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First example of double bond migration in the electrochemical CO_2 incorporation into (perfluoroalkyl)alkenes

Emmanuelle Chiozza[1], Marc Desigaud[1], Jacques Greiner[2]*, and Elisabet Duñach[1]*

[1] *Laboratoire de Chimie Moléculaire, associé au CNRS.*
[2] *Laboratoire de Chimie Bioorganique, associé au CNRS.*
Université de Nice-Sophia Antipolis, Parc Valrose, F-06108 Nice Cedex 2, France

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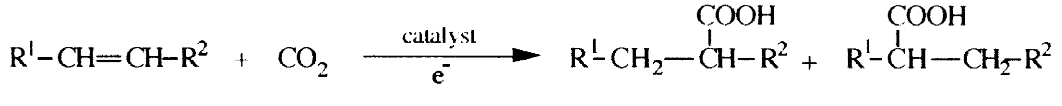
Abstract: The electrochemical, nickel-catalyzed addition of CO_2 to (perfluoroalkyl)alkenes leads to γ-fluoro-γ-(perfluoroalkyl)-β-alkenyl carboxylic acids, involving a double bond migration with loss of one fluorine atom.

Keywords: carboxylation; electrochemical reactions; olefins; perfluoroalkyl compounds

Within our interest in the carbon dioxide fixation into organic substrates for the synthesis of speciality products of the carboxylic acid family [1,2], we focussed our attention on the formation of carbon-carbon bonds between CO_2 and perfluoroalkylated alkenes. The perfluorinated chain being highly hydrophobic, the expected perfluoroalkylated carboxylic acids are precursors of amphiphilic molecules, of interesting applicability in the field of chemical and biomedical fields [3]. Thus, perfluoroalkylated amphiphilic materials are suitable as surfactants and co-surfactants to stabilize fluorocarbon-based emulsions for oxygen-carrying preparations and as components of vesicular structures to be used for drug encapsulation and delivery systems [4,5].

Although the incorporation of carbon dioxide into alkenes has been described with electron-rich transition-metal complexes in *stoichiometric* reactions [6-8], the *catalytic* process remains a challenging goal in CO_2 chemistry [1,2]. We have been interested in the CO_2 incorporation into unsaturated hydrocarbons by electrosynthesis, combined with the use of transition-metal catalysis [9]. Carboxylic acids could be obtained from alkenes and alkynes under mild conditions in a reductive hydrocarboxylation-type reaction [9-12] (eq. 1).



$$R^1\text{-}CH{=}CH\text{-}R^2 + CO_2 \xrightarrow[e^-]{\text{catalyst}} R^1\text{-}CH_2\text{—}\overset{COOH}{\overset{|}{C}H}\text{-}R^2 + R^1\text{-}\overset{COOH}{\overset{|}{C}H}\text{—}CH_2\text{-}R^2$$

Equation 1

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Thus, exo-norbornene carboxylic acid was obtained from norbornene and CO_2 in a nickel-catalyzed electrosynthesis [10]. However, no CO_2 insertion products were observed for unactivated aliphatic alkenes such as 1-octene [10].

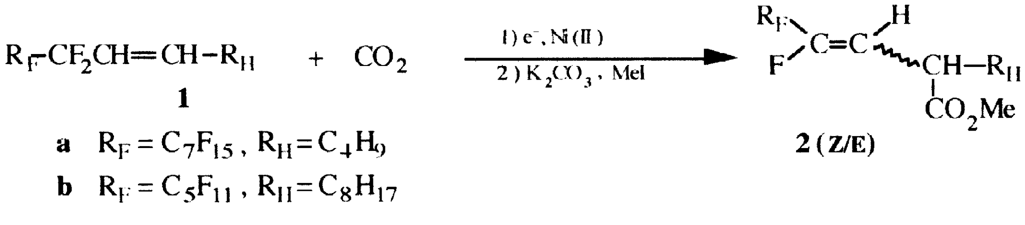
To broaden the scope of the CO_2 fixation reaction, we have been interested in its insertion on double bond substituted by perfluoroalkyl chain; such electron-deficient olefins should be activated towards electroreduction due to the presence of the perfluoroalkyl chain [13]. Except for the well-established anodic perfluorination [14] and cathodic trifluoromethylation [13,15,16], successful electrochemical reactions involving organofluorine compounds are still limited. To our knowledge, no examples of CO_2 insertion into perfluoroalkylated alkenes have been yet reported.

We present here our results on the electrochemical CO_2 fixation into perfluoroalkylated olefins **1a,b** (Scheme 1) in the presence of various nickel(II) complexes, used as the catalyst precursors. Thus, Ni(II) complexes such as $Ni(bipy)_3^{2+}$, $2BF_4^-$ (bipy = 2,2'-bipyridine) [12], and $Ni(cyclam)Br_2$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) [17] were used in catalytic amounts (10 mol%) for the electrocarboxylations. Substrates **1a,b** (E/Z = 90/10) were prepared by the well-known two-step procedure (i) radical addition of the corresponding perfluoroalkyl iodides on 1-alkenes and (ii) subsequent dehydroiodination of the intermediates [18,19].

Typical experimental electrosyntheses were carried out using a one-compartment cell fitted with a sacrificial magnesium anode [20] at atmospheric carbon dioxide pressure and the results of the carboxylations of **1a,b** are presented in Table 1.

Surprisingly, the expected carboxylic acids issued from a double bond hydrocarboxylation, according to eq. 1 were not obtained. Instead, the main reaction products were carboxylic acids **2** (mixture of E/Z regioisomers) (Scheme 1). Both perfluoroalkyl olefins **1a** and **1b** led to the β,γ-unsaturated acids **2**, which could be isolated and identified as their methyl esters (See NMR data in footnote of Table 1). Chemical shifts of fluorine atoms are in agreement with those of the literature data for similar compounds [21-23]. Products **2** are issued from a CO_2 incorporation on the hydrocarbon site of the initial double bond of **1** with a shift of the double bond position towards the perfluoroalkyl chain and loss of one fluorine atom from the allylic position.

At 20 °C, the best yields of carboxylation were obtained with the Ni-cyclam catalytic system; up to 92% of CO_2 incorporation into **1b** could be attained, while the Ni-bipy catalytic system led to lower alkene conversions.



Scheme 1: Electrocarboxylation of perfluoroalkylated alkenes.

The influence of the temperature on the electrocarboxylation of **1** was examined and showed that the Ni-bipy catalytic system was more efficient at 60 °C than at 20 °C; in contrast, the opposite effect occurred for the Ni-cyclam system. Among the carboxylic acids formed, the unsaturated compounds **2** constitute, hereagain, the main reaction products. Yields are similar to those obtained with the Ni-cyclam catalytic system at room temperature, although the regioselectivity Z/E is higher when cyclam is used as the ligand of nickel. Carboxylated by-products were essentially saturated analogs of **2** and dicarboxylic acids.

Table 1: Electrocarboxylation[a] of alkenes **1a,b**.

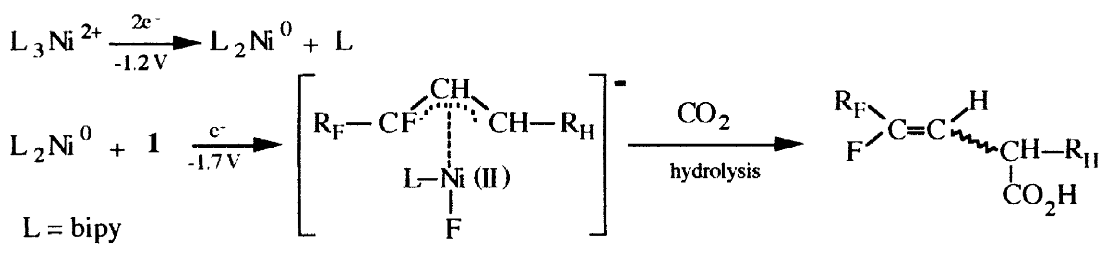
Starting alkenes	Catalyst precursor	T (°C)	% Carboxylation[b]	Esters[c]	
				% of **2**	**E/Z** ratio
1a	Ni (cyclam) Br_2	20	65	45	30/70
		60	35		
1a	Ni $(bipy)_3$ $(BF_4)_2$	20	20		
		60	58	30	45/55
1b	Ni (cyclam) Br_2	20	92	56	37/63
		60	34		
1b	Ni $(bipy)_3$ $(BF_4)_2$	20	30		
		60	86	50	45/55

[a] Electrocarboxylations were carried out with 2 mmol of **1a** or **1b** in anhydrous DMF (40 mL) at constant current intensity of 50 mA for 4 h, using tetrabutylammonium tetrafluoroborate (10^{-2} M) (Bu_4N^+,BF_4^-) as supporting electrolyte. The catalyst was introduced in a 10% molar ratio with respect to the substrate and carbon dioxide was bubbled through the solution at atmospheric pressure. To make purification and analysis easier, carboxylic acids in the crude mixture were esterified according to conventional method (K_2CO_3/MeI; 50 °C; 15 h) immediately after electrolyses and purified by column chromatography. All electrolyses were performed with Mg/stainless steel couple electrodes at 20 °C or 60 °C. No significant differences were found for experiments made with a carbon fiber or a nickel foam cathode.

[b] Calculated on recovered carboxylic acid methyl esters after electrosyntheses followed by esterification of the crude reaction mixtures.

[c] **Spectral data** ($CDCl_3$): Methyl ester **2a** (***Z***): RMN ^1H: 0.9 (3H, t, CH_3), 1.1 to 2.0 [6H, m, $CH_3(C\underline{H}_2)_3$], 3.6 (1H, m, CF=CH-C$\underline{H}$), 3.7 [3H, s, C(O)OC$\underline{H}_3$], 5.7 (1H, dd, CF=CH, $^3J_{HH} = 9$, $^3J_{FH} = 32$); RMN ^{19}F: -81.3 (3F, CF_3), -118.1 (2F, $C\underline{F}_2CF$=), -120.2 to -124.4 (8F, $4CF_2$), -126.7 (2F, $C\underline{F}_2CF_3$), -129.6 (1F, $CF_2C\underline{F}$=). Methyl ester **2a** (***E***): RMN ^1H: 0.9 (3H, t, CH_3), 1.1 to 2.0 [6H, m, $CH_3(C\underline{H}_2)_3$], 3.6 (1H, m, CF=CH-C$\underline{H}$), 3.8 [3H, s, C(O)OC$\underline{H}_3$], 5.9 (1H, dd, CF=CH); RMN ^{19}F: -81.3 (3F, CF_3), -117.2 (2F, $C\underline{F}_2CF$=), -120.2 to -124.4 (8F, $4CF_2$), -126.7 (2F, $C\underline{F}_2CF_3$), -129.1 (1F, $CF_2C\underline{F}$=).
Similar chemical shifts were observed for **2b** (***Z***) and **2b** (***E***).

Although more mechanistic work is needed to explain the carboxylation with allylic C-F bond activation, in the case of the Ni-bipy catalytic system we propose a first step of electrochemical two-electron reduction from Ni(II) to Ni(0) (Scheme 2). According to cyclic voltammetry results, the $[Ni(II)\ (bipy)_3]^{2+}$ reduction occurs at -1.2 V vs SCE in DMF



Scheme 2: Proposed electrocarboxylation mechanism.

containing Bu_4N^+, BF_4^- as supporting electrolyte [9]. However, no reaction took place at -1.2 V and the activation of the C-F allylic bond of **1** by the nickel complex occurs at more negative potentials, of -1.7 V. In the presence of CO_2, the proposed π-allyl-type complex is carboxylated regioselectively at its CH-end to afford, after hydrolysis, the corresponding β,γ-unsaturated carboxylic acid. This type of reactivity for the α-CF_2 group on the double bond has been once reported in a Friedel-Crafts reaction in the presence of $AlCl_3$ [24].

In the case of Ni(cyclam)Br_2 catalyzed carboxylation, a different mechanism might be operating, namely through electrogenerated Ni(I) species [25].

In conclusion, interesting and new results have been obtained for the fixation of CO_2 into perfluoroalkyl olefins. Good yields of carboxylic acids can be reached by a careful control of the reaction conditions and of the nature of the catalyst. The main carboxylic acids (or methyl esters) are derived from the incorporation of carbon dioxide on the C=C, with a double bond migration and loss of one flourine atom from the CF_2 in α. The formation of isomerized carboxylic acids from perfluoroalkyl olefins reveals an important influence of the perfluoroalkyl chain on the electroarboxylation reaction; no carboxylation occurred in the case of related alkyl olefins under the same reaction conditions. These results constitute the first example in which an allylic reactivity involving a double bond migration is observed in the case of electrochemical carboxylations.

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