also give **2a** in good yields (74%, 73%, and 70%, respectively, entries 2–4), while the yield of **2a** obtained with Pt or Ag as the cathode is only around 45% (entries 5 and 6). Specifically, in the case of a Zn cathode, no any mono- or di-carboxylic acid products were formed and phenylacetylene could be almost quantitatively recovered at the end of the electrolysis (entry 8). Moreover, in the Pt cathode case, we observed that a small amount of the mono-carboxylic acid (phenylpropiolic acid) was also generated and the surface of the cathode was usually covered by a thin gray matter, which might lead to the loss of Pt electrode activity. In addition, with a Ag cathode under 0.1 MPa of CO_2, the electrocarboxylation of phenylacetylene afforded a non-selective mixture of mono-and di-carboxylic acids (i.e., *cis*- and *trans*-cinnamic acids 29% yield, phenylpropiolic acid 15%, and phenylsuccinic acids 8%), which is similar to that reported in the literature.[34] In the present work, it is worthy to note that the products obtained with Ni cathode are the mixture of di-carboxylic acids instead of mono- and di-carboxylic acids, even under high or low pressure of CO_2. These experimental results show that the electrocarboxylation of phenylacetylene with CO_2 is strongly dependent upon the nature of cathode materials and reaction conditions. The practical reduction potential of phenylacetylene or CO_2 is associated with cathodic materials and reaction conditions. The excellent result of a nickel cathode may be linked with its catalytic activation for phenylacetylene and CO_2. The difference between Ni and Pt or Ag cathodes would further be discussed via cyclic voltammetries in Section 2.6.

According to our experimental results, the electrochemical route using Ni as the cathode and Al or Mg as the anode is feasible for the electrodicarboxylation of phenylacetylene with CO_2, in the absence of additional catalysts even at room temperature.

Table 1
Influence of electrode materials on the electrocarboxylation of phenylacetylene with CO_2[a]

Entry	Cathode	Anode	Yield[b] (%)	
			2a	**3a**
1	Ni	Al	88	5
2	Cu	Al	74	4
3	Cu–Sn alloy	Al	73	7
4	Stainless steel	Al	70	6
5	Pt	Al	40	5
6[c]	Ag	Al	45	3
7	Ni	Mg	83	4
8	Zn	Al	—	—
9[d]	Ni	Al	60	32

[a] Experimental conditions: room temperature, phenylacetylene (5 mmol), DMF (35 mL), current density 10 mA cm^{-2}, CO_2 3 MPa, and electricity 4 F mol^{-1}.
[b] Isolated yield based on the starting phenylacetylene.
[c] A small amount of phenylpropiolic acid was also detected.
[d] DMF and CO_2 were not further dried.

2.2. Influence of H_2O

From Table 1, it could be seen that a small amount of the saturated phenylsuccinic acid was also produced in all cases besides an unsaturated phenylmaleic anhydride as the main product, and found that the formation amount of saturated phenylsuccinic acids increased under the un-dried DMF solvent and CO_2 case (Table 1, entry 9). Thus, we deduce that the formation of saturated phenylsuccinic acids may be associated with the presence of residual water in the electrochemical system. In order to verify this point, we consciously added a small amount of H_2O to the electrolysis system. The obtained results are listed in Table 2. Under dry conditions, the obtained di-carboxylic acid almost is an unsaturated phenylmaleic anhydride (89% yield, Table 2, entry 1). However, the yield of unsaturated phenylmaleic anhydrides dramatically decreased from 89% to 3% and conversely the yield of saturated phenylsuccinic acids increased from 4% to 90% (entries 1–4) when a small amount of water (from 0.0 to 0.30 g) was added to 35 mL *n*-Bu_4NBr–DMF electrolyte solution. The experimental results further verify our deduction. The presence of water in the electrolysis system could provide protons to make phenylacetylene easily be reduced into styrene and finally result in the formation of saturated phenylsuccinic acids. Since it is very difficult to keep an absolute anhydrous state in the electrolysis system, the formation of an unsaturated phenylmaleic anhydride is always accompanied with a certain amount of saturated phenylsuccinic acids during the electrolysis.

Table 2
Influence of H_2O on the electrocarboxylation of phenylacetylene with CO_2[a]

Entry	H_2O (g)	Yield[b] of **2a** (%)	Yield[b] of **3a** (%)
1	0.00	89	4
2	0.10	50	42
3	0.20	11	80
4	0.30	3	90

[a] Experimental conditions: room temperature, phenylacetylene (4.5 mmol), DMF (35 mL), *n*-Bu_4NBr (0.05 mol L^{-1}), CO_2 3 MPa, current density 10 mA cm^{-2}, Al anode, Ni cathode, and electricity 4 F mol^{-1}.
[b] Isolated yield based on the starting phenylacetylene.

Table 3

Influence of conducting salts and solvents on the electrocarboxylation of phenylacetylene with CO_2[a]

Entry	Conducting salt	Solvent	Yield[b] (%)	
			2a+**3a**	**2a**/**3a**
1	*n*-Bu_4NBr	DMF	93	95:5
2	*n*-Bu_4NCl	DMF	89	85:15
3	*n*-Bu_4NI	DMF	73	90:10
4	Et_4NBr	DMF	70	85:15
5	*n*-Bu_4NBr	MeCN	20	80:20
6	*n*-Bu_4NBr	CH_3OH	—	—

[a] Experimental conditions: room temperature, phenylacetylene (5 mmol), solvent (35 mL), conducting salt (0.05 mol L^{-1}), CO_2 3 MPa, current density 10 mA cm^{-2}, electricity 4 F mol^{-1}, Al anode and Ni cathode.

[b] Isolated yield and the yield ratio of **2a**/**3a** based on the starting phenylacetylene, and data of GC–MS.

2.3. Influence of solvents and conducting salts

The effect of solvents (DMF, MeCN, and MeOH) and conducting salts (*n*-Bu_4NBr, *n*-Bu_4NCl, *n*-Bu_4NI, and Et_4NBr) on the electrocarboxylation of phenylacetylene with CO_2 was also carefully investigated. With DMF as the solvent, the electrolysis could efficiently afford the corresponding phenylmaleic anhydride (**2a**) and phenylsuccinic acid (**3a**) in good to excellent total yields (70–93%, Table 3, entries 1–4), whereas **2a** and **3a** were not detected in MeOH solvent case (entry 6). In addition, when conducting electrolysis in MeCN solvent, we found that the products precipitated on the surface of an Al anode so that the electrolysis could not be smoothly finished, and the electrolysis gave **2a** and **3a** in very low yield (20%, entry 5), together with other by-products (such as 2-propenoic acid). Different solvents lead to different results of electrolysis, which may be due to the difference in solubility of products or reactants and conducting salts in solvents. For conducting salts, at the same anion (Br^-) case, the electrolysis conducted with *n*-Bu_4NBr gave **2a** and **3a** in 93% total yield (entry 1), which was better than that of Et_4NBr (70%, entry 4). In the same cation (*n*-Bu_4N^+) case, *n*-Bu_4NBr or *n*-Bu_4NCl (89%, entry 2) seemed to be more effective than *n*-Bu_4NI (73%, entry 3). These results show that the electrochemical activation process of phenylacetylene or CO_2 is related with anions or cations of conducting salts. The activity of cations and anions for the reaction is *n*-$Bu_4N^+ > Et_4N^+$ and $Br^- > Cl^- > I^-$, respectively. Among these conducting salts and solvents examined, the combination of *n*-Bu_4NBr and DMF as the supporting electrolyte appears to be the most appropriate for the electrocarboxylation of phenylacetylene with CO_2.

2.4. Influence of electricity and temperature as well as carbon dioxide pressure

The electricity for electrolysis, temperature, and carbon dioxide pressure are also important factors for the electrochemical reaction system. Table 4 summarizes the effect of these factors on the electrocarboxylation of phenylacetylene with CO_2. It could be seen from Table 4 that the overall yield of **2a** and **3a** increased from 70% to 92% as the electricity passed through the electrolysis cell increased from 2 to 4 F mol^{-1} (Table 4, entries 1–3). When the electricity continued to increase up to 5 F mol^{-1}, the yield was almost unchanged (93%, entry 4). Considering the efficiency of current, we chose 4 F mol^{-1} as the optimal electricity for the electrolysis. The solubility of CO_2 in DMF solvent is limited under 0.1 MPa of CO_2. According to the basic principle of thermodynamics, lowering temperature or increasing CO_2 pressure is able to enhance the solubility of CO_2 in DMF solvent, which is beneficial for the electrocarboxylation of phenylacetylene with CO_2. Our experimental results also support this point. For example, under the same CO_2 pressure and electricity, the yield of **2a** and **3a** obtained at 10 °C or 25 °C is superior to that of the electrolysis at 35 °C (entries 3, 5, and 6). When carbon dioxide pressure increased from 0.1 to 3 MPa, the yield of **2a** and **3a** increased from 50% to 92% (entries 7–9 and 3). On the other hand, high pressure of CO_2 makes possible the electrochemical dicarboxylation of phenylacetylene with more concentrated solution and restricts the polymerization of phenylacetylene. But, carbon dioxide pressure is too high to favor the electrolysis. When carbon dioxide pressure increased up to 5 MPa, the voltage between anode and cathode increased dramatically so that the electrolysis was not successful (entry 10). Thus, carbon dioxide pressure should be controlled within an appropriate range (2–3 MPa).

Table 4

Influence of electricity and temperature as well as CO_2 pressure on the electrocarboxylation of phenylacetylene[a]

Entry	Electricity (F mol^{-1})	Temp (°C)	Pressure (MPa)	Yield[b] (%)	
				2a+**3a**	**2a**/**3a**
1	2	25	3	70	90:10
2	3	25	3	80	85:15
3	4	25	3	92	95:5
4	5	25	3	93	95:5
5	4	35	3	78	88:12
6	4	10	3	93	95:5
7	4	25	0.1	50	95:5
8	4	25	1	82	90:10
9	4	25	2	90	92:8
10	4	25	5	—	—

[a] Experimental conditions: phenylacetylene (4.5 mmol), *n*-Bu_4NBr (0.05 mol L^{-1}), DMF (35 mL), current density 5 mA cm^{-2}, Ni cathode and Al anode.

[b] Isolated yield and the yield ratio of **2a**/**3a** based on the starting phenylacetylene, and data of GC–MS.

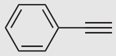
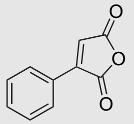
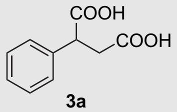
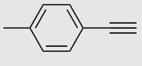
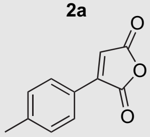
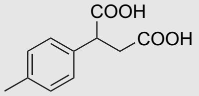
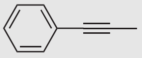
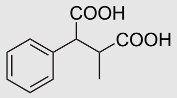
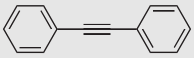
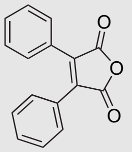
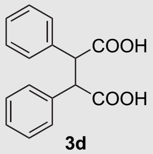
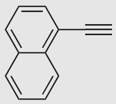
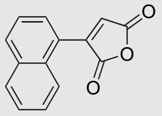
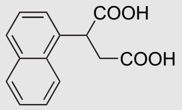
Based on the above investigations, the optimal conditions of the electrocarboxylation for phenylacetylene with CO_2 are summarized as follows: Ni as the cathode and Al (Mg) as the anode, *n*-Bu_4NBr–DMF as the supporting electrolyte, temperature of the electrolysis at 25 °C, CO_2 pressure at 2–3 MPa, and electricity at 4 F mol^{-1}.

2.5. Electrocarboxylation of phenylacetylene derivatives

In order to test the effectiveness and scope of this electrochemical route, several phenylacetylene derivatives were further electrocarboxylated under the above optimized electrolysis conditions. As shown in Table 5, the electrochemical route is also effective for the phenylacetylene derivatives in the absence of additional catalysts. The electrocarboxylation of *p*-tolylacetylene, 1-phenyl-1-propyne, 1,2-diphenylacetylene, and 1-ethynyl-naphthalene could afford the corresponding aryl-maleic anhydrides and 2-arylsuccinic acids in excellent total yields (94%, 82%, 91%, and 89%, respectively, Table 5, entries 2–5). In all cases, almost no any mono-carboxylic acids were formed in the present conditions. Earlier work of Wawzonek and Wearring has also showed that the electrolysis of 1,2-diphenylacetylene with carbon dioxide could give di-carboxylic acids (diphenylmaleic anhydride, diphenylfumaric acid, and *meso*-diphenylsuccinic acid).[36] It should be noted that the products obtained with the nickel complex-catalyzed electrocarboxylation of arylacetylenes are mono-carboxylic acids instead of di-carboxylic acids.[33] This means that the electrochemical reaction mechanism using Ni as the cathode is different from the one catalyzed by the nickel complex.

In addition, it should be pointed out that no oxalate or polyphenylacetylene was detected in our experiments although CO_2 radical anions could dimerize to oxalates and phenylacetylene radical anions could polymerize under certain conditions.

Table 5
Electrochemical dicarboxylation of phenylacetylene derivatives with CO_2[a]

Entry	Substrate (**1**)	Product (**2P**)	Product (**3P**)	Yield[b] (%)	
				2P+3P	**2P/3P**
1	 **1a**	 **2a**	 **3a**	93	95:5
2	 **1b**	 **2b**	 **3b**	94	90:10
3	 **1c**	 **2c**	 **3c**	82	85:15
4	 **1d**	 **2d**	 **3d**	91	95:5
5	 **1e**	 **2e**	 **3e**	89	75:25

[a] Experimental conditions: arylacetylene (5 mmol), DMF (35 mL), CO_2 3 MPa, room temperature, n-Bu_4NBr (0.05 mol L^{-1}), electricity 4 F mol^{-1}, current density 10 mA cm^{-2}, Ni cathode and Al anode.

[b] Isolated yield and the yield ratio based on the starting arylacetylenes, and data of GC–MS.

2.6. Electrochemical reaction mechanism

In our previous work,[35] it was observed that the result of a Ni cathode was almost the same as good as that of a Pt one for the electrodicarboxylation of styrene derivatives with carbon dioxide. Interestingly, in the present case, a Ni cathode appears to be more effective than a Pt or Ag one (Table 1, entries 1, 5, and 6). To understand the difference between Ni and Pt or Ag cathodes as well as the electrochemical reaction mechanism of arylacetylene with CO_2, we further checked the cyclic voltammetry of an n-Bu_4NBr–DMF solution containing phenylacetylene (model compound) in the absence or presence of CO_2 with Ni and Pt or Ag as the working electrodes. The obtained CV results are shown in Figures 1 and 2. It can be seen that the result of Ag electrode is obviously different

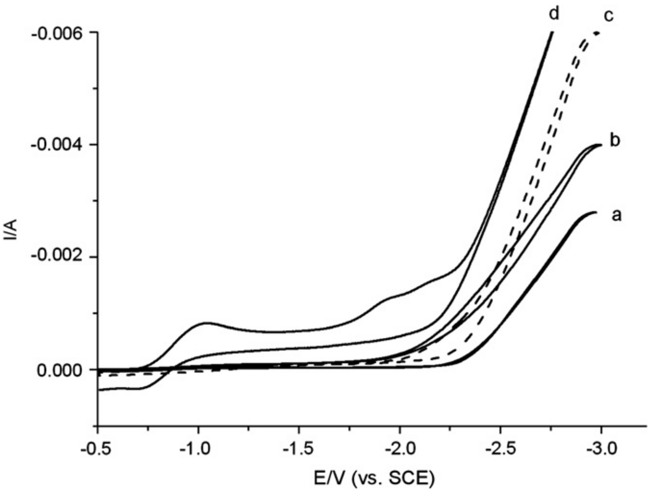


Figure 1. Cyclic voltammograms of a 0.05 mol L^{-1} n-Bu_4NBr–DMF solution (35 mL) containing 5.0 mmol phenylacetylene at room temperature, at the scan rate 100 mV s^{-1} with different working electrodes: (a) Pt; (b) cyclic voltammogram of 0.05 mol L^{-1} n-Bu_4NBr–DMF solution (35 mL) in the presence of CO_2 with Ni as a working electrode; (c) Ni; (d) Ag.

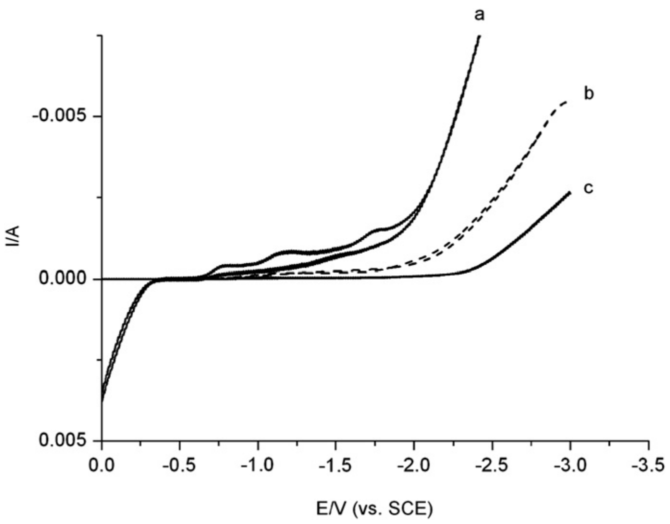
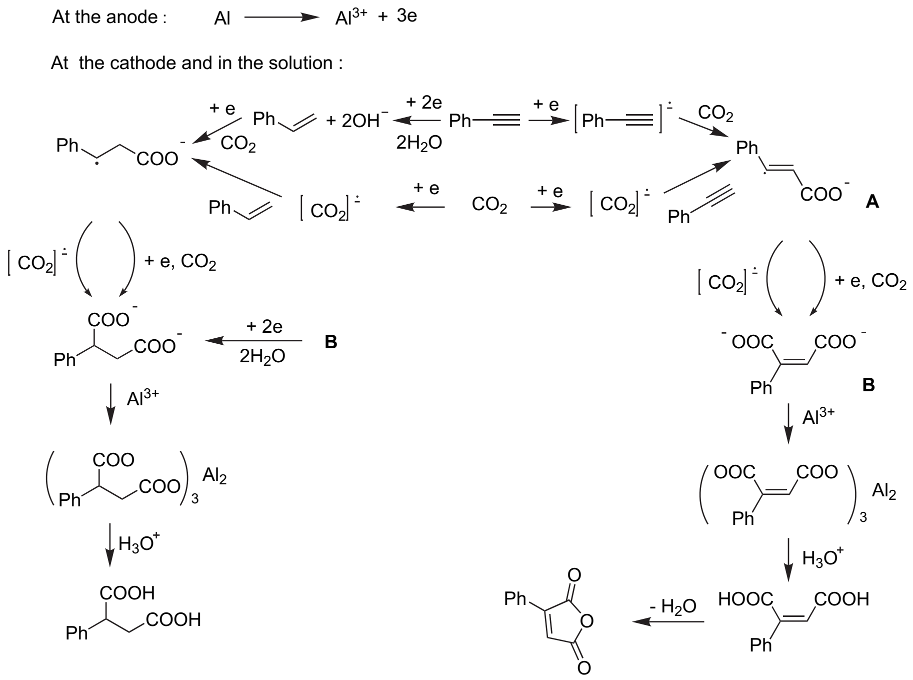


Figure 2. Cyclic voltammograms of a 0.05 mol L^{-1} n-Bu_4NBr–DMF solution (35 mL) containing 5.0 mmol phenylacetylene in the presence of CO_2 (0.1 MPa) at room temperature, at the scan rate 100 mV s^{-1} with different working electrodes: (a) Ag; (b) Ni; (c) Pt.



Scheme 2. Electrochemical reaction mechanism of phenylacetylene with CO_2.

from those of Ni and Pt. In the absence of CO_2, two reduction peaks of phenylacetylene were observed within −0.5 to −2.0 V versus SCE in the case of Ag electrode (Fig. 1d), while no reduction peaks appeared at the same reduction potentials with Pt and Ni as electrodes (Fig. 1a and c). In the presence of CO_2 (Fig. 2), a similar behavior could be observed, and in Figure 2a (Ag as the electrode), other reduction peak and an oxidation peak are also observed. At −2.25 V versus SCE, the reduction current of phenylacetylene also appears with Ni as the working electrode (Figs. 1c and 2b), whereas it is still zero in the Pt working electrode case (Figs. 1a and 2c). The CV results mean that the activity of electrode is Ag>Ni>Pt for the reduction of phenylacetylene, and that a Ag cathode results in more non-selective reduction products than Ni or Pt one. The activity of electrode is too high or too low to favor the electrodicarboxylation of phenylacetylene with CO_2. A Pt cathode gave di-carboxylic acids in low yield (Table 1, entry 5) due to its low activity. Compared with a Ag or Pt electrode, a Ni cathode seemed to be more appropriate for the electrodicarboxylation of phenylacetylene with CO_2. Moreover, due to the catalytic role of a Ni cathode, the tendency of reduction reaction of phenylacetylene approximates to that of CO_2 (see Fig. 1b and c). Consequently, it was considered that a single-electron reduction of CO_2 and phenylacetylene almost could take place at the same time during the electrolysis with nickel as the cathode. When phenylacetylene is added to n-Bu_4NBr–DMF electrolyte solution in the presence of CO_2, the change of reduction current at −2.0 to −2.5 V versus SCE is attributed to the one-electron or two-electron reduction processes of CO_2 and phenylacetylene (Fig. 2b).

Based on our experimental results, a possible electrochemical reaction mechanism of phenylacetylene with CO_2 is outlined in Scheme 2. When the electrolysis was performed under anhydrous conditions, phenylacetylene or CO_2 on the surface of a nickel cathode first got electrons to form radical anions almost at the same time. Then, the attack of CO_2 radical anions to phenylacetylene or the reaction of phenylacetylene radical anions with CO_2 gave an intermediate **A** (carboxylate radical anion). Further reaction of **A** with CO_2 radical anions, or reaction of **A** with CO_2 after **A** getting one electron, afforded a dicarboxylate anion **B**, followed by capturing of the anion by Al^{3+} ions generated at the anodic Al metal to form stable aluminum carboxylates. Finally, a phenylmaleic anhydride was formed via the dehydration of phenylmaleic acids during the acidification of the metal carboxylates with 2 mol L^{-1} aqueous HCl. If there was a small amount of water in the electrolysis system, an unsaturated dicarboxylate anion **B** would be further reduced to the saturated phenylsuccinic acids. On the other hand, phenylacetylene might first be reduced to styrene in the presence of water. Then, further reduction of styrene with CO_2 gave the saturated phenylsuccinic acids, as previously reported.[35] The presence of water leads to the formation of saturated phenylsuccinic acids, which is confirmed by our experiments (Table 2, entries 2–4). The electrochemical reaction of phenylacetylene with CO_2 becomes complex due to the presence of water. The detailed mechanism is needed to study further.

3. Experimental section for the electrochemical dicarboxylation of arylacetylenes with carbon dioxide

3.1. General methods

The electrocarboxylations of arylacetylenes with CO_2 were carried out in the high-pressure stainless-steel undivided cell fitted with a nickel (or copper, platinum, silver, etc.) sheet (2 cm×3 cm×0.02 cm) as the cathode and an aluminum (or magnesium) plate (2 cm×3 cm×0.05 cm) as the anode, being similar to that described in our previous paper.[35] Prior to the electrolysis, the two electrodes were cleaned with detergent and diluted hydrochloric acid, washed with distilled water, and then dried. In a typical procedure, n-Bu_4NBr (1.75 mmol), dried DMF solvent (35 mL), and phenylacetylene (5 mmol) were first added to the cell in turn. Carbon dioxide was then charged into the desired pressure after the cell was sealed. The electrolysis was performed at a suitable constant current until 4 F mol^{-1} of starting substrates had been passed through the cell at room temperature. The electrolyte solution was continuously stirred by a magnetic stirrer during the electrolysis. At the end of the electrolysis, the solvent was distilled off at reduced pressure, and the residue was acidified with 2 mol L^{-1} aqueous HCl and extracted with diethyl ether (4×25 mL). The ether phase was washed twice with distilled water. After evaporation of ether, the obtained product was dried in a vacuum oven at 60 °C for 6 h. The crude product was further purified by re-crystallization or using planar chromatography and column chromatography (eluent: petroleum ether–EtOAc), and was characterized by FTIR, mass spectra, and ^1H and ^{13}C NMR.

^1H and ^{13}C NMR were measured on a DRX-400 (Bruker) spectrometer with acetone-d_6 as solvent in the presence of $SiMe_4$ as an internal standard. Fourier transform infrared (FTIR) spectrum and mass spectra or GC–MS analyses were performed on TENSOR27 and Shimadzu QP5050A spectrometers, respectively. Elemental analyses were carried out in a Heraeus CHN-O-RAPID Elemental Analyzer. Melting points were determined on X-4 Mel-Temp apparatus and were uncorrected. Cyclic voltammetric experiments were carried out in an Auto LAB (PGSTAT30) electrochemical working station, with a nickel or a platinum sheet as a working electrode and a saturated calomel electrode (SCE) as a reference electrode.

3.1.1. *Phenylmaleic anhydride (**2a**)*

IR (neat): 1766, 1702 cm^{-1}. ^1H NMR (acetone-d_6): δ 7.29–7.31 (m, 1H, Ph), 7.33–7.35 (m, 2H, Ph), 7.51 (s, 1H), 7.56–7.58 (m, 2H, Ph). ^{13}C NMR (acetone-d_6, 100 MHz): δ 167.6, 166.6, 143.8, 135.4, 129.9, 129.5, 128.5, 128.1. MS (EI): m/z 174 (M$^+$). Pale yellow solid, mp: 119–120 °C (Ref. 118–119 °C).[37]

3.1.2. *p-Tolylmaleic anhydride (**2b**)*

IR (neat): 1760, 1701 cm^{-1}. ^1H NMR (acetone-d_6): δ 2.32 (s, 3H), 7.16–7.19 (m, 2H, Ph), 7.23–7.26 (m, 2H, Ph), 7.43 (s, 1H). ^{13}C NMR (acetone-d_6, 100 MHz): δ 168.4, 167.3, 143.7, 138.6, 132.7, 130.6, 130.0, 128.5, 21.2. MS (EI): m/z 188 (M$^+$). Pale yellow solid, mp: 107–109 °C (Ref. 106–108 °C).[37]

3.1.3. *2-Methyl-1-phenylmaleic anhydride (**2c**)*

IR (neat): 1773, 1695 cm^{-1}. ^1H NMR (acetone-d_6): δ 2.19 (s, 3H), 7.28–7.31 (m, 1H, Ph), 7.34–7.38 (m, 2H, Ph), 7.55–7.57 (m, 2H, Ph). ^{13}C NMR (acetone-d_6, 100 MHz): δ 169.9, 168.6, 137.8, 137.3, 136.5, 129.2, 128.5, 127.8, 17.3. MS (EI): m/z 188 (M$^+$). Pale yellow solid, mp: 149–151 °C. $C_{11}H_8O_3$ (188.18) calcd: C 70.21, H 4.29; found: C 70.31, H 4.23.

3.1.4. *2,3-Diphenylmaleic anhydride (**2d**)*

IR (neat): 1760, 1680 cm^{-1}. ^1H NMR (acetone-d_6): δ 7.15–7.17 (m, 2H, Ph), 7.37–7.43 (m, 4H, Ph), 7.50–7.52 (m, 4H, Ph). ^{13}C NMR (acetone-d_6, 100 MHz): δ 169.3, 137.5, 136.8, 129.5, 128.7, 128.0. MS (EI): m/z 250 (M$^+$). Pale yellow solid, mp: 158–159 °C (Ref. 157–158 °C).[36]

3.1.5. *1-(Naphthalen-2-yl) maleic anhydride (**2e**)*

IR (neat): 1765, 1699 cm^{-1}. ^1H NMR (acetone-d_6): δ 7.33–7.37 (m, 1H), 7.47–7.51 (m, 3H), 7.54 (s, 1H), 7.56–7.59 (m, 1H), 7.88–7.93 (m, 2H). ^{13}C NMR (acetone-d_6, 100 MHz): δ 167.6, 166.1, 144.1, 135.1, 132.5, 131.8, 129.9, 129.1, 128.3, 127.3, 126.9, 126.5, 125.5, 121.8. MS (EI): m/z 224 (M$^+$). Yellow solid, mp: 143–145 °C. $C_{14}H_8O_3$ (224.20) calcd: C 75.00, H 3.60; found C 75.10, H 3.56.

3.1.6. *2-Phenylsuccinic acid (**3a**)*

IR (neat): 1701 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.65 (dd, J_1=12.0 Hz, J_2=4.0 Hz, 1H), 3.12 (dd, J_1=10.2 Hz, J_2=4.0 Hz, 1H), 4.07 (q, J=5.1 Hz, 1H), 7.25–7.28 (m, 1H, Ph), 7.33–7.38 (m, 4H, Ph), 10.89 (s, 1H), 11.18 (s, 1H). ^{13}C NMR (acetone-d_6, 100 MHz): δ 174.3, 173.4, 139.6, 129.6, 128.7, 128.1, 47.7, 38.0. MS (EI): m/z 194 (M$^+$). White solid, mp: 166–168 °C (Ref. 168 °C).[27]

3.1.7. *2-p-Tolylsuccinic acid (**3b**)*

IR (neat): 1703 cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.26 (s, 3H), 2.48 (dd, J_1=8.0 Hz, J_2=4.0 Hz, 1H), 2.93 (dd, J_1=12.0 Hz, J_2=4.0 Hz, 1H), 3.83 (q, J=4.0 Hz, 1H), 7.11–7.17 (m, 4H, Ph), 11.80 (s, 1H), 12.22 (s, 1H). ^{13}C NMR (acetone-d_6, 100 MHz): δ 174.8, 173.3, 137.6, 136.7, 130.1, 128.5, 47.5, 38.2, 21.0. MS (EI): m/z 208 (M$^+$). White solid, mp: 198–200 °C.

3.1.8. *2-Methyl-1-phenylsuccinic acid (**3c**)*

IR (neat): 1705 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.31 (d, J=4 Hz, 3H), 3.08–3.13 (m, 1H), 3.74 (t, J=12 Hz, 1H), 7.24–7.30 (m, 1H, Ph), 7.32–7.36 (m, 4H, Ph), 10.78 (s, 1H), 11.02 (s, 1H). ^{13}C NMR (acetone-d_6, 100 MHz): δ 174.9, 173.0, 137.7, 129.2, 128.5, 127.5, 43.0, 42.0, 16.1. MS (EI): m/z 208 (M$^+$). White solid, mp: 216–218 °C.

3.1.9. *2,3-Diphenylsuccinic acid (**3d**)*

IR (neat): 1710 cm^{-1}. ^1H NMR (acetone-d_6): δ 4.24 (s, 2H), δ 7.09–7.15 (m, 2H, Ph), 7.35–7.39 (m, 4H, Ph), 7.42–7.48 (m, 4H, Ph), 11.32 (s, 2H). ^{13}C NMR (acetone-d_6, 100 MHz): δ 174.4, 138.3, 131.5, 129.4, 128.5, 47.8. MS (EI): m/z 270 (M$^+$). Pale yellow solid, mp: 220–222 °C (Ref. 222 °C).[36]

4. Conclusions

In conclusion, a simple and efficient electrochemical route with nickel instead of noble metal (Pt or Ag) as the cathode and Al as the anode has been developed for the electrochemical dicarboxylation of arylacetylenes with CO_2 without additional catalysts at mild conditions (room temperature). A nickel cathode itself could effectively catalyze the reduction reactions of arylacetylenes with CO_2. With nickel as the cathode as well as the catalyst, the electrochemical route appears much simple and more efficient. Under the optimized conditions (i.e., n-Bu_4NBr–DMF as the supporting electrolyte, temperature of the electrolysis at 25 °C, pressure of CO_2 at 2–3 MPa, and electricity at 4 F mol^{-1}), the electrochemical route could afford the corresponding aryl-maleic anhydrides and 2-arylsuccinic acids in excellent total yields (82–94%). The present work might be helpful to further extend the application scope of carbon dioxide.

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References and notes

1. Kaneco, S.; Katsumata, H.; Suzuki, T.; Ohta, K. *Electrochim. Acta* **2006**, *51*, 3316.
2. Kaneco, S.; Iiba, K.; Katsumata, H.; Suzuki, T.; Ohta, K. *Electrochim. Acta* **2006**, *51*, 4880.
3. Koleli, F.; Ropke, T.; Hamann, C. H. *Electrochim. Acta* **2003**, *48*, 1595.
4. Schrebler, R.; Cury, P.; Suarez, C.; Munoz, E.; Gomez, H.; Cordova, R. *J. Electroanal. Chem.* **2002**, *533*, 167.
5. Gattrell, M.; Gupta, N.; Co, A. *J. Electroanal. Chem.* **2006**, *594*, 1.
6. Fauverque, J. F.; De Zelicourt, Y.; Amatore, C.; Jutand, A. *J. Appl. Electrochem.* **1990**, *20*, 338.
7. Fauverque, J. F.; Jutand, A.; Francois, M. *J. Appl. Electrochem.* **1988**, *18*, 109.
8. Damodar, J.; Krishna Mohan, S. R.; Jayarama Reddy, S. R. *Electrochem. Commun.* **2001**, *3*, 762.
9. Otero, M. D.; Batanero, B.; Barba, F. *Tetrahedron Lett.* **2006**, *47*, 2171.
10. Isse, A. A.; Ferlin, M. G.; Gennaro, A. *J. Electroanal. Chem.* **2005**, *581*, 38.
11. Tokuda, M.; Kabuki, T.; Katoh, Y.; Suginome, H. *Tetrahedron Lett.* **1995**, *36*, 3345.
12. Kamekawa, H.; Senboku, H.; Tokuda, M. *Electrochim. Acta* **1997**, *42*, 2117.
13. Senboku, H.; Fujimura, Y.; Kamekawa, H.; Tokuda, M. *Electrochim. Acta* **2000**, *45*, 2995.
14. Silvestri, G.; Gambino, S.; Filardo, G. *Acta Chem. Scand.* **1991**, *45*, 987.
15. Koshechko, V. G.; Titov, V. E.; Lopushanskaya, V. A. *Electrochem. Commun.* **2002**, *4*, 655.
16. Scialdone, O.; Amatore, C.; Galia, A.; Filardo, G. *J. Electroanal. Chem.* **2006**, *529*, 163.
17. Sialdone, O.; Sabatino, M. A.; Belfiore, C.; Galia, A.; Paternostro, M. P.; Filardo, G. *Electrochim. Acta* **2006**, *51*, 3500.
18. Scialdone, O.; Galia, A.; Isse, A. A.; Gennaro, A.; Sabatino, M. A.; Leone, R.; Filardo, G. *J. Electroanal. Chem.* **2007**, *609*, 8.
19. Chan, A. S. C.; Huang, T. T.; Wagenknecht, J. H.; Miller, R. E. *J. Org. Chem.* **1995**, *60*, 742.
20. Feroci, M.; Orsini, M.; Rossi, L.; Sotgiu, G.; Inesi, A. *J. Org. Chem.* **2007**, *72*, 200.

21. Gennaro, A.; Sanchez, C. M.; Isse, A. A.; Montiel, V. *Electrochem. Commun.* **2004**, *6*, 627.
22. Ramesh Raju, R.; Krishna Mohan, S.; Jayarama Reddy, S. R. *Tetrahedron Lett.* **2003**, *44*, 4133.
23. Tascedda, P.; Weidmann, M.; Dinjus, E.; Duñach, E. *Appl. Organomet. Chem.* **2001**, *15*, 141.
24. Yang, H. Z.; Gu, Y. L.; Deng, Y. Q.; Shi, F. *Chem. Commun.* **2002**, 274.
25. Wang, Y.; Yuan, G. Q.; Zeng, Y. C.; Jiang, H. F. *Chin. J. Org. Chem.* **2007**, *27*, 1397.
26. Filardo, G.; Gambino, S.; Silvestri, G.; Gennaro, A.; Vianello, E. *J. Electroanal. Chem.* **1984**, *177*, 303.
27. Gambino, S.; Gennaro, A.; Filardo, G.; Silvestri, G.; Vianello, E. *J. Electrochem. Soc.* **1987**, *134*, 2172.
28. Dérien, S.; Clinet, J.-.C.; Duñach, E.; Périchon, J. *Tetrahedron* **1992**, *48*, 5235.
29. Ballivet-Tkatchenko, D.; Jean-Claude, F.; Tanji, J. *Appl. Organomet. Chem.* **2000**, *14*, 847.
30. Senboku, H.; Komatsu, H.; Fujimura, Y.; Tokuda, M. *Synlett* **2001**, 418.
31. Bringmann, J.; Dinjus, E. *Appl. Organomet. Chem.* **2001**, *15*, 135.
32. Wang, H.; Zhang, G. R.; Liu, Y. Z.; Luo, Y. W.; Lu, J. X. *Electrochem. Commun.* **2007**, *9*, 2235.
33. Dérien, S.; Duñach, E.; Périchon, J. *J. Am. Chem. Soc.* **1991**, *113*, 8447.
34. Koster, F.; Dinjus, E.; Duñach, E. *Eur. J. Org. Chem.* **2001**, 2507.
35. Yuan, G. Q.; Jiang, H. F.; Lin, C.; Liao, S. J. *Electrochim. Acta* **2008**, *53*, 2170.
36. Wawzonek, E.; Wearring, D. *J. Am. Chem. Soc.* **1959**, *81*, 2067.
37. Gabriele, B.; Veltri, L.; Salerno, G.; Costa, M.; Chiusoli, G. P. *Eur. J. Org. Chem.* **2003**, 1722.