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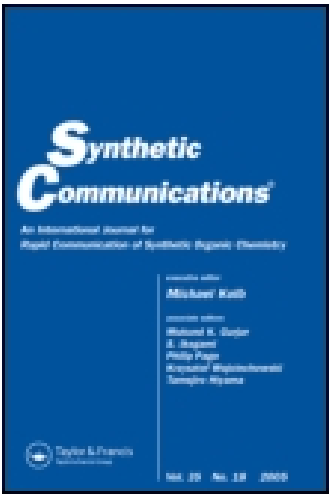

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ELECTROCATALYTIC CARBOXYLATION OF ARYLIC BROMIDES AT SILVER CATHODE IN THE PRESENCE OF CARBON DIOXIDE

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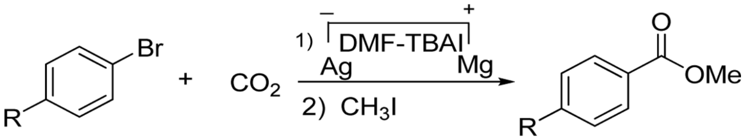
GRAPHICAL ABSTRACT



Abstract *A simple and efficient electrocatalytic carboxylation of arylic bromides has been developed using silver as cathode and magnesium as anode in* N,N-*dimethylformamide (DMF) under mild conditions. The influences of some key factors (such as the nature of cathode material, current density, and temperature) on this reaction were investigated. The investigations were extended to other arylic bromides under the optimized conditions, and the corresponding carboxylic acids were obtained in moderate to good yields (30–78%). The electrochemical behavior was studied at different electrodes (Ag, Cu, Ni, and Ti) by cyclic voltammetry, which showed significant electrocatalytic effect of the silver electrode toward the reductive carboxylation of arylic bromides.*

Keywords Arylic bromides; CO_2; electrocatalytic; silver cathode

INTRODUCTION

Carbon dioxide (CO_2) is the most abundant waste produced by human activities and one of the greenhouse gases.[1] However, CO_2 is recognized to be a naturally abundant, cheap, recyclable, and nontoxic carbon source that can sometimes replace toxic chemicals such as phosgene, isocyanates, or carbon monoxide.[2] As a result, CO_2 fixation has become an active area of research in green chemistry. Electrochemical carboxylation is one of the most useful methods for CO_2 fixation

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to organic molecules because it is a mild and easy-to-handle process. Carbanions can easily be genenrated by the electrochemical reduction of organic halides,[3] aromatic ketones,[4] and activated olefins,[5] and then carbon dioxide can work as an electrophile in the reaction of anion species to give carboxylic acids with one carbon elongation.

Benzoic acids are important intermediates in many natural and medicinally important compounds.[6] In recent years, metal-catalyzed carboxylation of aryl halides has become a powerful alternative to the classical synthetic approaches for these compounds.[7] Correa and Martin[8] used palladium complex as catalyst for the carboxylation of aryl bromides under 10 atmospheres of CO_2. In an electrochemical field, several metal complexes[9] (such as nickel and palladium complexes) have also been used as homogeneous catalysts for the electrochemical carboxylation of aryl halides, or else poisonous Hg was used as the electrode.[10] Although good current efficiencies were obtained with many of these catalytic systems, the presence of additive catalysts made the reaction system and the separation complicated, and it is also expensive and not friendly to the environment.

In the past years, a series of studies dealing with the reduction of organic halides at an Ag electrode have been reported.[11] It has been shown that such an electrode material exhibits extraordinary electrocatalytic activities toward the reduction process, especially in the case of bromides and iodides. In this work, we have investigated in detail the influences of operative parameters on the electrocarboxylation of arylic bromides in CO_2–saturated dimethylformamide (DMF) solution at the Ag cathode, aiming to optimize the process and exploit an applicable methodology. This method occurs under mild temperature and atmospheric pressure, avoiding the use of catalyst.

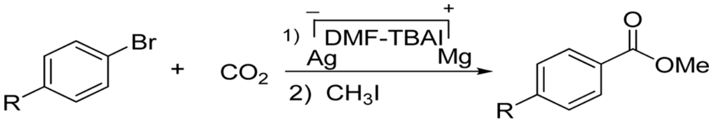
EXPERIMENTAL

Cyclic voltammograms were measured with a CHI660 electrochemical analyzer (CHI, USA). Silver (Ag), copper (Cu), nickel (Ni), and titanium (Ti) electrodes ($d = 2\,\text{mm}$) were used as working electrodes, respectively. The counterelectrode and the reference electrode were a platinum wire and Ag–AgI–0.1 M n-Bu_4NI in DMF, respectively. DMF was kept over 4-Å molecular sieves. Tetraethylammonium tetrafluoroborate ($TEABF_4$), tetrabutylammonium iodide (TBAI), and methyl p-(methoxycarbonyl) benzoate were used as received.

General Procedure for Electrochemical Carboxylation of Arylic Bromides

The galvanostatic electrolysis was carried out in a mixture of arylic bromides (0.1 M) and TBAI (0.1 M) in DMF (10 mL) under a slow stream of CO_2 in an undivided electrochemical cell equipped with a metallic ring cathode and a sacrificial Mg anode. The electrochemical carboxylation of arylic bromides and CO_2 followed the principle shown in Scheme 1.

After electrolysis, the residue was esterified by adding anhydrous K_2CO_3 (0.3 g) and CH_3I (0.6 mL) and stirring the mixture at 50 °C for 5 h. For the quantitative determination of benzoic acids by gas chromatography (GC), we converted the acids into their corresponding methyl esters. The solution was quenched by water and



Scheme 1. Electrocatalytic carboxylation of arylic bromides at Ag cathode in DMF-TBAI.

extracted with Et_2O, and the organic layers were dried over $MgSO_4$ and evaporated. The methyl esters corresponding to acids were isolated by column chromatography with petroleum ether/ethyl acetate mixtures as eluent. After isolation and identification of the products, working curves with n-decane as the internal standard were used for analysis of the electrochemical carboxylation. The methyl esters corresponding to acids were confirmed with ^1H NMR and GC-MS spectra. The spectral data of the products are given.

Methyl Benzoate

GC-MS (*m*/*z*, %): 136 (M^+, 11), 105 (29), 77 (16), 51 (5), 28 (100); ^1H NMR (500 MHz, $CDCl_3$): δ 8.03–7.41 (5H, m), 3.89 (3H, s).

Methyl p-Methoxybenzoate

GC-MS (*m*/*z*, %): 166 (M^+, 33), 135 (100), 107 (9), 77 (18), 64 (7); ^1H NMR (500 MHz, $CDCl_3$): δ 8.00–6.92 (4H, m), 3.89 (3H, s), 3.86 (3H, s).

Methyl p-Methyl Benzoate

GC-MS (*m*/*z*, %): 150 (M^+, 39), 119 (100), 91 (41), 65 (12), 39 (5); ^1H NMR (300 MHz, $CDCl_3$): δ 7.93–7.17 (4H, m), 3.86 (3H, s), 2.35 (3H, s).

4-Acetyl-benzoic Acid Methyl Ester

GC-MS (*m*/*z*, %): 178 (15), 163 (M^+, 100), 135 (20), 76 (7), 28 (37); ^1H NMR (500 MHz, $CDCl_3$): δ 8.14–8.00 (4H, m), 3.96 (3H, s), 2.65 (3H, s).

RESULTS AND DISCUSSION

Cyclic Voltammetric Behavior of Bromobenzene

Cyclic voltammograms recorded for reduction of bromobenzene at the Ag electrode in DMF containing 0.1 M $TEABF_4$ are depicted in Fig. 1. As shown in curve (a) of Fig. 1, no peaks were found. The curve (b) of Fig. 1 shows a single irreversible reductive peak (E_p) under a nitrogen atmosphere at -1.89 V that corresponds to two-electron reductive cleavage of the carbon–bromide bond. The voltammetry behavior of bromobenzene was very similar in appearence to those pictured in an earlier report pertaining to the cathodic behavior of alkyl halides at glass carbon electrodes.[12] The E_p of the bromobenzene is positively shifted from -1.89 V to -1.66 V

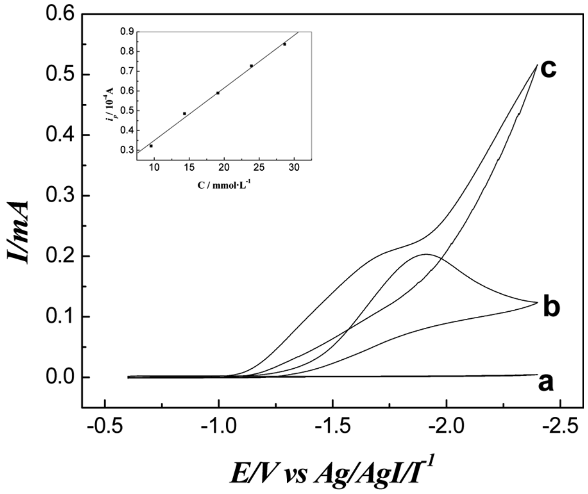


Figure 1. Cyclic voltammograms of bromobenzene recorded at Ag electrode in DMF–0.1 M $TEABF_4$. (a) DMF + $TEABF_4$; (b) a + 0.05 M bromobenzene; (c) b + CO_2. $v = 0.1\,V \cdot s^{-1}$, $t = 25\,°C$; Inset: linear relationship between i_p and concentration, $t = 25\,°C$, $v = 0.1\,V \cdot s^{-1}$.

after bubbling CO_2 into the solution. This indicates a rapid chemical reaction between CO_2 and electrogenerated radical anion. According to our previous study, the electrochemical reduction of CO_2 at the Ag cathode occurs at −2.13 V. The inset is the study of peak current (i_p) for the main reduction process of bromobenzene over the concentration range 10–30 mM, which revealed a linear relationship between i_p and concentration, showing that the reduction proceeds rather cleanly at the Ag electrode (that is, without serious filming effects).

To examine the electrocatalytic effect of the Ag electrode toward the reduction of bromobenzene, the voltammetry behaviors of bromobenzene were also investigated at the most commonly used cathodes [e.g., Cu, Ni, and Ti (Fig. 2)]. The reduction peak of bromobenzene at Cu electrode appeared at −1.87 V, which is similar to that required for its reduction at the Ag electrode (−1.89 V). Compared with the Ag electrode, an obvious thin film was formed at the Cu electrode surface after several voltammetry cycles, which was attributed to the absorption of electrogenerated intermediate species at the Cu electrode and will result in progressive degradation of the Cu cathode during the electrocarboxylation of arylic bromides. In addition, in our previously study,[13] we reported that Cu was also a good material for the reduction of CO_2. The two points mentioned previously are unfavorable to electrocarboxylation of bromobenzene. A broad reduction peak ($E_p \geq -2\,V$) appeared at the Ni or Ti electrode, which was considerably more negative than the E_p value obtained at Ag and very close to the reduction peak of CO_2.

Experimental Investigations on the Electrocarboxylation of Arylic Bromides

Bromobenzene was chosen as a model molecule to be investigated in detail, and then the investigations were extended to other arylic bromides. To optimize

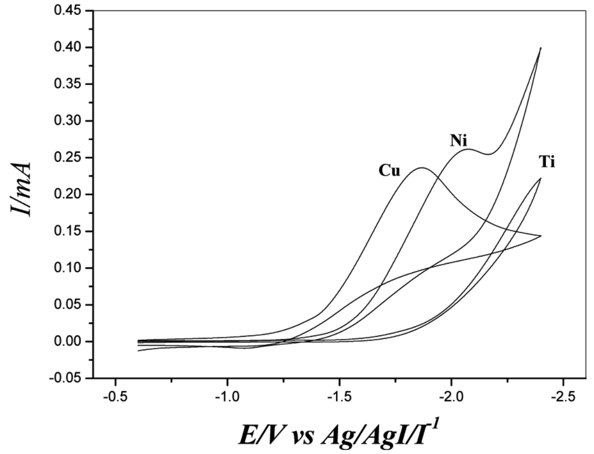


Figure 2. Cyclic voltammograms of bromobenzene in DMF–0.1 M $TEABF_4$ recorded at Cu, Ni, and Ti electrodes, $v = 0.1\,V \cdot s^{-1}$, $t = 25\,°C$.

the yields, we first focused our attention on the influences of various synthetic parameters of the process, such as the cathode electrode materials, current densities, and temperature. The results of the electrolysis are reported in Table 1.

Influence of cathode materials. The cyclic voltammograms demonstrated that Ag shows a significant electrocatalytic effect on the reduction of bromobenzene. To confirm this, we first investigated electrocarboxylation of bromobenzene at the Ag electrode (Table 1, entry 1) and then at Cu, Ni and Ti electrodes (Table 1, entries 2–4) for comparison. The electrocarboxylation yield decreased depending on the employed cathode materials in the following order: Ag > Cu> Ti > Ni. The electrolysis results accord with the result of cyclic voltammograms of bromobenzene. Owing

Table 1. Influence of various experimental parameters on the yield of benzoic acid[a]

Entry	Cathode	Current density ($mA \cdot cm^{-2}$)	Temp. (°C)	Yield[b] (%)
1	Ag	4.54	0	78
2	Ti	4.54	0	9
3	Ni	4.54	0	4
4	Cu	4.54	0	41
5	Ag	2.27	0	56
6	Ag	3.97	0	63
7	Ag	5.11	0	71
8	Ag	5.67	0	55
9	Ag	4.54	20	40
10	Ag	4.54	10	64
11	Ag	4.54	−10	65

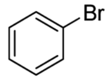
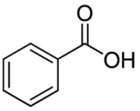
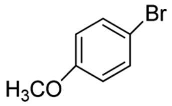
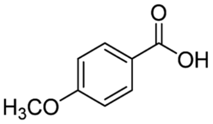
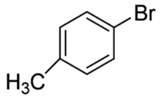
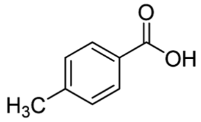
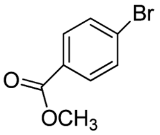
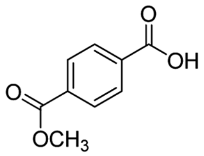
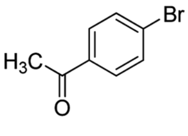
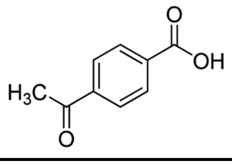
[a] General conditions: DMF = 10 mL, bromobenzene = 0.1 M, TBAI = 0.1 M, electric charge 2.5 F mol^{-1}, Mg as anode.

[b] GC yield, based on the starting bromobenzene.

to the very negative potentials required for the reduction of bromobenzene at Ni and Ti electrodes, concomitant reduction of CO_2 probably took place, which resulted in high consumption of charge and gave oxalate, CO and carbonate.[14]

Influence of current density. The yields are also strongly affected by the current density (Table 1, entries 1, and 5–8). The working electrode potential will become more negative with the increase in current density, so there will be other undesired reactions taking place on the electrode surface, such as the reduction of CO_2 or TBAI, which will decrease the carboxylation yield. Tributylamine was detected in GC-MS, which was generated by the dissociation of supporting electrolyte. On the other hand, the lower the current density is, the more positive the electrode potential will be. Thus, the proportion of the Faradaic current will decline, which will also decrease the carboxylation yield. As a result, the optimized current density is $4.54\,mA \cdot cm^{-2}$ on the electrodes of Mg-Ag.

Table 2. Electrochemical carboxylation of arylic bromides in DMF–TBAI[a]

Entry	Substrate	Product	Yield[b] (%)
1[c]			78
2[d]			69
3[e]			62
4[f]			60
5[g]			30

[a] General conditions: Ag cathode, Mg anode, $t = 0\,°C$.
[b] GC yield, based on the starting arylic bromides.
[c] This experiment (Table 1, entry 1) was repeated here for clarity.
[d] Current density $= 5\,mA \cdot cm^{-2}$, electric charge $= 2\,F\,mol^{-1}$.
[e] Current density $= 4\,mA \cdot cm^{-2}$, electric charge $= 2.5\,F\,mol^{-1}$.
[f] Current density $= 4.33\,mA \cdot cm^{-2}$, electric charge $= 2\,F\,mol^{-1}$.
[g] Current density $= 5\,mA \cdot cm^{-2}$, electric charge $= 2\,F\,mol^{-1}$.

Influence of temperature. To investigate the effect of the temperature on the electrochemical carboxylation of bromobenzene, electrolysis was carried out at different temperatures (Table 1, entries 1 and 9–11). According to the Arrhenius equation, the activation energy required for the electroreduction of bromobenzene decreased with increasing temperature. Conversely, the solubility of CO_2 in DMF solution also declined with elevating temperate. In view of the two contradictory factors, temperatures either too high or too low are unfavorable to the electrochemical carboxylation of bromobenzene. Hence, the optimal temperature is 0 °C.

Electrocarboxylation of other arylic bromides. To test the applicability of this electrochemical carboxylation, the investigation was extended to other arylic bromides. The results are reported in Table 2. In all cases, the corresponding carboxylic acids were obtained. It indicates that this electrochemical synthesis works well for arylic bromides.

CONCLUSION

In conclusion, we have demonstrated a simple and efficient electrochemical route with a silver cathode for electrocarboxylation of arylic bromides. The reaction does not need the presence of a catalyst and can be carried out under mild temperature and atmospheric pressure conditions. Under suitable conditions, arylic bromides were electrochemically reduced in the presence of CO_2 to the corresponding carboxylic acids. This electrochemical route appears to be a simple and efficient approach for electrocarboxylation of arylic bromides.

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