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Electrocatalytic carboxylation of aromatic ketones with carbon dioxide in ionic liquid 1-butyl-3-methylimidazoliumtetrafluoborate to α-hydroxy-carboxylic acid methyl ester

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ABSTRACT

A new electrochemical procedure for the electrocatalytic carboxylation of aromatic ketones with carbon dioxide in ionic liquid, 1-butyl-3-methylimidazolium tetrafluoborate ($BMIMBF_4$), to α-hydroxycarboxylic acid methyl ester was investigated for the first time. The electrochemical behavior of acetophenone in $BMIMBF_4$ was studied by cyclic voltammetry with a reduction peak at −1.9 V (vs. Ag). The electrolyses experiments were carried out in an undivided cell under mild conditions without any toxic solvents, catalysts and supporting electrolytes, followed by addition of an alkylating agent, affording the α-hydroxycarboxylic acid methyl ester in a moderate yield (62%). The results showed that the yields were strongly affected by various factors: temperature, current density, charge passed, electrode material and substrate concentration. Moreover, the ionic liquid was successfully recycled for this reaction.

1. Introduction

Carbon dioxide (CO_2) produced by combustion of fossil fuels is regarded as the most significant greenhouse gas; the increasing accumulation of CO_2 in the atmosphere has caused serious environmental problems [1]. On the other hand, CO_2 is a naturally abundant, economical, non-toxic and recyclable carbon source [2]. Thus, the conversion and utilization of CO_2 have attracted considerable attention in the whole world. The electrocarboxylation of various organic compounds with CO_2, which can replace phosgene and cyanides, is an environmental friendly and attractive approach to prepare valuable carboxylated products [3–9].

Direct electrocarboxylation of aromatic ketones with CO_2 has attracted a considerable interest as a method to obtain α-hydroxycarboxylic ester and its derivatives widely used as anti-inflammatory drugs [8–14]. Nevertheless, the use of toxic organic solvents, such as CH_3CN and DMF, and of large amounts of supporting electrolyte makes it more complex to recover the solvents. With the growing demand of environmental friendly technologies, efforts should be devoted to avoid the use of volatile solvents.

Ionic liquids, molten salts with melting points close to room temperature, are obtained by combination of large organic cations (*N*,*N*-dialkylimidazolium, phosphonium, pyridinium, quaternaryammonium, etc.) with a variety of anions, such as BF_4^-, PF_6^-, and $AlCl_4^-$ [15,16]. Recently, ionic liquids have been used as green reaction media in organic synthesis due to their wide electrochemical potential window, high ionic conductivity, good solvating ability and low vapour pressure. Up to now, several research groups have reported electrochemical fixations of CO_2 with various organic compounds to obtain valuable carboxylated products [15–19].

Conversely, to our best knowledge, investigations concerning chemical fixation of CO_2 with aromatic ketones in ionic liquids have not been reported. Herein, we began studying the electrocarboxylation of aromatic ketones in CO_2-saturated ionic liquid $BMIMBF_4$ (Scheme 1). The aim of this investigation was to set-up a simple and efficient electrochemical route for the incorporation of CO_2 into aromatic ketones in $BMIMBF_4$ to yield α-hydroxycarboxylic acid methyl esters, under mild conditions without supporting electrolyte and catalysts, giving a safer and more environmental friendly process for CO_2 fixation.

2. Experimental

2.1. Chemicals

The ionic liquid $BMIMBF_4$ (with a purity of more than 99%) was dried under vacuum at 120 °C until cyclic voltammetric results indicated that there was no detectable water, as the presence of water would narrow the electrochemical potential window of the

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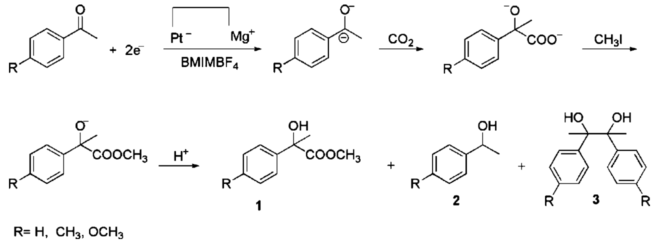

Scheme 1.

ionic liquid BMIMBF$_4$ [20,21]. The purity of CO$_2$ and argon (Ar) was 99.99%. Unless otherwise noted, the reagents and solvents were used as received from commercial suppliers.

2.2. Typical electroanalytical and electrolysis procedure

The electroanalytical experiments were carried out using CHI660B electrochemical station (Shanghai Chenhua Instrument Company) in an undivided cell, with glassy carbon electrode (GC, d = 3 mm) as the working electrode, platinum (Pt, area = 1 cm^2) foil as the counter electrode and Ag wire as the reference electrode. Prior to the experiments, all electrodes were polished mechanically (the GC electrode was polished until a mirror-like surface was obtained) with sand paper and then were sonicated (KQ-50DE) in ethanol for 5 min to remove any microparticulates. Finally, all the electrodes were cleaned with diluted hydrochloric acid and double distilled water and then were dried with Ar gas.

The electrolysis experiments were conducted in a standard undivided glass cell equipped with a metallic cathode (area = 2 cm^2) and a magnesium rod (Mg, d = 0.5 cm) sacrificial anode. The galvanostatic electrolysis was performed by using a CT2001C battery test system (Wuhan Land Company, China) with two electrodes, whereas the potentiostatic electrolysis was carried out using CHI660B electrochemical station with three electrodes. Prior to each test, BMIMBF$_4$ (5 mL) with definite concentration of aromatic ketone was bubbled with CO$_2$ for 30 min to be saturated. Then a suitable constant current (or potential) was applied and continuous CO$_2$ flow was maintained throughout the duration of the whole electrolysis experiment. After a certain amount of charge (Q) had been supplied to the electrode, the electrolysis was interrupted. Then CH$_3$I (3-fold excess) was added as an alkylation agent and the mixture was stirred at 55 °C for 6 h. After that the reaction mixture was extracted with diethyl ether (Et$_2$O, 3× 5 mL). Then the combined organic layers were acidified with 2 mol dm^{-3} aqueous HCl and dried over anhydrous Na$_2$SO$_4$. After evaporation of the Et$_2$O under reduced pressure, the crude product was obtained. This product was purified by column chromatography with petroleum ether/ethyl acetate mixtures.

Gas chromatography–mass spectra (GC–MS) were recorded with HP 6890/5973 GC–MS an Agilent 1100 series. HNMR spectra were obtained with a Varian INOVA-300 spectrometer using tetramethylsilane (TMS) as internal standard and deuterated chloroform (CDCl$_3$) as solvent.

2-Hydroxy-2-phenylpropionic acid methyl ester: GC–MS (m/z, %): 180 (M$^+$, 29), 148 (9), 121(22), 104 (100), 77 (39), 51 (11), 32 (24). H NMR: δ 7.2–7.6 (m, 5H, –ArH), 3.7 (s, 3H, –COOCH$_3$), 3.9 (s, 1 H, –OH), 1.8 (s, 3H, –CH$_3$).

Methyl-2-hydroxy-2-p-tolylpropanoate: GC–MS (m/z, %): 194 (M$^+$, 45), 135 (21), 118 (100), 91 (39), 77 (7), 65 (8), 43 (8). H NMR: δ 7.1–7.5 (4H, –ArH), 3.8 (s, 3H, –COOCH$_3$), 3.7 (s, 1H, –OH), 2.3 (s, 3H, –ArCH$_3$), 1.8 (s, 3H, –CH$_3$).

2-Hydroxy-2-(4-methoxyphenyl)propionate acid methyl ester: GC–MS (m/z, %): 210 (M$^+$, 12), 152 (24), 133(100), 103 (15), 91 (18), 77 (12), 43 (18). H NMR: δ 7.0–7.5 (4H, –ArH), 3.8 (s, 3H, ArOCH$_3$), 3.7 (s, 1H, –OH), 3.7 (s, 3H, –COOCH$_3$), 1.8 (s, 3H, –CH$_3$).

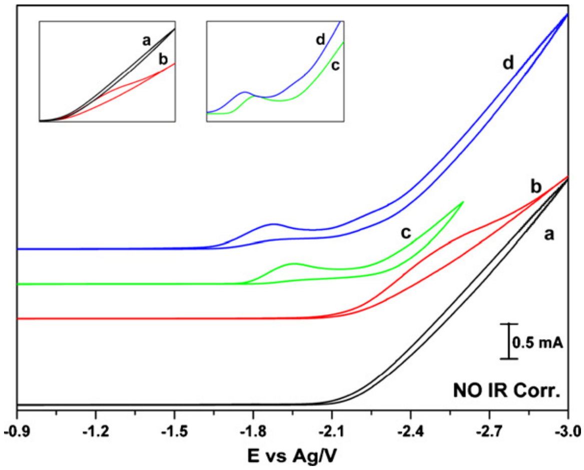

Fig. 1. Cyclic voltammograms recorded with glassy carbon electrode: (a) neat BMIMBF$_4$, (b) BMIMBF$_4$ saturated with CO$_2$, (c) BMIMBF$_4$ containing 0.02 mol dm^{-3} acetophenone and (d) as (c) saturated with CO$_2$.

3. Results and discussion

3.1. Cyclic voltammetry of acetophenone in BMIMBF$_4$

Acetophenone was chosen as the model molecule to be investigated. Cyclic voltammograms (CV) of acetophenone in BMIMBF$_4$ on GC electrode were recorded at the scan rate of 10 mV s^{-1} in an undivided cell at 25 °C with Pt foil as counter electrode and an Ag wire as the reference electrode.

As shown in Fig. 1a, after bubbling Ar gas for 20 min, there was no reduction peak in the sweeping region from −0.9 V to −3.0 V in neat BMIMBF$_4$. It should be noted that the cathodic current began to increase at around −2.1 V, due to the reduction of BMIMBF$_4$ [17,18]. Fig. 1b illustrates that there is no obvious reduction peak in the sweeping region and no enhancement of the current density before −2.1 V in BMIMBF$_4$ saturated with CO$_2$, demonstrating that CO$_2$ does not begin to reduce in this potential window. After addition of acetophenone (0.02 mol dm^{-3}) to neat BMIMBF$_4$, the cathodic current starts to increase at around −1.7 V (Fig. 1c), and a distinct reduction peak appears at about −1.9 V; this peak is attributed to the two successive one electron reduction of acetophenone to ketyl radical anion then to a dianion [10–12,22,23]. The voltammetric behavior of the acetophenone is strongly modified by addition of CO$_2$ to the solution of BMIMBF$_4$ containing acetophenone. In fact, after saturating the solution with CO$_2$, a significant positive shift of the peak potential (Ep) from −1.9 V to −1.7 V and a little increase of the reduction current were observed (Fig. 1d), possibly because of rapid chemical reaction between the electrogenerated anion radical and CO$_2$ [10–12,22–24]. In addition, it is noteworthy that Ep of acetophenone is more positive than that of CO$_2$, which provides a possible potential window to perform the electroreduction of acetophenone without interference from reduction of CO$_2$.

The effect of the scan rate on the CV behavior of acetophenone in BMIMBF$_4$ was examined at 25 °C. The results are presented in Fig. 2. As shown, the reduction peak shifted toward negative potential, and the cathodic peak current enhanced with increasing the scan rate from 5 to 80 mV s^{-1}. The peak current varies linearly with $v^{1/2}$, indicating that the electrode process is controlled by diffusion rather than adsorption [11,25–27].

The effect of acetophenone concentration on the CV behavior of model molecule in BMIMBF$_4$ was also studied on GC electrode at a