

Electrochemical Selective Incorporation of CO₂ into Terminal Alkynes and Diynes

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Dedicated to Prof. E. G. Jäger on the occasion of his 65th birthday

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Electrochemical incorporation of CO₂ into terminal alkynes and diynes on silver cathodes occurred selectively, to afford monocarboxylic acid derivatives in good yields. The electro-

lyses were carried out in one-compartment cells fitted with magnesium anodes, under mild conditions.

Introduction

Carbon dioxide is an abundant and low-cost carbon source for the production of fuels and organic chemicals.^[1] The development of novel and selective reactions capable of forming C–C bonds from CO₂ and organic substrates constitutes an important topic, avoiding the use of toxic CO or phosgene, and using CO₂ as an environmentally friendly reagent.^[2]

Of the selective and catalytic reactions involving carbon dioxide as a C-1 building block for the synthesis of fine chemicals, electrochemical methods have been shown to have a wide range of applications.^[3] The direct electrochemical reduction of carbon dioxide requires relatively negative reduction potentials (–2.2 V vs. SCE in an aprotic medium),^[4] and the use of several catalytic systems has been reported.^[3]

The fixation of CO₂ into organic substrates may involve its reactivity in nucleophilic reactions^[5] or its activation by coordination to low-valent transition metal complexes. In this case, new C–C bonds can be formed by simultaneous activation by the metal center, both of the organic substrate and of the carbon dioxide.^[6–8]

We have been particularly interested in the incorporation of CO₂ into unsaturated hydrocarbons, such as alkynes and diynes. Ni⁰ complexes have been reported to mediate the C–C coupling of disubstituted alkynes and CO₂ for the formation of α,β -unsaturated carboxylic acids in stoichiometric reactions at carbon dioxide pressures around 1 atm.^[9] At higher CO₂ pressures ($p_{\text{CO}_2} \geq 50$ atm), the synthesis of pyrones from alkynes^[10] and diynes^[11] has been achieved.

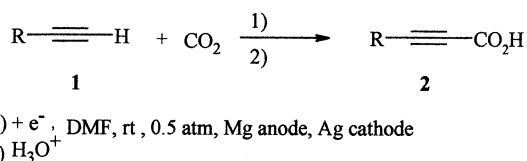
Nickel(II)-catalyzed electrochemical reactions for the fixation of carbon dioxide into unsaturated hydrocarbons

have also been reported.^[12,13] Thus, terminal alkynes regioselectively afforded α,β -unsaturated carboxylic acids in a reductive hydrocarboxylation-type reaction, when Ni(bpy)₃²⁺·2BF₄ was used as the catalyst precursor (bpy = 2,2'-bipyridine).^[14]

The electrocarboxylation of terminal alkynes in the presence of Ni(cyclam)Br₂ resulted in the corresponding alkynylcarboxylic acid, in a stoichiometric process.^[15] The electrochemical, uncatalyzed carboxylation of diphenylacetylene has also been reported,^[16] but a nonselective mixture of reduced and carboxylated compounds was obtained.

Results and Discussion

We report here a simple electrochemical carboxylation procedure for the selective conversion of terminal alkynes into α,β -alkynyl carboxylic acids under mild conditions (Scheme 1). The electrocarboxylations were carried out in DMF, in single-compartment cells fitted with magnesium anodes.^[17,18] Electrolyses were performed at room temperature and at a CO₂ pressure of 0.5 atm. Up to now, the reported selective electrocarboxylation processes involving nonactivated, unsaturated hydrocarbons needed the presence of a catalytic system.^[12,13] We report here that, depending on the nature of the cathodic material used, the carboxylation reaction of terminal alkynes does not need the presence of metal catalysts to afford selective CO₂ incorporation.



Scheme 1. Electrochemical carboxylation of terminal alkynes

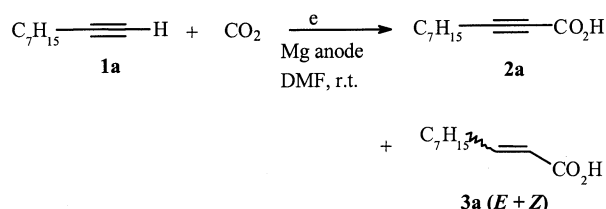
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a) Influence of the Cathodic Material

Some preliminary tests were carried out on the electroreductive behavior of 1-nonyne (**1a**) in the presence of CO₂ at different cathodic materials. Silver plate, nickel foam, Pt foil, or carbon fiber cathodes were used. The results of the electrocarboxylations are presented in Table 1.

Table 1. Influence of the cathodic material on the electrocarboxylation of 1-nonyne (**1a**)



Entry ^[a]	Cathode	Products	Yield (%)	Selectivity for 2a among the carboxylic acids (methyl esters)
1	Ag	1a 2a	5 90	95%
2	Ni	1a 2a 3a	35 55 5	85%
3	Pt	1a 2a 3a	35 5 40	8%
4	C	1a 3a	75 20	—

^[a] For experimental details, see Exp. Sect.

Interestingly, **1a** was electrochemically carboxylated on a silver plate cathode to afford 2-decyanoic acid (**2a**) in 90% yield (Entry 1), whereas under the same conditions, but on a nickel foam cathode, the same substrate produced a mixture of **2a** and 2-decenoic acid (**3a**) with incomplete conversion (Entry 2). On a platinum surface, only 5% of **2a** was obtained, the main product being the reduced carboxylic acid **3a** (mixture of *cis* and *trans*) formed in 40% yield (Entry 3). The electrocarboxylation of **1a** on a carbon fiber cathode (Entry 4) afforded a low degree of conversion and reductive carboxylation to **3a** in 20% yield.

The same reactivity trends could be observed in cases of electrocarboxylations of 1,8-nonadiyne (**1b**). The second triple bond of the starting material was not reduced, nor carboxylated. The electrochemical process showed a very strong and interesting chemoselectivity for monofunctionalization of a symmetrically disubstituted substrate.

b) Influence of the Solvent

The influence of the solvent in the electrocarboxylations of **1a** and **1b** in DMF and acetonitrile was examined. As shown in Table 2, the electrolyses in DMF resulted in much

higher carboxylation yields and selectivities than those in acetonitrile.

Table 2. Influence of the solvent and of the CO₂ pressure in the electrocarboxylations of **1a** and **1b**, with Mg/Ag electrode couples

Entry	Substrate	Solvent	CO ₂ pressure [atm]	Yield of carboxylic acid methyl esters of 2a or 2b
1	1a	DMF	5	2a 5%
2	1a	DMF	0.5	2a 90%
3	1a	MeCN	0.5	2a 10%
4	1b	DMF	5	2b 5%
5	1b	DMF	0.5	2b 90%
6	1b	MeCN	0.5	2b 5%

c) Influence of Carbon Dioxide Pressure

We performed the electrocarboxylation reactions of **1a** and **1b** in DMF at 5 atm of CO₂ and at 0.5 atm of CO₂, and the results are shown in Table 2.

Electrolyses were performed with 1 mmol of **1** at constant current (50 mA) over 3 h, which corresponds to a passage of 5.4 F/mol of **1**. The carboxylation reaction should theoretically consume 1 F/mol of **1**. The electrolyses thus occurred with faradic yields for carboxylic acids **2** and **3** in the range of 15–20% at a pressure of 0.5 atm. The incomplete conversions after the passage of 1 F/mol of **1a** are accounted for by a different electroreduction reaction, which in this system corresponds to the direct reduction of CO₂ (see Scheme 3).

In reactions performed at 5 atm of CO₂, the yields of **2a** or **2b** were very low after 3 h of electrolysis. These low yields indicate an important parallel carbon dioxide reduction process, as confirmed by the formation of oxalic acid as the main product in these electrolyses. This CO₂ homocoupling side reaction increased with higher CO₂ pressures, as shown by the results in Table 2. For Entries 1 and 4, the faradic yield of CO₂ reductive coupling to oxalate was as high as 90–95%. We found that a CO₂ pressure of 0.5 atm was the best compromise for alkyne reactivity versus CO₂ electroreduction on silver surfaces.

d) Cyclic Voltammetry

Studies by cyclic voltammetry were carried out with diyne **1b** and CO₂. Figure 1 and 2 present the behavior of **1b** in DMF containing tetrabutylammonium tetrafluoroborate (TBABF₄) for two different diyne concentrations, in the absence and in the presence of CO₂.

In the absence of carbon dioxide (Figure 1), a nonreversible reduction peak of **1b** was observed at –1.9 V vs. Ag/AgCl (curve a), the intensity of which increased upon further addition of the diyne (curve b). In the presence of CO₂ (Figure 2, curve c), the same irreversible behavior could be observed with a further reduction peak at –2.5 V, presumably due to the reduction of carbon dioxide under these conditions.

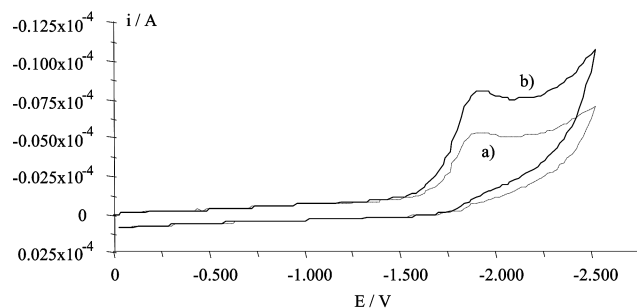


Figure 1. Cyclic voltammograms of a DMF solution (10 mL) containing TBABF₄ (1 M), at 20 °C, at 100 mV/s on a carbon fiber working electrode, reference electrode Ag/AgCl; curve a) addition of **1b** (0.1 mmol); curve b) addition of **1b** (0.2 mmol)

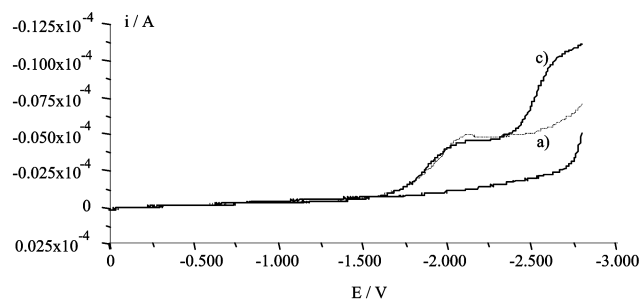


Figure 2. Cyclic voltammograms of a DMF solution (10 mL) containing TBABF₄ (1 M), at 20 °C, at 100 mV/s on a carbon fiber working electrode, reference electrode Ag/AgCl; curve a) addition of **1b** (0.1 mmol); curve c) same as curve a) but after addition of CO₂ at 20 °C, 1 atm

e) Electrocarboxylation of Alkynes and Diynes

Several alkyne and diyne derivatives were carboxylated using an Mg anode and an Ag cathode as the pair of electrodes, in DMF at room temperature and at a CO₂ pressure of 0.5 atm. The results are presented in Table 3. The obtained carboxylic acids were esterified in the reaction mixture by the presence of methyl iodide, in order to facilitate the extraction and the analysis of the products as the corresponding methyl esters.

The reactivity trends already noted for **1a** and **1b** (Entries 1 and 2) were also observed for the electrocarboxylation of 1-octyne (**1c**) and 1,7-octadiyne (**1d**) (Entries 3 and 4). Excellent yields of the corresponding monocarboxylic acids were obtained in all cases. Cyclohexyl acetylene (**1e**) produced 3-cyclohexylpropionic acid (**2e**) in 80% yield (Entry 5).

The presence of an ether function in 1-methoxy-3-butyne (**1f**) was compatible with the reaction conditions and 5-methoxypentynoic acid (**2f**) was formed in 80% yield (Entry 6). However, no CO₂ incorporation occurred in the case of the analogous unprotected 3-butyne-1-ol. Dipropargyl ether (**1g**) also underwent a single CO₂ incorporation, affording dialkynyl monocarboxylic acid **2g** in 90% yield (Entry 7).

The selectivity of alkyne carboxylation versus alkene carboxylation was examined in the case of 3-methylbut-3-en-1-yne (**1h**) (Entry 8), and of 3-butyne-1-pentynyl ether

Table 3. Electrocarboxylation of terminal acetylenic derivatives on a silver cathode surface

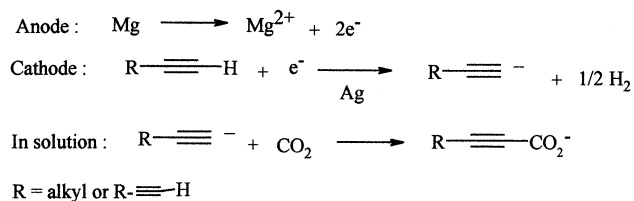
Entry	Substrate	Product (methyl esters)	Yield (%)
1	1-nonyne, 1a	$\text{C}_7\text{H}_{15}-\text{C}\equiv\text{C}-\text{CO}_2\text{H}$ 2a	90
2	1,8-nonadiyne, 1b	$\text{C}\equiv\text{C}-(\text{CH}_2)_5-\text{C}\equiv\text{C}-\text{CO}_2\text{H}$ 2b	90
3	1-octyne, 1c	$\text{C}_6\text{H}_{13}-\text{C}\equiv\text{C}-\text{CO}_2\text{H}$ 2c	90
4	1,7-octadiyne, 1d	$\text{C}\equiv\text{C}-(\text{CH}_2)_5-\text{C}\equiv\text{C}-\text{CO}_2\text{H}$ 2d	90
5	cyclohexylacetylene, 1e	$\text{C}_6\text{H}_{11}-\text{C}\equiv\text{C}-\text{CO}_2\text{H}$ 2e	80
6	1-methoxy-3-butyne, 1f	$\text{CH}_3\text{O}-(\text{CH}_2)_2-\text{C}\equiv\text{C}-\text{CO}_2\text{H}$ 2f	80
7	dipropargyl ether, 1g	$\text{CH}_3\text{O}-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{H}$ 2g	90
8	3-methyl-3-buten-1-yl, 1h	$\text{CH}_3-\text{C}(\text{CH}_3)=\text{CH}-\text{C}\equiv\text{C}-\text{CO}_2\text{H}$ 2h	70
9	3-butyne-1-pentynyl ether, 1i	$\text{CH}_3\text{O}-(\text{CH}_2)_3-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-\text{CO}_2\text{H}$ 2i	80
10	4-octyne, 1j	1j	>95%

(**1i**) (Entry 9). The main carboxylation product for both substrates arose from single CO₂ incorporation into the terminal position of the triple bond. Further carboxylation of the double bond occurred only at low ratios.

Phenylacetylene was very reactive under the reaction conditions and produced a nonselective mixture of mono- and dicarboxylated compounds, together with some reduced products. The reactivity of internal triple bonds versus terminal triple bonds was also examined. Thus, internal 4-octyne (**1j**) exhibited no reactivity under the standard reaction conditions and could be quantitative recovered at the end of the electrolysis.

f) Mechanistic Aspects

For the one-compartment cell electrolysis procedure used here, we have, at the anode, the oxidation of the magnesium rod into Mg²⁺ ions in solution (Scheme 2). At the cathode, the reduction of the organic substrate takes place.

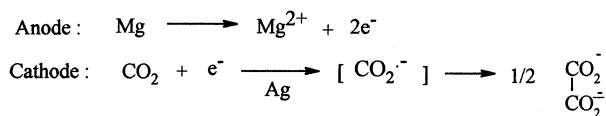


Scheme 2. Electrochemical reaction at the electrodes and in solution

The absence of reactivity observed for internal alkynes and the selectivity in the monocarboxylation of α,ω -diynes prompted us to propose a mechanism in which the first step is the deprotonation of the terminal alkyne by direct electrochemical reduction on the silver surface, as the cathodic reduction step. This deprotonation, with H_2 evolution, should be followed by reaction of the acetylide with CO_2 acting as an electrophile. In the presence of the Mg^{II} ions, issuing from the anodic oxidation, the coupling reaction affords the alkynylcarboxylate as a magnesium salt.

In the case of α,ω -diynes, the first terminal alkyne cathodic reduction and carboxylation produces an Mg^{2+} monocarboxylate. The presence of the anionic carboxylate species should disfavor their approach towards the cathode and therefore the further reduction of its remaining alkyne unit. This fact could explain the high selectivity towards diyne monocarboxylation.

Furthermore, the lack of carboxylation of 3-butyne-1-ol can be explained similarly. For this substrate, initial deprotonation of the alcohol function to the corresponding alkoxide occurs before the alkyne reduction. Thus, the negatively charged alkoxide inhibits further reduction of the terminal triple bond. As a cathodic side reaction, the direct electroreduction of CO_2 in DMF forms oxalate, through the radical anion of CO_2 (Scheme 3).^[4] In solution, magnesium oxalate is formed. At the end of the electrolysis, these oxalate ions, in the presence of methyl iodide, are esterified to dimethyl oxalate, which could be found in the reaction mixtures.

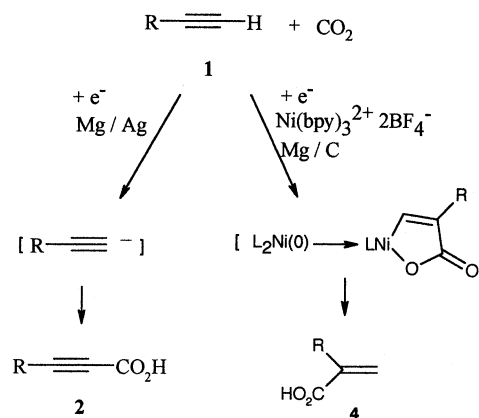


Scheme 3. Oxalate formation as a cathodic side reaction

It is interesting to compare the results of the uncatalyzed electrocarboxylation on Ag cathodes with those of the analogous nickel-catalyzed reactions on carbon fiber cathodes. Nickel(II) in association with 2,2'-bipyridine has been reported to catalyze CO_2 incorporation into terminal alkynes^[12] or diynes,^[13] yielding α,β -unsaturated acids **4** in a reductive hydrocarboxylation-type reaction, using an Mg anode. In this process, the cathodic reaction involves reduction of Ni^{II} to Ni^0 , which is followed by the formation of oxanickelacycles as intermediates in the C–C bond formation, with further recycling of the Ni^{II} species (Scheme 4).

In the case of an Ag cathode, the use of Ni–bpy as the catalytic system in the electrochemical carboxylation of **1c** produced **4c** as the main compound in 30% yield, together with **2c** and dimers and trimers of **1c**. These results indicate that a change in the reaction conditions, such as the nature of the cathodic material, may strongly influence the results of the electrochemical reaction. In the case of an Ag cathode, there is a strong interaction between the surface and the electrogenerated acetylide, which can explain the high reaction selectivity.

On the other hand, CO_2 is adsorbed and/or reduced differently and selectively, according to the nature of the cath-



Scheme 4

odic material. This factor plays an important role in the CO_2 electroreductive side reaction, and therefore on the faradic yield of the carboxylation.

Conclusions

In conclusion, we have developed a very simple electrochemical method that selectively affords monoalkynylcarboxylic acids from alkynes and diynes. The reaction does not need the presence of a catalyst and can be carried out under very mild pressure and temperature conditions. The carboxylation reaction is chemoselective: It permits monofunctionalization of α,ω -diynes but not the carboxylation of internal triple bonds.

Interestingly, terminal alkynes have for the first time demonstrated selective reduction of the terminal C–H bond on silver cathodes. The change in the cathodic material modified the mechanism and the chemoselectivity of the reaction, changing the nature of the carboxylic acid formed in the carboxylation process.

Experimental Section

General: All solvents were dried and degassed by standard methods. DMF was freshly distilled from calcium hydride before electrolyses.

Electrochemical Procedure: A DMF (25 mL) solution of nBu_4NBF_4 (0.3 mmol) and the alkyne (1 mmol) was electrolyzed in a single-compartment cell fitted with an Mg anode and a silver cathode under carbon dioxide (0.5 atm) and nitrogen at room temperature. The electrodes were connected to a DC power supply and a current of 50 mA was applied between them for 3 h. The consumption of **1** was monitored by GC analysis of aliquots withdrawn from the reaction mixture. The apparent current density was 0.25 A/dm² (applied voltage ca. 3–15 V). The faradic yields were in the range of 30–40%. The reaction mixture was esterified directly in DMF by addition of anhydrous K_2CO_3 (4 mmol) and methyl iodide (12 mmol) and stirring the mixture at 50 °C for 12 h. The solution was hydrolyzed with 20 mL of 0.1 M HCl solution and extracted with Et_2O . The organic layer was washed with H_2O , dried with $MgSO_4$, and concentrated. The methyl esters corresponding to the

carboxylic acids were isolated and analyzed by GC-MS, FT-IR, and ¹H and ¹³C NMR. The products are known compounds and their spectroscopic data were compared to those of authentic samples.

Instrumentation and Cell: Cyclic voltammetry experiments were performed with P.A.R. Scanning Potentiostat model 362 equipment, and were carried out at 25 °C, using Pt or carbon fiber microelectrodes (Tacussel). All potentials are quoted with respect to Ag/AgCl electrode at room temperature, which correspond to a potential difference from that of Fc/Fc⁺ of –0.55 V in DMF/*n*Bu₄N⁺BF₄[–]. Controlled constant intensity electrolyses were carried out using a stabilized constant current supply (Sodilec, EDL 36.07). The electrochemical one-compartment cell is a cylindrical glass vessel of approx. 40 mL volume, equipped with a silver plate cathode (20 cm²) and a magnesium rod anode immersed to 3 cm, such as that reported in ref.^[17]

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