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NOTE

Electrocatalytic reduction of CO_2 for the selective carboxylation of olefins†

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Electroreduction of $[CpFe(CO)_2]_2$ (Fp_2) in the presence of carbon dioxide makes possible the formation of the 1:1 adduct $[Cp(CO)_2Fe—CO_2]^-$, which is catalytically reduced at −1.8 V vs SCE liberating $[Cp(CO)_2Fe]^-$ and $CO_2^{\cdot -}$. The generation of $CO_2^{\cdot -}$ at a potential close to the standard value allows regioselective carboxylation of styrene and isoprene with turnover number of 200 per Fp_2. The first step of the carboxylation appears to be the addition of $CO_2^{\cdot -}$ to the unsubstituted carbon atoms of the olefin. Copyright © 2000 John Wiley & Sons, Ltd.

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INTRODUCTION

Electroreductive coupling between olefinic substrates and CO_2 is known to be a preparative method for dicarboxylic acids derivatives.[1] The voltage required for electrolysis is governed by the reduction properties of the olefin–CO_2 system. Accordingly, good to poor yield and selectivity were observed. For activated olefins reduced at a less cathodic potential than CO_2, two mechanisms have been proposed for initiation: either the nucleophilic attack of the olefin radical-anion on CO_2 or a redox catalysis followed by coupling of the olefin and CO_2 radical-anions.[2,3] Our approach in this field came from our interest on CO_2 activation by transition metal complexes[4] and on selective functionnalization of olefins by appropriate conjunction of activation modes.[5] We report here the role of $[CpFe(CO)_2]_2$, Fp_2, in the regioselective electrocarboxylation of styrene and isoprene.

RESULTS

The electrochemical reduction of Fp_2 has been shown to be a two-electron process leading to $2Fp^-$, which is reoxidized to the starting complex (EC mechanism).[6] Accordingly, cyclic voltammetry at a scan rate of 0.1 V s^{-1} exhibited irreversible cathodic and anodic peaks at $E_p = -1.55$ V and −0.96 V respectively (Fig. 1a). Addition of styrene or isoprene did not promote any changes. By contrast, the addition of CO_2 led to an additional cathodic peak at −1.8 V (Fig. 1b), which was found to be catalytic as CO_2 concentration increased (Fig. 1c). It was therefore of interest to study more deeply this system by generating Fp^- and examining its electroactivity under CO_2. It is noteworthy that the chemical reaction between Fp^- and CO_2 has been reported to give the 1:1 adduct $[Fp—CO_2]^-$.[7] The *in situ* preparation of Fp^- was performed by controlled potential electrolysis of Fp_2 (10^{-2} M) at −1.80 V. Then, changes in Fp^- concentration upon CO_2 admission were recorded

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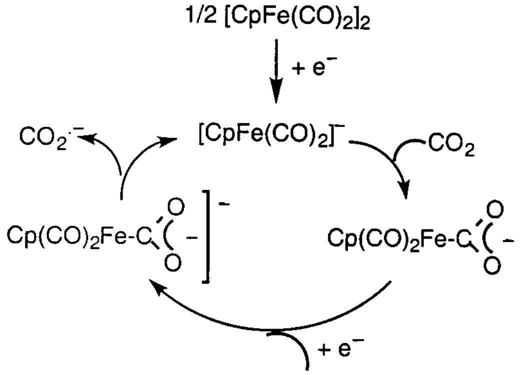


Scheme 1.

by amperometry at +0.3 V, a potential at which Fp^- is oxidized. Upon admission of CO_2, the current decreased progressively. The IR spectrum of the solution exhibited ν(C=O) bands of the carbonyl ligands at 2015 and 1950 cm^{-1}, corresponding to those of $[Fp—CO_2]^-$;[7] the ν(CO) of the carbonato ligand was obscured by the solvent. The voltammogram at a rotating gold electrode showed practically no current at the level of either Fp_2 reduction ($E_{1/2} = -1.50$ V) or Fp^- oxidation ($E_{1/2} = -0.96$ V), whereas a current associated with the catalytic wave at $E_{1/2} = -2.0$ V was present. The cyclic voltammetry of the same solution at a stationary gold electrode confirmed the disappearance of Fp_2 and the presence of $[Fp—CO_2]^-$ and Fp^-. These results show that $[Fp—CO_2]^-$ is reduced at −1.8 V to produce an unstable species that splits into Fp^- and $CO_2^{\cdot-}$. As Fp^- is regenerated, it reacts again with CO_2 in a catalytic cycle, as depicted in Scheme 1.

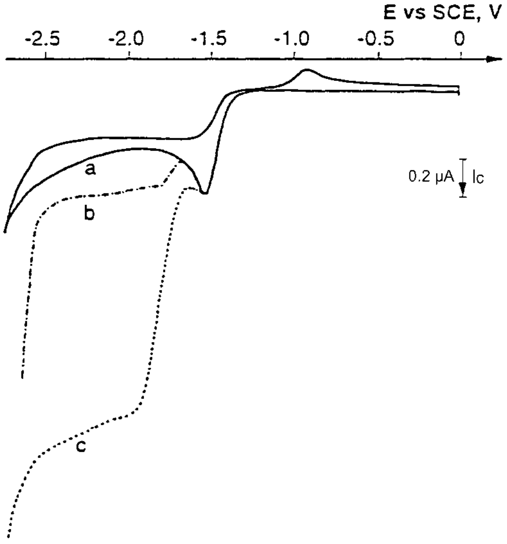
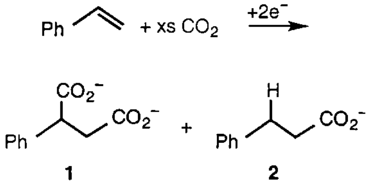


Figure 1 Voltammogram (scan rate 0.1 V s^{-1}) in DMF–0.1 M $TBABF_4$ on a gold microelectrode of: (a) Fp_2 (10^{-2} M), (b) Fp_2–CO_2, (c) with more CO_2.

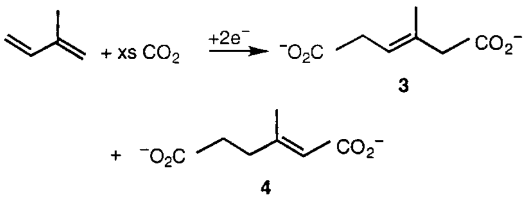
Controlled potential electrolysis of a 70 ml *N*,*N*-dimethylformamide–tetrabutylammonium hexafluorophosphate (DMF–$TBAPF_6$) solution containing Fp_2 (0.13 mmol), styrene (60 mmol), and CO_2 (9 bar) led to the carboxylated products **1** and **2** (Eqn [1]), at the reduction potential of $[Fp—CO_2]^-$.



[1]

After the passage of 200 *F* mol^{-1} of Fp_2, compound **1** was the major product formed with a chemical yield of 78% and a current efficiency of 45% ($2e^-$ per mole of **1**). In the absence of Fp_2, the electrolysis occurred at −2.3 V, for the same current density, and compound **1** was again preponderant (chemical yield: 70%; current efficiency: 40%). The other product, **2**, corresponds to the regioselective carboxylation at the β carbon atom and the addition of one hydrogen atom at the α carbon of the double bond. Experiments conducted in the presence of 110 mmol of H_2O, under the same conditions, pointed out that residual water was responsible for the hydrogenation. Compound **2** was formed selectively in the absence of Fp_2 (chemical yield: 77%; current efficiency: 67%), whereas with Fp_2 the ratio **1**:**2** = 1.3 (chemical yield and current efficiency close to 98%). These results show that the major effect of Fp_2 is to operate the carboxylation of styrene at a less negative potential, at a value corresponding to the catalytic wave described in Scheme 1.

A more spectacular effect of Fp_2 was revealed for isoprene. At the reduction potential of $[Fp—CO_2]^-$, electrolysis of a 70 ml DMF–$TBAPF_6$ solution



[2]

containing Fp_2 (0.13 mmol), isoprene (60 mmol), and CO_2 (2.5 bar) led to the carboxylated products **3** and **4**, resulting from the regioselective 1,4-dicarboxylation (Eqn [2]). After the passage of 200 $F\ mol^{-1}$ of Fp_2, the chemical yield was 97% and the current efficiency 72%, with a selectivity **3**:(**3** + **4**) = 83%. In the absence of Fp_2, electrolysis took place at -2.6 V. The reaction was not selective in the carboxylation of isoprene: oxalate was found (current efficiency of 30%) together with **3** and **4** (current efficiency 20%).

DISCUSSION

The results described in this paper show that the electrogeneration of $[Fp—CO_2)]^-$ from Fp_2 and CO_2 leads to a catalytic reduction of CO_2 into $CO_2^{\cdot -}$ through the decomposition of $[Fp—CO_2)]^{2-}$ into Fp^- and $CO_2^{\cdot -}$. The generation of $CO_2^{\cdot -}$ at a potential close to the standard value (-2.21 V vs SCE in DMF)[8] allows the regioselective carboxylation of styrene and isoprene with turnover numbers of 200 F per Fp_2. The first step of the carboxylation appears to be the addition of $CO_2^{\cdot -}$ to the unsubstituted carbon atoms of the olefin.

EXPERIMENTAL

All reactions were carried out under argon atmosphere using standard Schlenk techniques. DMF from Aldrich was distilled under reduced pressure over CaH_2 and kept over 3 Å molecular sieves. $TBAPF_6$ from Fluka was recrystallized from $EtOH–H_2O$ and vacuum dried at 100 °C overnight before use. Fp_2 was prepared according to Ref. 9.

The electrochemical experiments were conducted in DMF. Bulk electrolyses were performed under CO_2 pressure in a thermostated stainless steel reactor fitted with electric leads. The three compartments of the cell were separated by glass fritts. The working electrode was a mercury pool (29 cm^2), the counter electrode aluminum foil, and the reference electrode Ag–AgCl. Electrolysis was carried out with a current density of 7 $mA\ cm^{-2}$ using an AMEL 552 potensiostat equipped with a Solea–Tacussel IG5-LN coulometer. The experiments were stopped after 2500 C.

The gas phase was analyzed by gas chromatography (GC) for CO and hydrogen, then the reactor was depressurized, and the solution from the cathodic compartment was distilled under reduced pressure at room temperature. The residue, containing the reaction products, was reacted with MeI–MeCN to esterify the carboxylated salts for GC analysis. The concomitant formation of TBAI was titrated with a solution of $AgNO_3$. This procedure allowed one to calculate the chemical yield in carboxylation. A further treatment with diazomethane permitted one to check if any carboxylic acids were present; this was not the case. Identification of the products was performed by ^1H NMR and mass spectrometry, after extraction with diethyl ether and separation by liquid chromatography. The yield in methyl esters was determined by GC (10% Carbowax 20M on Gaz Chrom Q) with suitable internal standards.

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