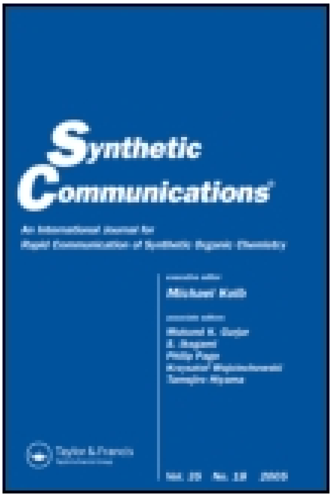

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Electrochemical Carboxylation of 2-Iodoaromatic Compounds

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ABSTRACT

The electrochemical reduction of a series of 2-iodoaromatic substituted compounds in acetonitrile under an atmospheric pressure of carbon dioxide leads to ortho-substitued aromatic carboxylic acid. The maximum yield of acid obtained by electrolysis performed in a diaphragmless cell at low temperature (5°C) with a sacrificial magnesium anode and by the use of a low current density was slightly higher than 70%.

Key Words: Electrochemical carboxylation; 2-Iodoaromatic substituted compounds; Carbon dioxide.

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INTRODUCTION

The C–X bond of organic halides can be cleaved through electrochemical reduction under suitable conditions. In most cases and in particular with substituted aromatic or aliphatic halides, the generated carbanion after two electron transfer can react with electrophile derivatives as carbon dioxide to lead the corresponding carboxylic acids.[1–6] Nevertheless, this reaction maybe competed with the protonation reaction by residual water.[7,8]

On the other hand, previous work has shown the possibility of electrochemical carboxylation of a large variety of compounds such as aldehydes and ketones [9] or gem-dihalides.[10] In the present paper, we report a promising procedure for the synthesis of ortho-substituted benzoic acid derivatives by reductive carboxylation of 2-iodoaromatic compounds (Sch. 1) in aprotic media. Coulometric and analytical results are discussed.

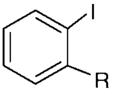
RESULTS AND DISCUSSION

Cyclic voltammetry was carried out in acetonitrile (ACN) solution with tetrabutylammonium tetrafluoroborate ($TBATF_4$) as supporting electrolyte. The voltammograms of compounds **1a**, **1b**, and **1c** show one irreversible wave (Fig. 1).

This wave is attributed to the cleavage of the C–I bond after two electrons transfer.[11] The compounds **1d** and **1e** exhibit two irreversible peaks. The first one corresponds to the cleavage of C–I bond, while the second is attributed to the reduction of the carbonyl function.[12]

Table 1 shows that the first peak potentials E_p of **1e** is less cathodic than that of the other studied compounds, owing to the electron withdrawing effect of the carboxylic substituent.

In CO_2 saturated acetonitrile solution, only a slight increase of the cathodic peak was observed at a scan rate of 0.05 V sec^{-1} (Fig. 2).



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	1a	**1b**	**1c**	**1d**	**1e**
R	NH_2	OME	CH_2OH	NCO	COOH

Scheme 1.

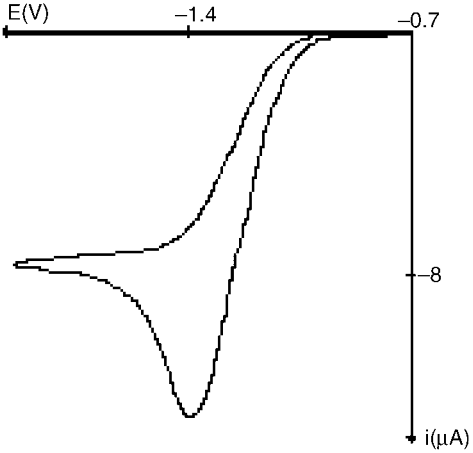


Figure 1. Cyclic voltammogram of **1a** in ACN–TBAP 0.1 M. Hanging mercury drop electrode (area ~ 1 mm^2). Reference electrode: Ag/AgI/I$^-$ 0.1 M. Concentration: $C = 5 \times 10^{-3}$ M. Sweep rate: $v = 50\,\mathrm{mV\,sec^{-1}}$.

This result suggests the occurrence of an interaction between the reduced iodoaromatic compounds and carbon dioxide.

In fact E_p varies linearly with the logarithm of the scan rate (Fig. 3), the average slope $\partial E_p/\partial \log v$ is equal to 60 mV per decade and the value of the peak width is about 120 mV at a scan rate of 0.1 V sec^{-1}.

These data are in agreement with a reduction controlled by the kinetic of the heterogeneous electron transfer. The lower value for the transfer coefficient α ($\alpha \approx 0.2$–0.4) indicates that the reduction potential is more negative than the standard potential of the rate determining electron transfer.

Table 1. Characteristic of cyclic voltammetric curves of some *o*-iodoaromatic compounds in ACN–TBAP 0.1 M.

	First peak		Second peak	
Substrates	E_p (V) vs. SCE	I_p (μA)	E_p (V) vs. SCE	I_p (μA)
1a	−1.60	3.1	—	—
1b	−1.61	2.9	—	—
1c	−1.75	3.5	—	—
1d	−1.70	3.2	−1.85	6.30
1e	−1.08	2.8	−1.77	3

Note: Hanging mercury drop electrode. Reference electrode: SCE 3 M. Concentration: $C = 5 \times 10^{-3}$ M. Sweep rate: $v = 100\,\mathrm{mV\,sec^{-1}}$.

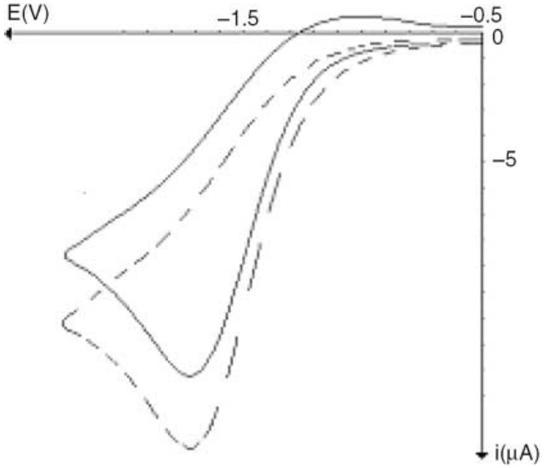


Figure 2. Cyclic voltammogram of **1b** in the presence of CO_2 in ACN−TBAP 0.1 M. Hanging mercury drop electrode (area $\sim 1\,mm^2$). Reference electrode: Ag/AgI/I^- 0.1 M. Sweep rate: $v = 50\,mV\,sec^{-1}$. Concentration: $C = 3 \times 10^{-3}\,M$.

So, the reduction of the 2-iodoaromatic compounds followed a mechanism where electron transfer and cleavage of the carbon−halogen bond take place simultaneously at the working electrode (Eq. 1, Sch. 2).

A fast reduction of the radical entity may occur at the working potential owing to the very negative potential required for the reduction of the substrates (Eq. 2, Sch. 2).

The anion maybe trapped by the carbon dioxide to give the corresponding carboxylate (Eq. 3, Sch. 2).

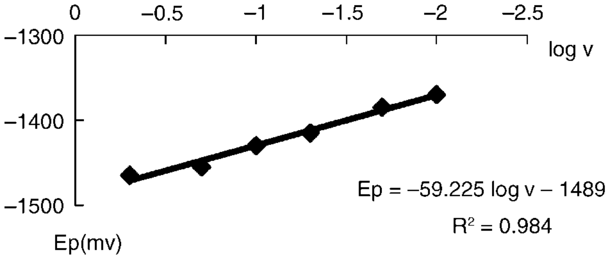
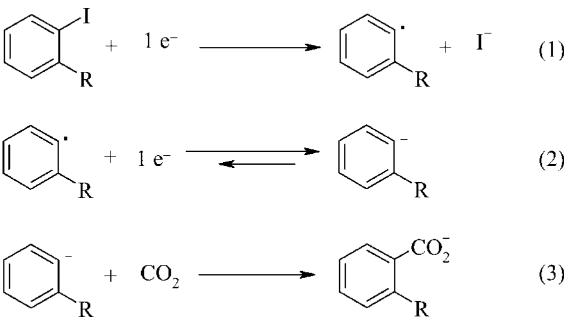


Figure 3. Variation of the peak potential of **1b** in ACN−TBAP 0.1 M as a function of the scan rate range. Hanging mercury drop electrode. Reference electrode: Ag/AgI/I^- 0.1 M. Concentration: $C = 2.5 \times 10^{-3}\,M$.



Scheme 2.

However, the chemical yield is never equal to 100% because of the competing protonation reaction by residual proton impurities.

The preparative electrolysis of compound **1a**–**1d** conducted in acetonitrile solution under a slow stream of carbon dioxide gas with magnesium anode, gave the corresponding aromatic carboxylic acid in good yield after consumption of 2 faraday per molecule. This confirms the above suggested mechanism. The anodic process which consists of oxidation of magnesium anode may contribute to the stabilisation of the electrogenerated carboxylate anion by neutralisation of the Lewis acidity of Mg^{2+}. Indeed when a platinum anode is used instead of a magnesium or zinc electrode, a lower yield of orthobenzoic acid is achieved (Table 2).

In the same conditions, the macroelectrolysis of **1e** leads only to benzoic acid because of a rapid autoprotonation reaction of the electrogenerated anion by the substrate.

On the other hand, we investigated the effect of some parameters like the current density, the temperature, and the number of transferred electron on the yield of the corresponding anthranilic acid and *o*-methoxy benzoic acid followed by HPLC method.

Table 2. Effect of the anode nature on the yield of some orthobenzoic acids get after reductions of **1a** and **1b** in presence of carbon dioxide.

Anode nature	Yield of anthranilic acid (%)	Yield of *o*-methoxy benzoic acid (%)
Platinum	5	6.2
Aluminum	44.60	47.80
Magnesium	45.20	74.31
Zinc	62	51.10

Table 3. Variation of the yield of anthranilic acid with the temperature.

Temperature (°C)	Yield of anthranilic acid (%)
5	62
10	56
20	59

The experimental results showed (Table 3), a slight decrease of the electrocarboxylation yield upon increasing the temperature. This behaviour maybe ascribed to a decrease of solubility of carbon dioxide, since the CO_2 dissolution reaction is exothermic.[13]

Moreover, the electrocarboxylation yield (Table 4) is increased by lowering the current density.

Aromatic acids have been identified by spectroscopic methods and their spectral characteristics are summarised below:

2a. Yield: 59%; m.p: 144°C (lit. 144–146°C); IR $\nu_{C=O} = 1680\,cm^{-1}$; NMR: ^1H, 7.2 (s, 2H); 6.8–8.0 (μ, 4H); 11 (s, 1H); ^{13}C, 111, 116, 116.58, 131.84, 133.99, 150.80, 170.70.

2b. Yield: 63%; m.p: 99°C (lit. 98–100°C); IR $\nu_{C=O} = 1672\,cm^{-1}$; NMR: ^1H, 3.60 (s, 3H); 7.4–7.9 (μ, 4H); 10.90 (s, 1H); ^{13}C, 53, 126.8, 127.8, 128.15, 128.75, 130.8, 140, 171.

2c. Yield: 54%; IR $\nu_{C=O} = 1672\,cm^{-1}$; NMR: ^1H, 2.2 (s, 1H); 4.6 (s, 2H); 7.2–7.5 (m, 4H); 10.50 (s, 1H); ^{13}C, 65, 126.87, 127.18, 127.81, 128.42, 128.71, 140.96, 170.50.

2d. yield: 69%; IR $\nu_{C=O} = 1666\,cm^{-1}$; NMR: ^1H, 3.3 (s, 4H); 7.3–7.85 (μ, 4H); ^{13}C, 61.5, 127.3, 124.7, 128.15, 128.85, 131.3, 134.1, 166.3.

2e. Yield: 75%; m.p: 206°C (lit. 206–208°C); IR $\nu_{C=O} = 1713\,cm^{-1}$; NMR: ^1H, 11.50 (s, 1H); 7.4–8.20 (μ, 5H); ^{13}C, 128.31, 128.59, 129.33, 130.24, 133.65, 133.90, 172.49.

Table 4. Effect of the current density on the yield of anthranilic and *o*-methoxy benzoic acids.

Current density ($mA\,cm^{-2}$)	Yield of anthranilic acid (%)	Yield of *o*-methoxy benzoic acid (%)
5	63.10	74.31
10	62	68.37
20	55	61.56

EXPERIMENTAL

The IR spectra ($CHCl_3$) were determined on a Perkin–Elmer 1000 PC spectrophotometer. The NMR spectra were recorded on a Brucker AC 300 MHz spectrometer in $CDCl_3$ containing tetrametylsilane as an internal standard.

All the experiments are performed in ACN purchased from Fluka and was dried over anhydrous magnesium sulphate $MgSO_4$, distilled under vacuum and kept over activated alumina. The supporting electrolyte is 0.1M $TBATF_4$ (Fluka). It was used without further purification.

The cyclic voltammetry measurements were performed using a PAR scanning potentiostat model 362. The cell was a three-electrode type with hanging mercury drop as a working electrode, a platinum wire as counter electrode and SCE 3 M or $Ag/AgI/I^-$ 0.1 M system as a reference electrode.

Macroscale electrolysis is carried out in an undivided cell on a stirred mercury pool as a cathode and a magnesium anode. The current density is controlled by a Tacussel-type PJT 35-2 potentiostat and the amount of electricity is measured with a Tacussel IG5 integrator. All the electrolyses were carried out under continuous bubbling of carbon dioxide in the solution containing 0.1 M of the substrate (the corresponding mass of substrate, about 1 g was dissolved in 50 mL of a solution of acetonitrile containing the supporting electrolyte). At the end of the electrolysis, the catholyte was acidified by HCl 2M solution, then extracted by diethyl oxide and the organic solution was dried over $MgSO_4$. The yields obtained analytically are followed by HPLC using Perkin–Elmer liquid chromatography equipped with C18 column and an auto control UV detector. The eluting solution was 70% acetonitrile–30% phosphate buffer.

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