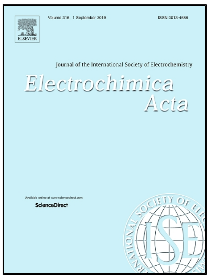

Electrocarboxylation of halobenzonitriles: An environmentally friendly synthesis of phthalate derivatives

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Electrocarboxylation of halobenzonitriles: An environmentally friendly synthesis of phthalate derivatives.

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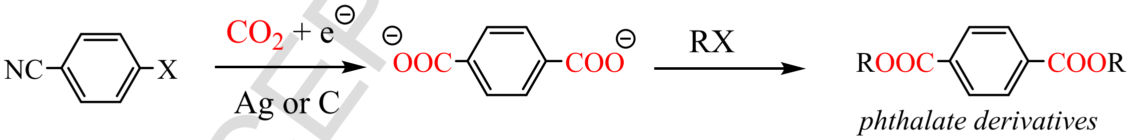
Abstract

This manuscript presents an efficient approach for producing high valuable compounds using CO_2 as building block. The methodology employed is based on electrochemical techniques, which allow performing eco-friendly chemistry solutions and maintaining the aim of offering a potential long-term strategy for reducing the CO_2 emissions in the atmosphere, while obtaining useful compounds, such as aromatic acids and phthalate derivatives. This work describes the electrochemical reduction behavior of 4-halobenzonitrile compounds using Glassy Carbon and Silver as cathodes under inert and carbon dioxide atmosphere. Controlled potential electrolysis of 4-halobenzonitriles under CO_2 allows obtaining, in very good yields, the corresponding mono- and di-carboxylated organic compounds in CO_2-saturated solutions of dimethylformamide containing 0.1 M of tetrabutylammonium tetrafluoroborate. Electro-catalytic effects are seen when Ag is used a cathode, which give very high yields, especially as regards di-carboxylated products. The methodology offers a new "green" route for the synthesis of different phthalate derivatives, which can be potentially used for making plastic polymers in a more environmentally friendly way.

Keywords: Carboxylation • Electrochemistry • Electrolysis • 4-halobenzonitrile • Cyclic voltammetry

TOC:



Highlights:

Disclosure of electrochemical reduction mechanism of halobenzonitrile compounds using Glassy Carbon and Silver cathodes under inert and CO_2 atmosphere.

Electrocarboxylation of halobenzonitriles for producing high valuable compounds using CO_2 as building block.

Tuning electrochemical reactivity of CO_2 using Silver cathodes.

New "green" route for the synthesis of different phthalate derivatives.

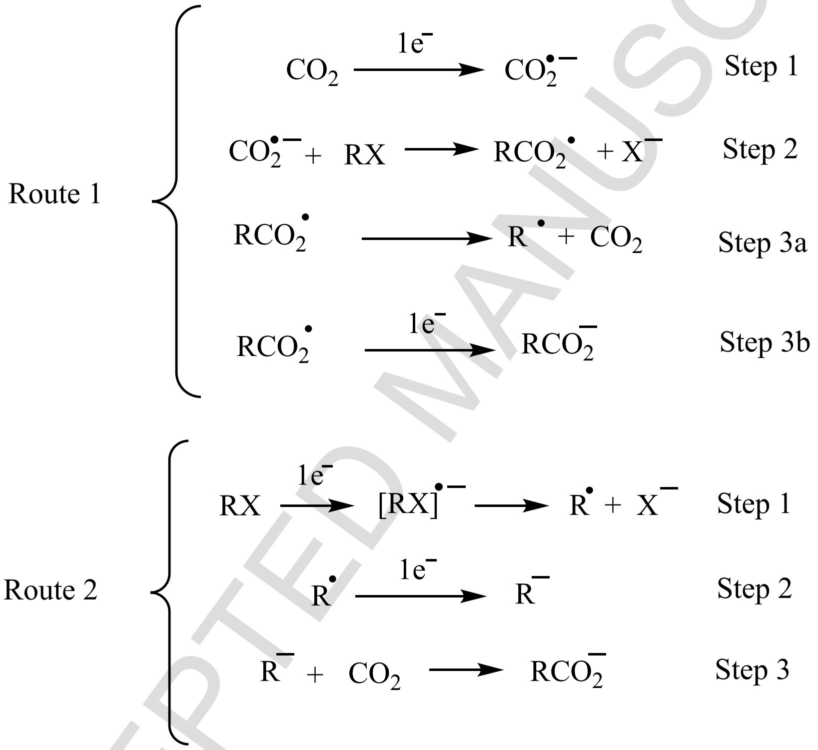
1. Introduction

The increasing concentration of CO_2 in the atmosphere is a fact that threatens the economy and the sustainability of the planet. In spite of the precautions and actions that have been taken for reducing the emissions arising from fuel consumption processes, more efficient and sustainable ways to ameliorate the climate change problem still need to be investigated, not only for improving the quality life, but also because non-renewable sources are, indeed, limited and still in high demand world-wide[1–3]. Possible alternatives for reducing CO_2 emissions are using low carbon-rich forms as fuel, and capturing and storing CO_2, and for what seems to be the most practical approach is to use it as a carbon building block for producing high valuable compounds[4,5]. In this sense, one of the problems associated with the chemical utilization of CO_2 is related to its inherent thermodynamic stability and kinetic inertness, hence, direct or indirect activation of the functionalization process is required. On the other hand, the use of CO_2 as C1 feedstock has some advantages as an abundant, non-toxic, non-flammable, and a quite easily available resource[6].

Transformation of CO_2 studies to either convert the CO_2 into more reduced forms or use it as a carboxylating agent in combination with different molecules, have been widely described in the literature. There are also a few examples reported where the CO_2 acts as a C1 building block, including: methane[7–9], methanol[10,11], ethylene glycol[12,13], polyurethanes, urea[14] cyclic carbonates (propylene carbonate)[15–18], carbamates[19–21], and ibuprofen[22–25]. Nevertheless, these transformations are normally associated with high pressures and/or temperatures, low efficiency processes, formation of byproducts, multiple synthetic steps, etc. In the present work, we have developed an electrochemical method in order to overcome those disadvantages, that is, a more environmentally respectful strategy for the utilization of CO_2 to produce high value-added products, and at the same time, a potential way to confront the climatic change at a long-term perspective. In fact, electrochemistry can be seen as a branch of Green Chemistry as it is in accordance with a set of principles for reducing the use of hazardous substances in the design of processes and manufacture of chemical products[26]. The benefits of using electrochemical experiments include mild chemical and process conditions, easy control, high process selectivity, novel chemistry available, safer operation, electrons as inexpensive reagents in comparison with the typical redox agents. In addition, the electrons are capable of acting as heterogeneous catalysts able to be easily isolated from the products.

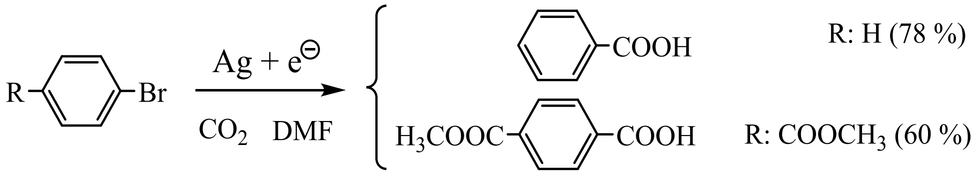
Classical electrochemistry of CO_2 consists of the electro-reduction of the molecule in the presence of an organic aprotic or protic solvent and supporting electrolyte. Apart from the solvent, the nature of the working electrode (WE), the temperature, and the concentration are other important factors. These can be more or less adjustable, not only for tuning the reduction potential of CO_2 but also to modulate the subsequent formation of different products (such us oxalate, carbonate, carbon monoxide, etc.)[27,28].

The electrochemical promoted approaches for achieving carboxylated organic valuable products can mainly be tackled in strategies (Scheme 1). In the first approach, the electrochemical generation of the CO_2 radical anion ($CO_2^{\cdot -}$) requires a fairly negative potential (Scheme 1, route 1)[29], making this option costly in terms of energy consumed. In the second approach (Scheme 1, route 2), the electrochemical reduction takes places in the organic molecule (for instance, an organic halide RX); which is a more easily reducible compound than CO_2. After being reduced ($RX^{\cdot -}$), cleaves into the anion halide (X^-) and the organic radical ($R^{\cdot}$) (step 1). The electro-generated radical can be further reduced to form the corresponding organic anion (R^-) (step 2). If this organic anion is stable enough in the electrolytic media, it will nucleophilically attack the CO_2 dissolved in the solution, and therefore the CO_2 molecule would be added, leading to a carboxylate derivative (RCO_2^-) (step 3).



Scheme 1. Electrochemical strategies used for the synthesis of carboxylated products

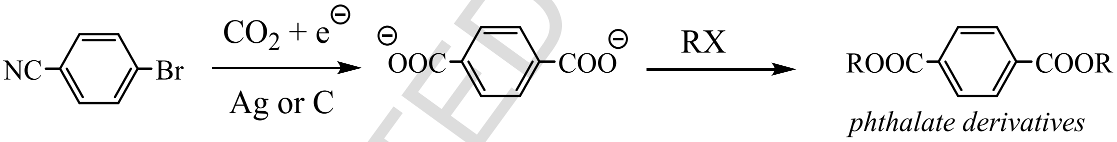
There are some examples in the literature following the second carboxylation strategy. Gennaro *et.al* have reported electro-reduction processes that lead to carboxylation of different organic[30–32], and non-organic compounds in various solvents and/or working electrodes[33–36]. In one of these studies, they showed that exhaustively controlled potential electrolysis (at -1.5 V vs SCE) of electrochemical reduction of benzyl halides in acetonitrile, using silver as working electrode, under of CO_2 atmosphere at 25ºC, yielded up to c.a. 45% of phenylacetic acid[36] Zhang *et al* also investigated the electro-catalytic carboxylation of bromobenzene derivative using a silver cathode in the presence of CO_2 (at 0ºC) achieving a 78% yield, Scheme 2[37].



Scheme 2. Electrolysis of aryl bromides in the presence of CO_2 in DMF using Ag as working electrode[37].

According to the above mentioned electrocarboxylation strategies and previous studies published[36,37], the use of halobenzonitriles seems to be an ideal starting material for obtaining carboxylated products. The presence of the CN group in the molecule would help to reduce the energy required for the reduction process, since it would act as an electrophore. Thus, the carbon-halogen bond cleavage reaction will occur at less negative potential. Note, that the nature of the electrode would also modify the reduction potential value, so the use of Ag as cathode due to its electrocatalytic properties would also help to decrease the reduction potential value.

Thus, the aim of this study is to valorize CO_2 using halobenzonitriles as a starting material for obtaining carboxylated derivatives using a "green" electrochemical route. The electrocatalytic properties of using Ag instead of C as cathode in the electrochemical reduction mechanism of 4-halobenzonitriles will also be analyzed. It is important to note that the synthesis of dicarboxylated compounds using this strategy would potentially open a very versatile and sustainable approach for making plastic polymers in a foreseeable future (Scheme 3).



Scheme 3. Electrochemical strategy used in this work for synthesizing phthalate derivatives

2. Experimental section

2.1. Reagents

All the commercially available reagents were purchased with the maximum purity and used without previous purification. Solvents: Chloroform, SDS, Carlo Erba, for HPLC stabilized with ethanol, ≥ 99.9%. Deuterated chloroform ($CDCl_3$), Euriso-top, 99.8%. Dichloromethane, Carlo Erba, for HPLC, stabilized with ethanol, ≥ 99.9%. Diethyl ether, SDS, Carlo Erba, purity ≥ 99.0% (GC). *N*, *N'*-dimethylformamide (DMF), SDS, for synthesis. Toluene, SDS, pure for synthesis. Supporting electrolytes: tetrabutylammonium tetrafluoroborate ($TBABF_4$), Sigma-Aldrich, 99%. Electro-active substances: 4-Bromobenzonitrile, Sigma-Aldrich, 99%. 4-Cyanobenzoate methyl ester, Sigma-Aldrich, 99%. 4-Chlorobenzonitrile, Sigma-Aldrich, 99%. 4-Fluorobenzonitrile, Sigma-Aldrich, 99%. 4-Iodobenzonitrile, Sigma-Aldrich, 99%. 9-Fluorenone puriss., Fluka, ≥ 99%. Benzonitrile, Sigma-Aldrich, 99%. Carbon Dioxide, Linde, purity ≥ 99.9993%. Dimethyl terephthalate, Fluka, ≥ 99.0% (GC). Other reagents: 2-Bromoethylbenzene, Sigma-Aldrich, 98%. Hydrochloric acid (HCl), Sigma-Aldrich, reactive 37%. Bromoethane (BrEt), Sigma-Aldrich, 98%. Methyl iodide (CH_3I), Sigma-Aldrich, 2.0 M solution in tert-butylmethyl ether, and anhydrous sodium sulfate, Na_2SO_4, Sigma-Aldrich, 99.0%.

2.2. *Methodology*

2.2.1. *Cyclic voltammetry*

Firstly, a solution of the electro-active substance is prepared with a known concentration (between 10 and 16 mM) containing 0.10 M of a supporting electrolyte (tetrabutylammonium tetrafluoroborate, $TBABF_4$) in 10 ml of dimethylformamide (DMF). Once the solution is introduced into the cell, it is deoxygenated (or CO_2 removed) through an influx of an inert gas, Ar or N_2, a process that is repeated between measurements when the cell is opened to clean the working electrode. The working electrode is a vitreous carbon disk of 1mm diameter. It is polished using a 1 mm diamond paste before each new measurement with a mixture of lubricant and ethanol. The electrochemical used for the set-up of the three-electrode system is conical. The counter electrode is a Pt disk of < 1 mm diameter. All the potentials are reported versus an aqueous saturated calomel electrode (SCE) isolated from the working electrode compartment by a salt bridge. The salt solution of the reference calomel electrode is separated from the electrochemical solution by a salt-bridge ended with a frit, which is made of a ceramic material, allowing ionic conduction between the two solutions and avoiding appreciable contamination. Ideally, the electrolyte solution present in the bridge is the same as the one used for the electrochemical solution, to minimize junction potentials. The cyclic voltammetry studies are performed for each concentration of electro-active substance at different scan rates between 0.1 and 1.0 $V \cdot s^{-1}$. Overall, the I-E curves obtained lead to the determination of the electrochemical (E_p, ΔE_p, $I_p/(c \cdot (v)^{1/2})$), and thermodynamic parameters (E^o) of the target molecule.

2.2.2. *Controlled Potential Electrolysis*

For preparing the solutions to be electrolyzed, a known amount of the 4-halobenzonitrile is firstly dissolved in DMF/0.1M $TBABF_4$. The solution is then deoxygenated with an influx of an inert gas (N_2 or Ar), and an initial voltammogram is recorded before starting the electrolysis. The solution is then saturated with CO_2 (determined because no increase in intensity is observed in the I-E response, despite continuing bubbling CO_2 into it), and the electrolysis is immediately started. The applied potential for the reduction of the electro-active substance is about 100 mV more negative than the corresponding reduction wave. A graphite rod was used as a working electrode and a Pt as a counter electrode, isolated from the solution by a salt bridge with electrolyte solution, and an SCE was used as a reference electrode, which was also separated from the solution by a salt bridge. The electrolysis is finished, either when the desired charge is consumed according to the Faraday's Law, or when the initial intensity has been reduced by over 90% (exhaustive electrolysis). At this point, 4 equivalents of an alkylating agent are added (R-Y: R: methyl, ethyl, or 2-ethylbenzene; Y: I or Br) to the solution and kept under constant N_2 bubbling for 15-20 minutes.

The electrolyzed samples are then extracted with ether/HCl 1M in the same proportion. The products that are more soluble in acid water (HCl 1M) (x3) being extracted from the organic phase, and later with H_2O (x2). The aqueous acid phase is finally extracted using ether. The resulting organic phase is dried with anhydrous sodium sulphate, filtered, and evaporated in a rotating evaporator. To finish, the crude reaction is analyzed using ^{1}H-NMR and GC-MS and compared with pure samples.

Typical Procedure for Preparative Electrolysis − Generation of isolated carboxylated products by preparative Electrolysis: a solution solution of the halobenzonitrile (50-100 mg), which contains 0.1 M $TBABF_4$ is electrolyzed following the above-mentioned procedure. Four equivalents of the alkylaying agent were added at the end of the electrolysis. After that the electrochemical cell was bubbled with nitrogen for 10 minutes. Later an extraction with ether/HCl 1M was performed, and the crude product [or mixture of product(s)] was purified or separated by chromatography on silica gel eluting with mixtures of hexane/dichloromethante (40:60). The yield obtained for isolated products in pure form were a 5 % less than the firstly determined for the non-purified crude.

Benzonitrile: GC-MS (70 eV): m/z (%): 103.0 (100) [M+], 76.0 (36) [M+ - CN], 63.0 (4), 52.0 (6), 51.0 (12).

4-cyanobenzoate methyl ester: GC-MS (70 eV): m/z (%): 161.0 (22) [M+], 130.0 (100) [M+- CH3O], 102.0 (44) [M+- C2H3O2], 75.0 (14%), 51.0 (8). 1H-NMR (250 MHz, CDCl3) δ (ppm): 3.96 (s, 3H), 7.75 (d, 8.33 Hz, 2H), 8.14 (d, 8.33 Hz, 2H).

Dimethyl terephthalate: GC-MS (70 eV): m/z (%): 194.0 (18) [M+], 163.0 (100) [M+ - CH3O], 135.0 (22) [M+ - C2H3O2), 120.0 (8) [M+ - C3H6O2], 103.0 (13) [M+ - C3H6O3], 92.0 (3), 76.0 (13) [M+ - C4H6O4]. 1H-NMR (250 MHz, CDCl3) δ (ppm): 3.95 (s, 6H), (s, 8.10 Hz, 4H).

Diethyl terephthalate: GC-MS (70 eV): 175.0 (13) [M$^+$], 147.0 (34) [M$^+$ - C_2H_5], 130.0 (100) [M$^+$ - C_2H_5O], 102.0 (42) [M$^+$ - $C_3H_5O_2$], 87.0 (5), 75.0 (13) [M$^+$ - $C_4H_5O_2N$].

Terephthalic acid monoethyl ester: GC-MS (70 eV): m/z (%) 194.0 (11) [M$^+$], 166.0 (35) (M$^+$ - C_2H_5], 149.0 (100) [M$^+$ - C_2H_5O], 121.0 (17) [M$^+$ - $C_3H_5O_2$], 104.0 (6) [M$^+$ - $C_3H_6O_3$], 76.0 (9) [M$^+$ - $C_4H_6O_4$], 65.0 (20), 51.0 (5).

4-cyanobenzoate ethyl ester: GC-MS (70 eV): m/z (%): 222.1 (6) [M$^+$], 194.1 (20) [M$^+$ - C_2H_5], 177.1 (100) [M$^+$ - C_2H_5O], 166.0 (35), 149.0 (86) [M$^+$ - $C_3H_5O_2$], 132.0 (2) [M$^+$ - $C_4H_{10}O_2$], 121.0 (19) [M$^+$ - $C_5H_{10}O_2$], 104.0 (24) [M$^+$ - $C_5H_{10}O_3$], 76.0 (23) [M$^+$ - $C_6H_{10}O_4$], 65.1 (21), 51.0 (4).

Diethyl terephthalate: GC-MS (70 eV): 175.0 (13) [M^+], 147.0 (34) [M^+ - C_2H_5], 130.0 (100) [M^+ - C_2H_5O], 102.0 (42) [M^+ - $C_3H_5O_2$], 87.0 (5), 75.0 (13) [M^+ - $C_4H_5O_2N$].

Terephthalic acid monoethyl ester: GC-MS (70 eV): m/z (%) 194.0 (11) [M^+], 166.0 (35) (M^+ - C_2H_5], 149.0 (100) [M^+ - C_2H_5O], 121.0 (17) [M^+ - $C_3H_5O_2$], 104.0 (6) [M^+ - $C_3H_6O_3$], 76.0 (9) [M^+ - $C_4H_6O_4$], 65.0 (20), 51.0 (5).

4-cyanobenzoate ethyl ester: GC-MS (70 eV): m/z (%): 222.1 (6) [M^+], 194.1 (20) [M^+ - C_2H_5], 177.1 (100) [M^+ - C_2H_5O], 166.0 (35), 149.0 (86) [M^+ - $C_3H_5O_2$], 132.0 (2) [M^+ - $C_4H_{10}O_2$], 121.0 (19) [M^+ - $C_5H_{10}O_2$], 104.0 (24) [M^+ - $C_5H_{10}O_3$], 76.0 (23) [M^+ - $C_6H_{10}O_4$], 65.1 (21), 51.0 (4).

Diphenethyl terephthalate: GC-MS (70 eV): m/z (%) 374.4 [M^+], 253.1 (6) [M^+ - C_8H_9O], 149.0 (12) [M^+ - $C_{16}H_{18}O$], 121.1 (5) [M^+ - $C_{17}H_{18}O_2$], 104.1 (100) [M^+ - $C_{17}H_{18}O_3$], 91.1 (5) [M^+ - $C_{17}H_{15}O_4$], 77.1 (3) [M^+ - $C_{18}H_{17}O_4$], 65.1 (5), 51.1 (1).

4-cyanobenzoate phenethyl ester: GC-MS (70 eV): m/z (%) 251.3 [M^+], 130.0 (28) [M^+ - C_8H_9O], 104.1 (100) [M^+ - C_9H_9ON], 91.1 (13) [M^+ - $C_9H_6O_2N$], 77.1 (M^+ - $C_{10}H_8O_2N$], 65.1 (5), 51.1 (5).

3-phenylpropionitrile: GC-MS (70 eV): m/z (%): 131.1 (25) [M^+], 103.1 (3) [M^+ - 91.1 (100) [M^+ - C_2H_2N], 77.1 (5) [M^+ - C_3H_4N], 65.1 (12), 51.1 (7).

Benzoate phenethyl ester: GC-MS (70 eV): 226.3 [M^+], 104.1 (100) [M^+ - C_8H_9O], 91.1 (8) [M^+ - $C_8H_7O_2$], 77.0 (33) [M^+ - $C_9H_9O_2$], 65.0 (4), 51.0 (10).

2.2.3. Instrumentation

The cyclic voltammetry at different scan rates and controlled potential electrolysis are performed using a PAR 273A potentiostat controlled by a computer. Powersuite software is used for data acquisition and data treatment.

^{1}H NMR spectra were recorded on a Bruker DPX360 (360 MHz) spectrometer and GC-MS analysis were performed using an Agilent Technologies 6850 GC instrument with a 5975C detector.

3. Results and Discussion

3.1. Electrochemistry of 4-halobenzonitriles under N_2 atmosphere

A study has been conducted order to establish the optimal experimental conditions for the optimal electrochemical capture of CO_2, the electrochemical behavior of 4-halobenzonitriles (F, Br, Cl and I derivatives). Cyclic voltammograms of a 10 ml solution in DMF using 0.1M of tetrabutylammonium tetrafluoroborate (TBABF4) were recorded at different scan rates (from 0.10 a 1.0 V s^{-1}) using Ag (solid lines) or Glassy Carbon (GC, dotted line) as working electrodes under N_2 atmosphere for each halobenzonitrile derivative (Figure 1).

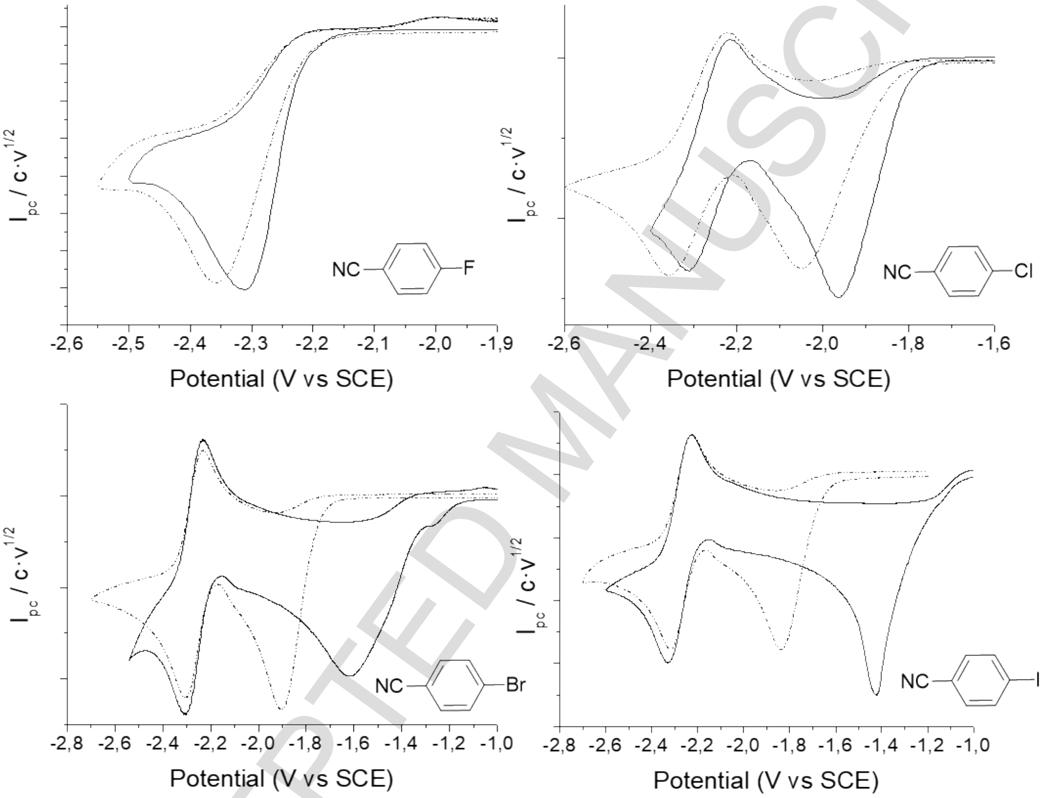


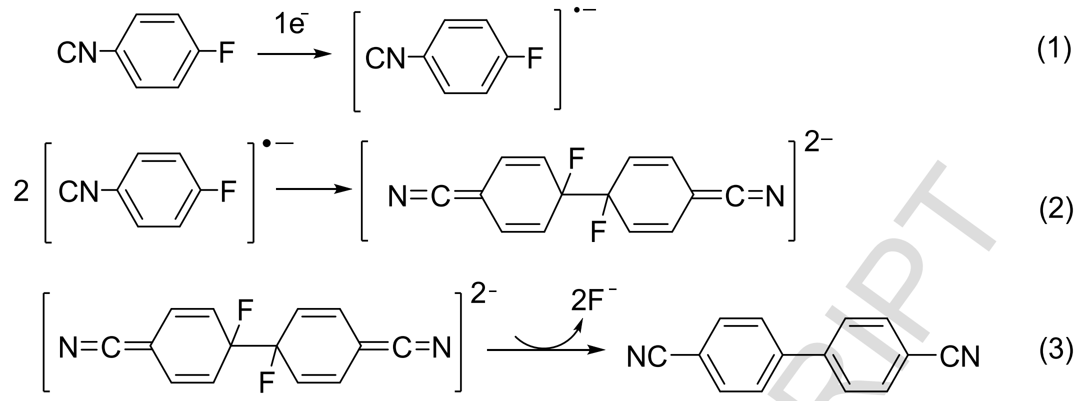
Figure 1. Cyclic voltammograms of 5-15 mM 4-halobenzonitriles (X: F, Cl, Br and I) solutions using Ag (solid line) and GC (dotted lines) in DMF/0.1M $TBABF_4$ under nitrogen atmosphere. Scan rate: 0.5 $V \cdot s^{-1}$.

As it can be deduced from Figure 1, two different electrochemical pathways can be distinguished. The 4-fluorobenzonitrile shows only an electron transfer process, whereas the other halobenzonitrile derivatives show two electron transfer processes up to -2.5 V. Focusing on the first electron transfer process, all the compounds show an irreversible two electron reduction wave (Table 1). The peak width values (ΔE_{pc}) greater than 56mV reveal a slow electron transfer process. According to previously reported cyclic voltammetry studies performed in our laboratory[38–40], the second electron transfer process seen when $X \neq F$ corresponds to one electron transfer process, is attributed to the electrochemical reduction of benzonitrile. Thus, the benzonitrile moiety is the initial electron acceptor, and the cyano group acts as an intramolecular catalyst of the halogen atom removal when X ≠ F. The electrochemical parameters of the electrochemical reduction of 4-halobenzonitriles are summarized in Table 1. It is worth noting the shape of the cyclic voltammograms recorded at the same for each compound when either GC or Ag is used as a working electrode. The presence of halogen substituents in the aromatic compounds, electron withdrawing groups (because of higher electronegativity), makes easier to reduce them. A closer look to the E_{pc} values of halobenzonitriles reveals However, there is another effect related to the fact that their lone pair can be incorporated that their tendency to gain electrons and get reduced follow the order I > Br > Cl>F, which indicated that the halogen lone pair can be incorporated in conjugation of the systems affecting the reduction potential values. However, a closer look reveals that, for all the halobenzonitriles studied, the use of Ag to enable the compound to be reduced at less negative potential values demonstrates the electrocatalytic effects of this material.

Table 1. Electrochemical parameters associated to the first reduction wave of 5-15 mM of 4-halobenzonitrile solutions (X: F, Cl, Br, and I) contained in 10 ml DMF/0.1M $TBABF_4$ under N_2 atmosphere, using Ag or GC as WEs, respectively, Pt as counter-electrode, and SCE as reference electrode.

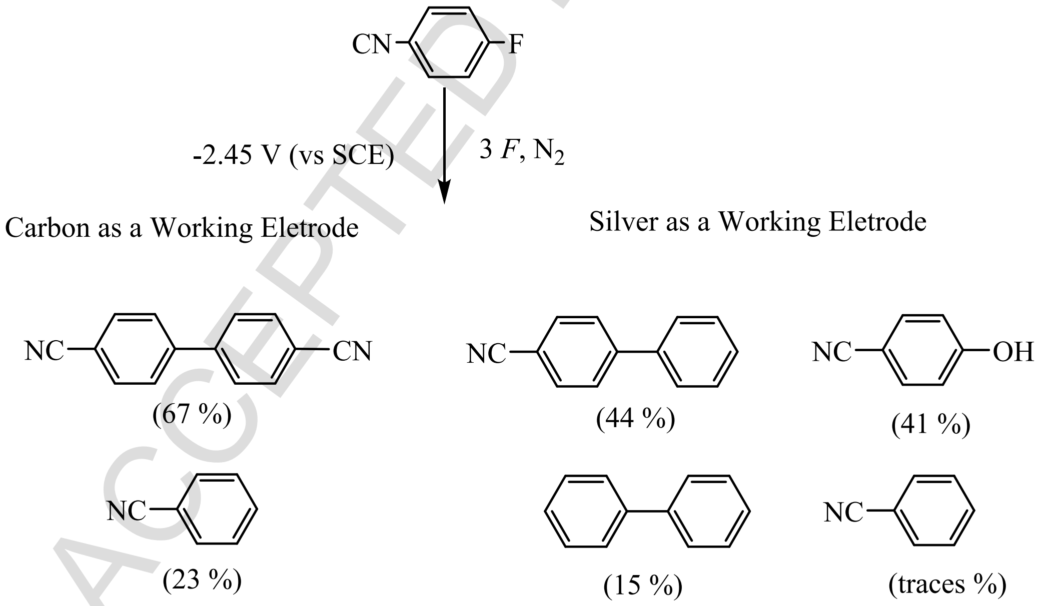
4-Halobenzonitriles	Ag			GC		Electrocatalytic effect: $E_{pc}(Ag)-E_{pc}(GC)$ (mV)
	Number of electrons	E_{pc} (V)	ΔE_{pc} (mV)	E_{pc} (V)	ΔE_{pc} (mV)	
F	2	**-2.35**	80	-2.38	80	**30**
Cl	2	**-1.95**	90	-2.04	100	**90**
Br	2	**-1.75**	210	-1.94	110	**190**
I	2	**-1.46**	50	-1.84	110	**380**

In order to demonstrate the electrochemical reduction mechanism of halobenzonitriles in our experimental conditions, controlled-potential electrolysis was performed after the first reduction wave. In the case of 4-fluorobenzonitrile, exhaustively controlled potential electrolysis experiments were performed at -2.45 V (Vs SCE), using 20 mM solutions in DMF/0.1M $TBABF_4$. The distribution of products obtained after the reduction of the sample depended on the nature of the electrode. In the case of using a carbon graphite rod as cathode, the products obtained were benzonitrile and 4,4'-dicyanobibenzene, which is in good agreement with previously reported studies using Pt as a cathode (Scheme 4). The formation of 4,4'-biphenyldicarbonitrile from 4-fluorobenzonitrile can be rationalized by a dimerization reaction of 4-fluoro-benzonitrile anion radical (Scheme 4, step 2), which decomposes by the elimination of two fluoride anions, leading to the corresponding dimer (step 3).



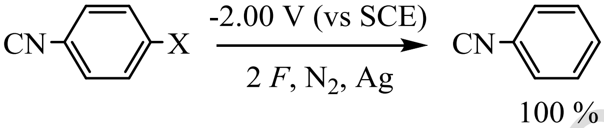
Scheme 4. Proposed mechanism for the formation of 4,4'-biphenyldicarbonitrile from 4-F-benzonitrile.

Benzonitrile and dimer derivatives are also obtained when silver (Ag) foil was used as working electrode, (Scheme 5). In this sense, the electrochemical reduction mechanism appears to be the same in both cases, although the use of silver seems to favor a de-cyanidation process of the products formed, probably due to an adsorption process of the reduction intermediates at the electrode surface. The presence of 4-hydroxybenzonitrile can be explained due to the reactivity of the reactant (4-F-benzonitrile) in the medium after the electrolysis.



Scheme 5. Electrolysis of a 16 mM solution of 4-F-benzonitrile in DMF/0.1M $TBABF_4$, applying a potential of -2.45 V (vs SCE), consuming 3 F of charge, under a N_2 atmosphere, using silver foil as WE, a Pt counter-electrode, and a SCE reference electrode.

Controlled potential electrolysis experiments of Cl, Br, and I halobenzonitriles (applying a reduction potential value of ~0.1 V more negative than its first reduction potential wave using either using C graphite or Ag) reveal the quantitative formation of benzonitrile after the passage of 2 F under nitrogen atmosphere (Scheme 6). The formation of benzonitrile is related to a bond cleavage reaction coupled to the initial electron transfer process. The benzonitrile radical formed is reduced at this potential value, yielding the corresponding anion, which is protonated in last step. Those results are in good agreement with previous work published in the literature using a C electrode, as a working electrode[38,39,41].



Scheme 6. Electrolysis of 10 mM of 4-halobenzonitrile solutions in DMF/0.1M $TBABF_4$ under N_2 atmosphere using Ag as a working electrode.

From these electrochemical results obtained under inert atmosphere, it is possible to conclude that in the case of Cl, Br and I benzonitrile derivatives the electrocarboxylation process should take place through a nucleophilic attack between the benzonitrile anion and CO_2. Whereas, in the case of 4-F-benzonitrile the electrocarboxylation process would be triggered through a reaction between of 4-F-benzonitrile radical anion and CO_2.

3.2. Electrochemistry of 4-halobenzonitriles under CO_2 atmosphere

Cyclic voltammetry of the different 4-halobenzonitriles (X: F, Cl, Br and I) are performed using Ag and GC under CO_2 atmosphere (Figure 2). In the case of 4-Br, 4-Cl and 4-I, when either GC or Ag were used as a working electrode two reduction peaks were observed at the same reduction potential values, which were previously determined under inert atmosphere for each electrode. Hence, the first one is related to the reduction of the 4-halobenzonitrile, whereas the second one is related to the reduction of benzonitrile. Note that under CO_2 atmosphere, the benzonitrile reduction peak turns irreversible and increases dramatically its peak current value, which indicates that benzonitrile is acting as an organic mediator (catalyst) for the reduction of CO_2 (Scheme 7). In the case of 1-Fluorobenzonitrile only an increase in the cathodic peak current value is detected since the reactant and products (benzonitrile and 4,4'-biphenyldicarbonitrile) , which act as a catalyst appear at the same potential values[28,42]. Note that at low CO_2 concentration (5 mM, Figure 2D), it is possible to distinguish a third reduction peak at c.a. -2.4 V vs. SCE. According to previous studies performed in our research group, this new reduction peak corresponds to a CO_2 direct reduction at the surface of silver electrode[43].

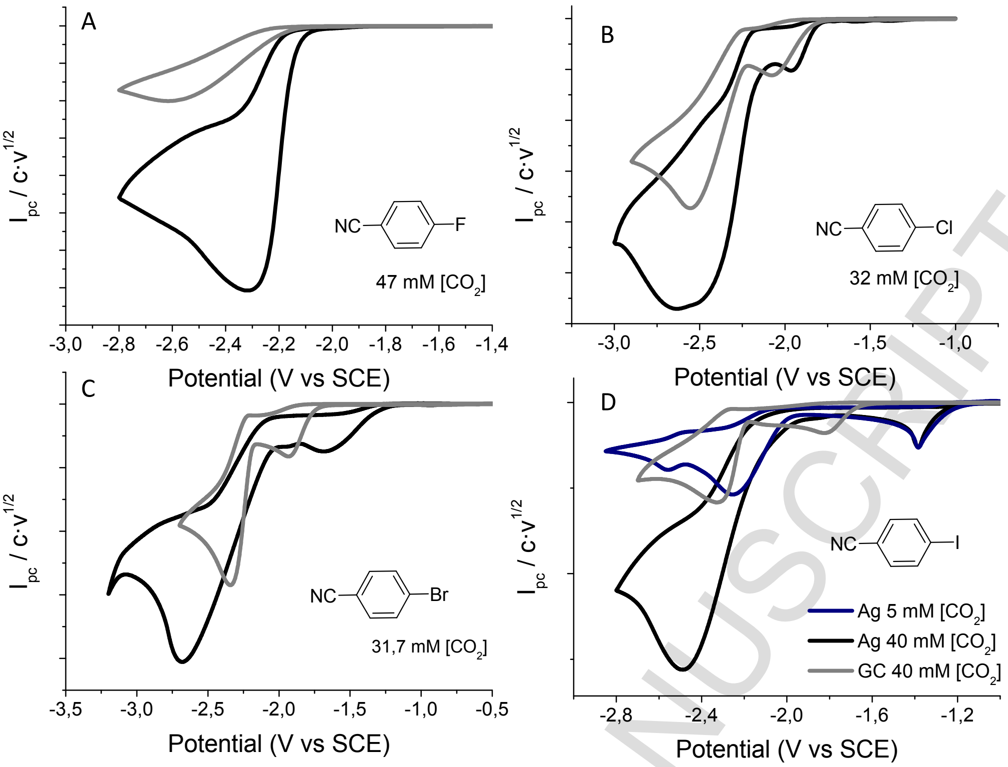
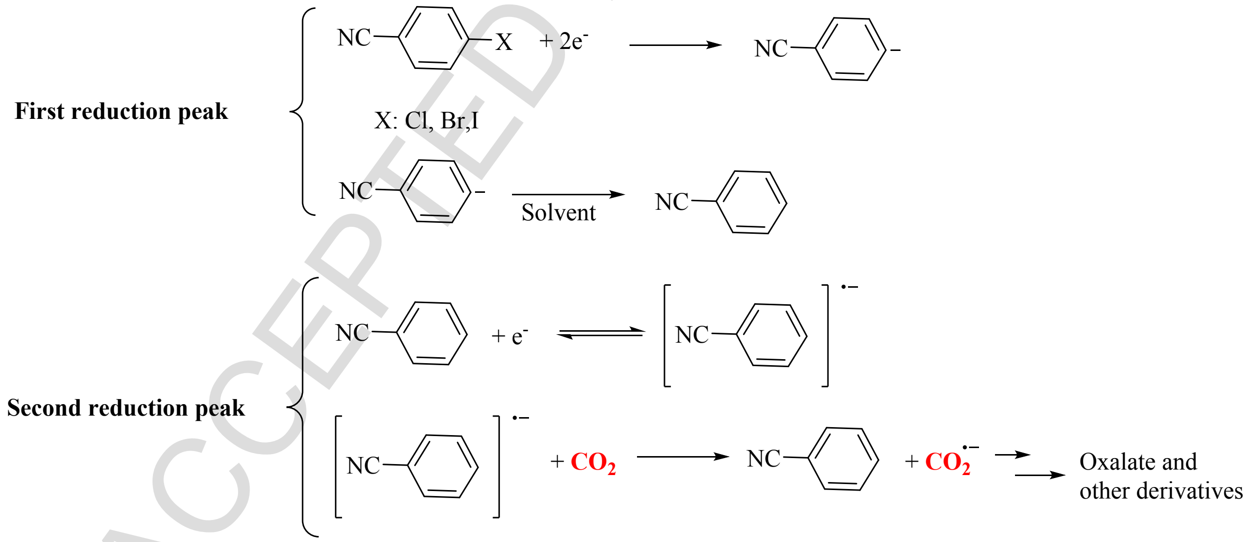


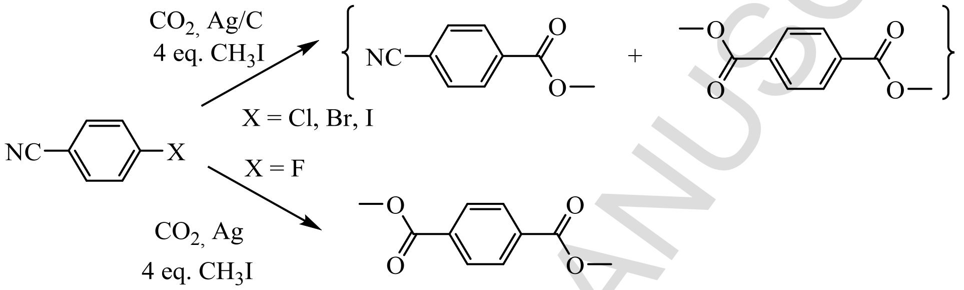
Figure 2. Cyclic voltammograms of 5-15 mM 4-halobenzonitriles (X: F, Cl, Br and I) solutions using Ag (black lines) and GC (grey lines) in DMF/0.1M TBABF$_4$ under at scan rate: 0.5 V·s^{-1} under CO$_2$ atmosphere.



Scheme 7. Mechanism proposal for the reduction of 4-Cl, 4-Br and 4-I using GC electrode under saturated CO$_2$ atmosphere.

Electrolysis of 4-halobenzonitriles (X: F, Cl, Br, and I) are performed using a Ag foil or C$_{graphite}$ bar, applying potentials ~0.1 V more negative than the previously determined the first reduction wave of each 4-halobenzonitrile (Table 2) in CO$_2$-saturated solutions with ~12 mM of the organic compound in DMF and an excess of supporting electrolyte (0.1M of TBABF$_4$ for Ag or TEABF$_4$ for C). After the consumption of the desired charge, an alkylating agent, methyl iodide (CH_3I), was added to facilitate the separation of the products.

The results of these experiments are depicted in Table 2 (entries 1-7 and 10-14). A general trend is observed in all the cases independently of the nature of the electrode, Ag or C, and the total charge passed (from 1.7 to 4.5 F). When 4-Br-, 4-Cl-, and 4-I-halobenzonitriles solutions are electrolyzed a mix of mono- (4-cyanobenzoate methyl ester) and di-carboxylated (dimethyl terephthalate) products are obtained after the chemical treatment of the sample (Scheme 8 and Table 2, entries 1-7, and 10-14). In contrast, with X = 4-F-, only the di-carboxylated compound is formed (Table 2, entries 1-3). In addition, in all the cases when the total charge passed increases, less reactant remains, and the percentage of di-carboxylation increases.



Scheme 8. Electrolysis of 10-14 mM 4-halobenzonitrile (X: F, Cl, Br, I) CO_2-saturated solutions in DMF/0.1M $TBABF_4$ or $TEABF_4$, with an Ag foil or a $C_{graphite}$ rod as WEs and adding 4 equivalents of CH_3I at the end of each experiment.

Table 2. Products distribution obtained by electrolysis of 10 mM 4-halobenzonitriles (X: F, Cl, Br, and

I) CO_2-saturated solutions in DMF/0.1M $TBABF_4$ or $TEABF_4$, with a Ag foil or $C_{graphite}$, respectively, after adding 4 equivalents of the corresponding alkylating agent indicated on the right column. “Mono-” and “di-” terms refer to mono-carboxylated or di-carboxylated product.

WE	Entry	Halobenzonitrile (X)	C mol^{-1}	$E_{applied}$ (V vs SCE)	Alkylating agent	Yield (%) of carboxylated products	
						mono-	di-
Ag[a]	1	F	2.0	-2.45	CH_3I	0	11
	2	F	3.5	-2.45	CH_3I	0	20
	3	F	4.5	-2.75	CH_3I	0	40
	4	Cl	2.1	-2.05	CH_3I	20	40
	5	Cl	3.5	-2.05	CH_3I	31	49
	6	Br	2.3	-1.80	CH_3I	36	29
	7[b]	Br	4.5	-1.90	CH_3I	1	87
	8	Br	4.5	-1.80	Br-CH_2CH_3	10	90
	9	Br	4.5	-1.80	2-Br-CH_2CHPh	17	49
	10	I	2.0	-1.80	CH_3I	39	31
	11	I	3.5	-1.80	CH_3I	28	67
$C_{graphite}$	12	Cl	1.7	-2.15	CH_3I	15	23
	13	Br	2.0	-2.10	CH_3I	27	18
	14	I	1.7	-2.10	CH_3I	16	12

[a] 100% of conversion ratios, the reactant was the only product apart from the electrocarboxylation products recovered at the end of the experiment. [b] In this case a 12 % of benzonitrile was obtained at the end of the process, it can be attributed to the application of a higher negative reduction potential value. Under these conditions, CO_2 can be also reduced and react with the halobenzonitrile derivative (Scheme 1 – Steps 1-3a). Finally, a radical cleavage in the Kolbe reaction of the monocarboxylated product ($R\text{-}CO_2^{\cdot}$) will occur leading to benzonitrile and CO_2[44].

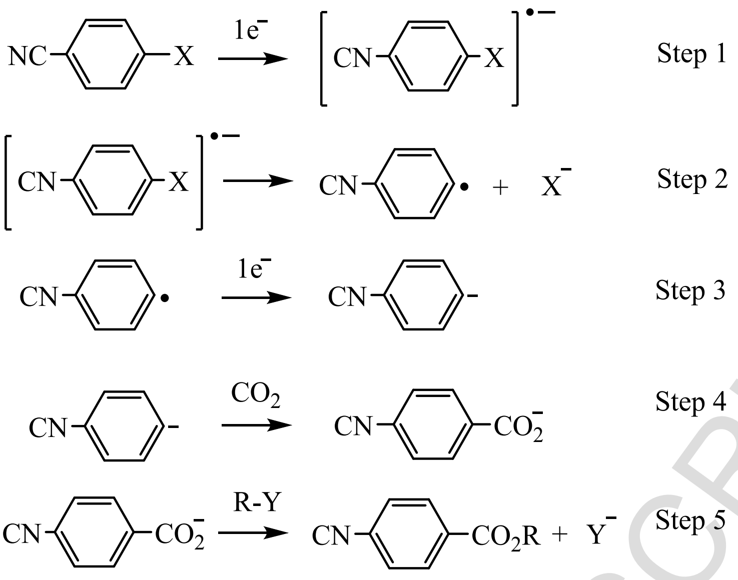
A closer look at Table 2 revealed that, when C is used as a cathode, moderate yields of carboxylated products were obtained (from 24 % to 45 %) using high reduction potential values (c.a. -2.00 V vs. SCE, entries 12-14) when non-fluorinated benzonitrile is used. When fluorobenzonitrile is used as a starting material, no carboxylated products were obtained using C graphite as a working electrode The observed reactivity can be related to the ability of the aromatic radical anions to undergo cleavage of the carbon halogen bond, with the peculiarity that in our case there is a stable fluoride radical anion that dimerises[45].

Replacing C cathode, which acts as an inert electrode, by Ag cathode not only allows reducing the reduction potential value applied but also increasing the yield of carboxylation products (entries 4-11). Ag electrode is recognized as a powerful catalytic electrode in organic solvent, being its catalytic property ascribe to the adsorption between metal surface and halogenated substrate as well as its reduction intermediates and products. Hence, due to these adsorption processes that favors the stability of reduction intermediates after the same total charge passed, the same consumption of charge, the yield of carboxylation is higher for Ag, but also in global terms, carboxylation is 2-3 times for Ag.

The maximum yield of dimethyl terephthalate (87%, entry 7) is reached for controlled potential electrolysis of a bromobenzonitrile solution at -1.80 V (vs SCE) after the passage of 4.5 F under CO_2 atmosphere using Ag as a cathode. The use of 4-I-benzonitrile also allows obtaining carboxylation yields close to 100 % after the passage of 3.5 F. The ratio of % of di-carboxylation/charge consumed is the same in both cases, thus this could suggest that maybe the adsorption of the I-derived reactant (Figures 1) plays an important role for the carboxylation process.

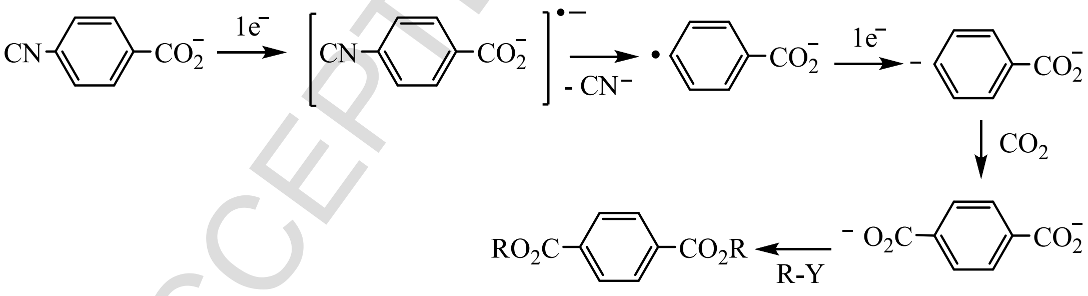
As it was previously mention, no carboxylated products were obtained using C graphite as a working electrode for fluorobenzonitrile. However, the use of silver as a working electrode enables a maximum yield of 40% of dimethyl terephthalate (entry 3) to be obtained after the passage of 4.5 F at of -2.75 V (vs SCE). It is worth noting that, after the passage of the same number of Farads, the total yield of electrocarboxylation products is as follows; I>Br>Cl>F. This fact can be explained by considering the bond dissociation energies (BDEs) of the Ar-X bonds.

On observing the above-mentioned results, it is plausible to propose a mechanism for the insertion of CO_2 in 4-halobenzonitriles (X: Cl, Br, and I) the following mechanism (Scheme 9). In a first step, the reduction of the 4-halobenzonitrile forms the correspondent radical anion, which rapidly cleaves to give the benzonitrile radical, and the corresponding halide (step 2). In a third step, the radical reduces at the electrode surface leading to the benzonitrile anion. In a further step, this anion can react with CO_2 under CO_2-saturated atmosphere, leading to 4-cyanobenzoate anion (step 4). Finally, the addition of iodomethane as alkylating agent (R-Y) yields the correspondent ester (step 5).



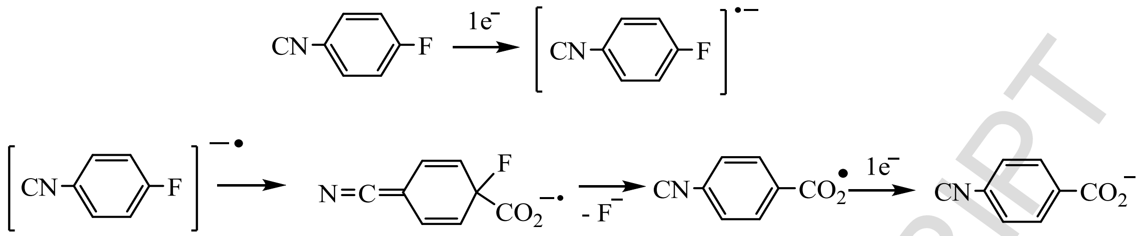
Scheme 9. Electrochemical Strategy for inserting CO_2 in 4-halobenzonitriles (X: Cl, Br, and I).

Note that the ratio of carboxylated products (4-cyanobenzoate methyl ester vs. dimethyl terephthalate) can be tune in function of the charge passed during the electrolysis. This fact should be related to the reduction of the 4-cyanobenzoate formed upon the electrolysis, this dianion can act as a nucleophile and react with the CO_2 (Scheme 10). Lately, the decyanation of dianion has taken place. This mechanism is supported by the detection of cyanide anion at the end of the electrolysis. Hence, the formation of the carboxylated di-substituted products is related to the reactivity of the nitrile group in presence of CO_2. Moreover, reductive decyanation processes for similar compounds has been previously reported in the literature[46–48].



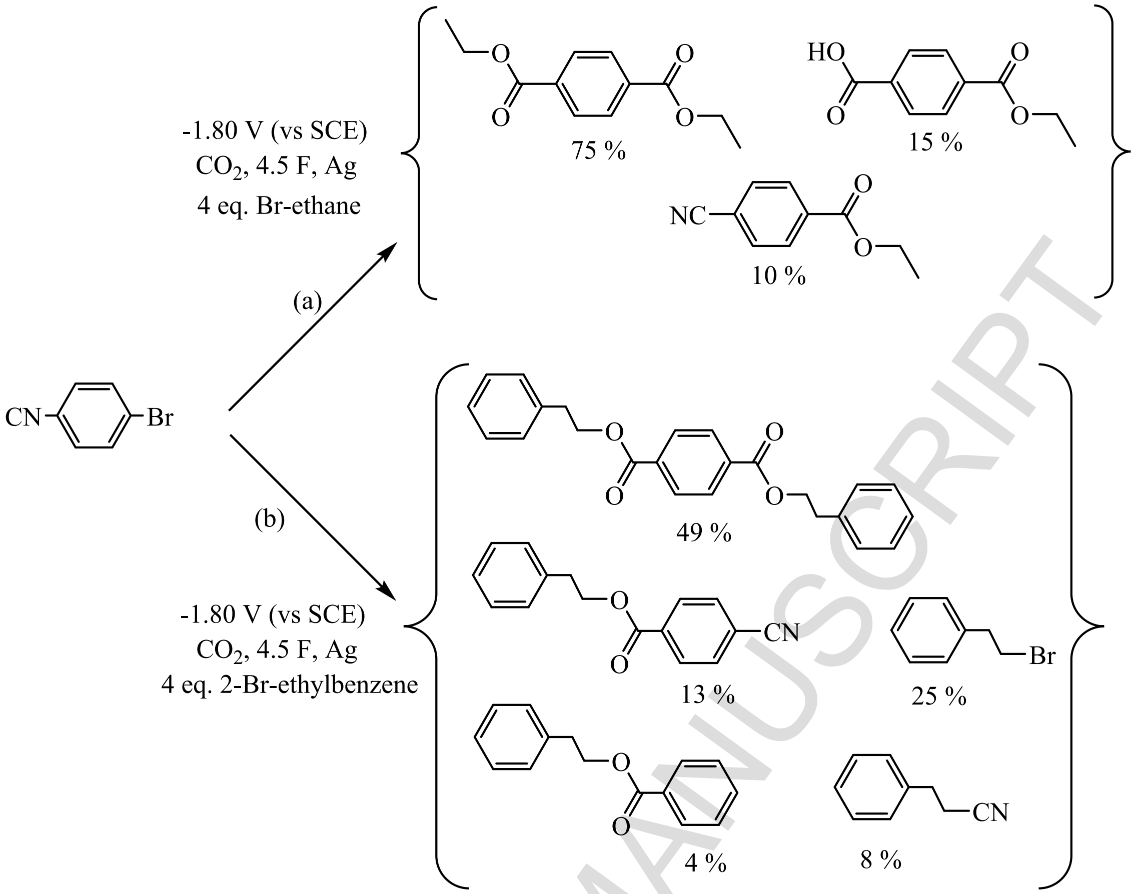
Scheme 10. Electrochemical reduction mechanism of 4-halobenzonitriles (X: Cl, Br, and I) under CO_2 atmosphere after the passage of 3-4 F.

In the case of 4-fluorobenzonitrile then only carboxylated product obtained after the electrocarboxylation process in Ag was the dimethyl terephthalate. In this case, the electrocarboxylation is very selective and enables yields of 40 % to be obtained, as has been previously pointed. The plausible electrocarboxylation mechanism is depicted in Scheme 10. The fluorobenzonitrile anion radical reacts with CO_2 instead of dimerization leading to a benzonitrile carboxylated derivate (Scheme 11). This derivate is not stable at high negative reduction processes values and further reduction are taking place following the same mechanism that the previously described for the rest of halobenzonitriles (Scheme 9). The process ends with the capture of CO_2, and further alkylation processes.



Scheme 11. 4-fluorobenzonitriles under CO_2 atmosphere electrochemical reduction mechanism

Once halobenzonitrile in CO_2 cathode electrochemical reduction mechanism as well as the electrocarboxylation conditions were optimized at the silver, other alkylation agents were used in other to check the potentiality of the methodology. 4-bromo-benzonitrile was selected as a starting material, since almost a 100 % of electrocarboxylation products were obtained using methyl iodide as a methylated agent (Table 2, Entry 9). Hence, controlled potential electrolysis, at –1.80 V vs. SCE, of a 10 mM DMF/0.1M $TBABF_4$ solution of 4-bromo-benzonitrile in a CO_2-saturated were performed using Ag foil as a working electrode. After, the passage of 4.5 F, four equivalents of two different alkylating agents: 1) bromoethane and (2-bromoethyl) benzene were added at the end of the electrolysis. In the first case, the analysis of the electrocarboxylation process yields 75% of diethyl terephthalate, 15 % of terephthalic acid mono-ethyl ester, and 10% 4-cyanobenzoate ethyl ester, Scheme 12 (Table 3, entry 8). Changing the alkylating agent for (2-bromoethyl) benzene, the analysis of the electrocarboxylation process revealed a 49% diphenethyl terephthalate, 13% 4-cyanobenzoate phenethyl ester, 8% 3-phenylpropionitrile, and 4% benzoate phenethyl ester, and 25 % of the alkylating agent is recovered (Scheme 12, Table 2, entry 9). As mentioned before, the presence of the 3-phenylproprionitrile molecule can be explained by the reaction between the removed cyanide anion from the reactant and the alkylating agent. Note that there is a steric hindrance effect on the efficiency of alkylation reaction.



Scheme 12. Electrolysis of 10-14 mM 4-bromobenzonitrile CO_2-saturated solutions in DMF/0.1M $TBABF_4$ with an Ag foil. At the end of the electrocarboxylation process the alkylation agent was added: a) bromoethane b) for (2-bromoethyl)benzene.

4. Conclusions

Electrolysis of 4-halobenzonitrile in CO_2-saturated employing a carbon graphite rods or silver foils as a cathode lead to the formation of mono-, and di-substituted products from moderate to almost quantitative yields. The maximum efficiency of the carboxylation process is achieved with the passage of c.a. 4F. It has also been demonstrated that the use of “small” alkylating agents, such as iodomethane or bromoethane, enables higher yields to be obtained in terms of carboxylation products, probably due to hindrance effects. The use of Ag as working electrode enables controlled potential electrolysis to be performed at less negative potential values. Hence, electrocatalytic effects are seen when Ag is used as cathode, giving very high yields in terms of di-carboxylated products, where two units of CO_2 are incorporated to one unit of halobenzonitrile. This “new” methodology offers a new “green” route for the synthesis of different phthalate derivatives, which can potentially be used for making plastic polymers in a more environmentally friendly way.

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