

Electrolytic Fixation of CO₂ by Electrocarboxylation of RX on Nanocrystalline TiO₂-Pt Cathode

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Electrolytic fixation of CO₂ was investigated by electrocarboxylation of organic halides (RX), and four esters (I, II, III, IV) were obtained in moderate yields. Electrochemical reduction esterifications of RX in the presence of CO₂ were carried out on nanocrystalline TiO₂-Pt electrode. The electrochemical behavior of RX in the presence of CO₂ was investigated by the technique of cyclic voltammetry, and the probable reaction mechanism was proposed.

Keywords CO₂, nanocrystalline TiO₂-Pt electrode, electrocarboxylation, organic halide (RX), ester

Introduction

Carbon dioxide is an abundant and low-cost “green carbon source” for production of organic chemicals and fuels.^{1,2} The chemistry of CO₂ is receiving increasing attention for a variety of reasons including its potential as a C₁ feedstock,³ the concentration of green-house gas in the atmosphere,⁴ and its possible use as a substrate for storing solar energy.⁵ The fixation of CO₂ is an important area of research.⁴ Although many fixation processes including the hydrogenation over heterogeneous and homogeneous catalysts at high temperature and electrochemical reduction have been proposed, one of the most essential matters in CO₂ fixation is to achieve it under an input energy as low as possible to avoid a secondary generation of CO₂. Because of this, the heterogeneous methanation of CO₂ at elevated temperatures is not a candidate for a practical fixation process, while electrochemical reduction taking place at room temperature seems to be promising. Electrochemical fixation of CO₂ have been attracting research interest recently.⁶ And esterification is one of the most fundamental and important reactions in organic synthesis.⁷

In this paper, we report for the first time electrolytic fixation of CO₂ on nanocrystalline TiO₂-Pt cathode by electrocarboxylation of RX (X=Br, Cl) at room temperature with four esters being obtained.

Results and discussion

Preparation and characterization of electrode

The nanocrystalline TiO₂-Pt modified titanium electrode (Ti/nano-TiO₂-Pt) was prepared by electrosynthesis precursor Ti(OEt)₄ directly hydrolyzed and electro-deposited Pt on nanocrystalline TiO₂ film.⁸ The mor-

phology of deposited Pt on the nano-TiO₂ electrode illustrated by the SEM image is shown in Figure 1. The results indicated that Pt was deposited on the porous surface of nano-TiO₂ and the average diameter of Pt particle was 60 nm. The Pt particle of such scattered state had enormous surface area so that the surface effect of the nanometer material improved the surface activation of Pt particle further.

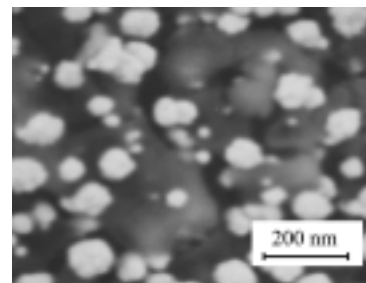


Figure 1 SEM photograph of the nanocrystalline TiO₂-Pt electrode.

Figure 2 shows CV for Pt electrode (area 0.04 cm²) and Ti/nano-TiO₂-Pt (area 0.04 cm²) electrode in 1 mol·L⁻¹ H₂SO₄ under argon near room temperature. It can be seen that the Ti/nano-TiO₂-Pt electrode has the electrochemical behavior of the Pt electrode⁹ and electrochemical activity is much higher than Pt electrode, which should be attributed to the nano-TiO₂ in coordination with Pt particle.

The electrochemical behavior of RX on nanocrystalline TiO₂-Pt electrode

The electrochemical behavior of RX on nanocrystalline TiO₂-Pt electrode was investigated by the technique

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Received January 13, 2004; revised June 14, 2004; accepted July 2, 2004.

Project supported by the Natural Science Foundation of the Anhui province in China (No. 00045317).

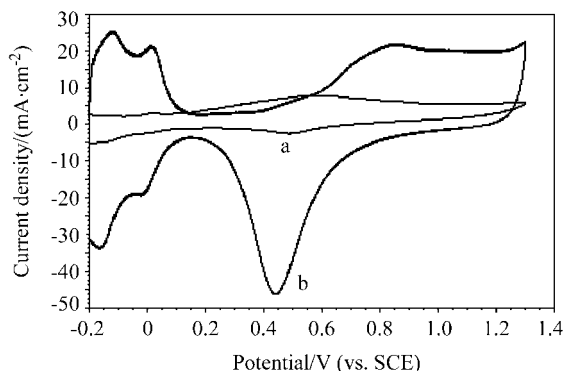


Figure 2 Cyclic voltammograms (CV) for Pt electrode (a) and Ti/nano-TiO₂-Pt electrode (b) in 1 mol·L⁻¹ H₂SO₄. The solution was Ar saturated. Scan rate, 0.1 V·s⁻¹.

of cyclic voltammetry. Figure 3 shows CV of PhCH₂Br in the absence and presence of CO₂ on nanocrystalline TiO₂-Pt electrode. In the absence of carbon dioxide (curve b), an irreversible reduction peak of PhCH₂Br was observed at -2.0 V (vs. SCE), and benzyl bromide has been reported to exhibit a, presumably two-electron, wave polarographically but to yield products arising from both carbanionic¹⁰ and presumed radical¹¹ intermediates in bulk electrolyses. In the presence of CO₂ (curve a), the onset potential of reductive current wave was observed in the presence of a positive potential and the current increased apparently. This increase in current is attributed to an electrocatalytic reaction between the electrogenerated species and CO₂. A reduction peak was observed at -2.4 V (vs. SCE) and an oxidation peak was observed at -1.0 V (vs. SCE) in Figure 3 (curve a), possibly due to the reduction of CO₂ and the oxidation of the product which was reduced by CO₂. As the reduction potential of RX is more positive than that of CO₂, the reduction of RX is easier than that of CO₂ on nano-TiO₂-Pt cathode.

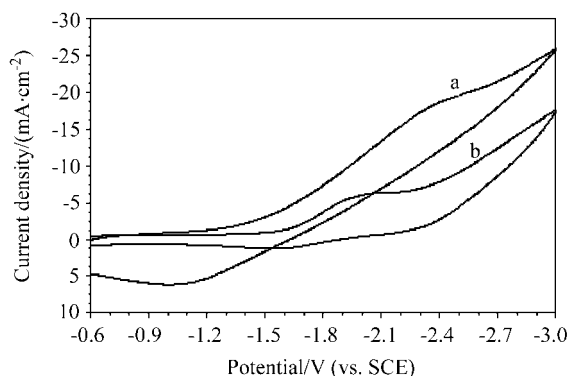


Figure 3 Cyclic voltammograms of RX (PhCH₂Br) on Ti/nano-TiO₂-Pt electrode in DMF containing 0.1 mol·L⁻¹ Bu₄NBr as supporting electrolyte at 20 °C. Scan rate, 0.1 V·s⁻¹. (a) solution saturated with CO₂; (b) solution under argon.

Electrolytic fixation of CO₂

Electrolytic fixation of CO₂ on nanocrystalline TiO₂-Pt cathode was achieved by electrocarboxylation of RX (X=Br, Cl) in DMF near room temperature, and four esters were obtained.

The results are summarized in Table 1. A range of RX was explored with comparable results. The electrocarboxylation of benzyl bromide (**1**) or benzyl chloride (**2**) in the presence of CO₂ gave the expected esterification product **I** exclusively in 47% or 42% yield, respectively (Entries 1 and 2). After purification by fractional column distillation, the electrocarboxylation of ethyl bromoacetate (**3**) afforded esterification product **II** in 41% yield in the similar reaction conditions (Entry 3). In contrast to **1**–**3**, when butyl bromide (**4**) or *n*-butyl chloride (**5**) was electrocarboxylated in the presence of CO₂, the esterification product **III** was obtained in the lower yield along with the coupled products as by-products.

Table 1 Electrocarboxylation of RX in the presence of CO₂ on Ti/nano-TiO₂-Pt cathode surface^a

Entry	RX	Current density ^{b/} (mA·cm ⁻²)	Time/ h	Product	Yield ^{c/} %
1	PhCH ₂ Br (1)	20	3.5	I	47
2	PhCH ₂ Cl (2)	20	4.0	I	42
3	BrCH ₂ COOC ₂ H ₅ (3)	20	4.0	II	43
4	<i>n</i> -C ₄ H ₉ Br (4)	12	8.0	III	10
5	<i>n</i> -C ₄ H ₉ Cl (5)	5	9.0	III	4
6	CH ₂ =CHCH ₂ Br (6)	15	3.2	IV	27

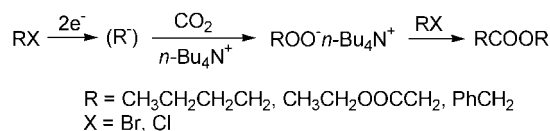
^a Solution initially had 0.1 mol·L⁻¹ supporting electrolyte. ^b The current density was expressed versus the area of the cathode. ^c Isolated yield based on current. **I**: PhCH₂COOCH₂Ph, **II**: C₂H₅OOCCH₂COOCH₂COOC₂H₅, **III**: *n*-C₄H₉COOC₄H₉, **IV**: CH₃CH=CHCOOCH₂CH=CH₂.

The possible mechanism of the electrochemical reactions is proposed in Scheme 1. Electrochemical reduction of RX in the presence of CO₂ led directly to RCOOR. Electrolysis has been used as a means of trapping anion radicals¹² and anions from hydrocarbons and halides,¹³ respectively. The RCOOR was the major coupled product. Reaction of the R⁻ with CO₂ yields a carboxylate anion RCOO⁻. The counter ion is tetraethylammonium. In the presence of excess active halide the salt is rapidly converted to ester. It was established independently that tetraethylammonium carboxylates are rapidly converted to esters with active and even only moderately active halides in DMF.

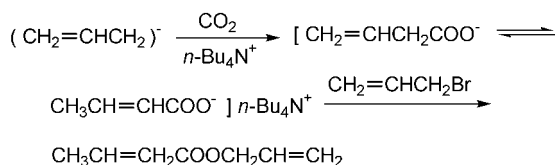
However, when allyl bromide (**6**) was used to react in the presence of CO₂, **IV** was acquired in mediate

yield as the major product. The possible mechanism is shown in Scheme 2. The reaction of the ally carbanion with CO₂ yields a carboxylate anion, [CH₂=CHCH₂COO⁻ ↔ CH₃CH=CHCOO⁻]*n*-Bu₄N⁺, which under conditions prevailing in the catholyte must become crotonate rather than 3-butenate. So when allyl bromide (**6**) was electroreduced in the presence of CO₂, the major coupled product was allyl crotonate.

Scheme 1



Scheme 2



Experimental

Materials and instruments

¹H NMR spectra were recorded in CDCl₃ on Bruker AM-300 instruments with Me₄Si as the internal standard. IR spectra were obtained with a Nicolet AV-360 spectrophotometer. Electrochemical experiments were performed on a CHI model 660A electrochemical workstation with a three-electrode system using Ti/nano-TiO₂-Pt as a working electrode, Pt wire as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. Electrolysis was carried out with an HYL-A current source. All potentials in the text refer to SCE.

DMF was distilled under reduced pressure from CaH₂ and RX was purified before use. Bu₄NBr was recrystallized from ethyl acetate and air dried. The water used was doubly distilled. And all electrodes were washed and dried before use.

General procedure for electrolytic fixation of CO₂ by electrocarboxylation of RX on nanocrystalline TiO₂-Pt cathode

The electrolysis cell for electrocarboxylation was a two-compartment H-cell, which was separated by a 15-mm diameter medium porosity frit. The Ti/nano-TiO₂-Pt cathode had an area of 10 cm² and the anode was of graphite. The mixed solution of *n*-Bu₄NBr or *n*-Bu₄NCl (0.1 mol·L⁻¹) and RX (0.4 mol·L⁻¹) in DMF (30 mL) were electrolyzed in the cathode compartment. The cell was then immersed in a cold water bath to dissipate the heat evolved by the electrolysis and to keep the temperature under 30 °C. Carbon dioxide was bubbled continuously through catholyte. After be-

ing electrolyzed, the catholyte was hydrolyzed with aqueous HCl and extracted with Et₂O, and the organic layer was dried over MgSO₄. After concentration, the residue was purified by column chromatography or reduced pressure distillation.

Benzyl phenylacetate (I): Benzyl phenylacetate was isolated by flash column chromatography on silica gel using ethyl acetate/hexane (V/V=1 : 40) as an eluent. Colorless liquid. ¹H NMR (300 MHz, CDCl₃) δ: 3.71 (s, 2H, CH₂COO), 5.17 (s, 2H, OCH₂), 7.27—7.41 (m, 10H, 2×Ph). IR ν: 1737 cm⁻¹.

Ethoxycarbonylmethyl ethyl malonate (II): Ethoxycarbonylmethyl ethyl malonate was isolated by reduced pressure distillation (140 °C/66.5 Pa). Colorless liquid. ¹H NMR (300 MHz, CDCl₃) δ: 1.24—1.30 (m, 6H, 2×CH₃), 3.46 (s, 2H, COCH₂CO), 4.16—4.25 (m, 4H, 2×CH₂), 4.64 (s, 2H, OCH₂CO). IR ν: 1740, 1755 cm⁻¹.

***n*-Butyl pentanoate (III):** *n*-Butyl pentanoate was isolated by reduced pressure distillation (85 °C/1330 Pa). Colorless liquid. ¹H NMR (300 MHz, CDCl₃) δ: 0.89 (t, *J*=6.0 Hz, 6H, 2×CH₃), 1.23—1.39 (m, 4H, 2×CH₂CH₂), 1.47—1.62 (m, 4H, 2×CH₂CH₂CH₂), 2.58 (t, *J*=6.3 Hz, 2H, CH₂COO), 4.10 (t, *J*=7.0 Hz, 2H, OCH₂). IR ν: 1745 cm⁻¹.

Allyl crotonate (IV): Allyl crotonate was isolated by flash column chromatography on silica gel using ethyl acetate/hexane (V/V=1 : 40) as an eluent. Colorless liquid. ¹H NMR (300 MHz, CDCl₃) δ: 1.89 (d, *J*=7 Hz, 3H, CH₃), 4.64 (d, *J*=5 Hz, 2H, OCH₂), 5.23—5.36 (m, 2H, =CH₂), 5.86—6.00 (m, 2H, 2×CH=), 6.98—7.06 (m, 1H, =CHCOO). IR ν: 1731 cm⁻¹.

Conclusion

In conclusion, electrolytic fixation of CO₂ on nanocrystalline TiO₂-Pt cathode can be reached by electrocarboxylation of RX in the presence of CO₂. The reaction does not need the presence of a catalyst and can be carried out under very mild pressure and temperature conditions. It is also worth noting that this reported method utilizes carbon dioxide as the starting C₁ carbon source and constitutes a new example in the field of green chemistry. The further utility of this method is in progress.

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(E0401132 CHENG, B.)