Electrochemistry Communications 43 (2014) 71–74

Contents lists available at ScienceDirect

Electrochemistry Communications

journal homepage: www.elsevier.com/locate/elecom

Short communication

Electrosynthesis of enantiomerically pure cyclic carbonates from CO_2 and chiral epoxides

Yan Xiao, Bao-Li Chen, Heng-Pan Yang, Huan Wang *, Jia-Xing Lu **

Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, Shanghai 200062, China

ARTICLE INFO

Article history:
Received 14 December 2013
Received in revised form 1 March 2014
Accepted 17 March 2014
Available online 24 March 2014

Keywords:
Electrosynthesis
Cyclic carbonates
CO_2
Chiral epoxides

ABSTRACT

In this paper, the one-step synthesis of enantiomerically pure cyclic carbonates has been developed by electrolyzing the chiral epoxides and CO_2 (0.1 MPa, rt) in an undivided cell with a 316 stainless steel (SS) cathode and a Mg sacrificial anode containing TEAI–MeCN as supporting electrolyte and solvent with a constant current. To deeply understand this reaction, the effects of various synthesis conditions were investigated using R-styrene oxide as the model compound. Under the optimized conditions, the maximum conversion is 67% with 96% selectivity and 98.8% ee value for R-styrene carbonate. Finally, the reaction mechanism has been proposed by comparative electrolysis and DFT calculation.

1. Introduction

CO_2 is one of the main gases which cause the greenhouse effect. Fortunately a number of methods can be used to convert CO_2 as a cheap, nontoxic and highly abundant C1 resource into useful organic chemicals. One of the most promising methodologies is the electrochemical utilization of CO_2 with epoxides for the synthesis of valuable cyclic carbonates which has been studied by some workers. However, most of these systems unfortunately have several drawbacks, including potentially toxic catalysts [1], expensive ionic liquids [2] and high CO_2 pressures [3]. In recent years, the electrosynthesis of styrene carbonate [4] and propylene carbonate [5,6] from CO_2 and corresponding oxides has been achieved under atmospheric CO_2 pressure and at ambient temperature in MeCN without a catalyst by Buckley and our lab, respectively.

Nowadays, for the important roles in industry and medicine, the enantiomerically pure cyclic carbonates coming from the insertion of CO_2 into enantiomerically pure epoxides or racemic epoxides have been reported frequently, which were catalyzed by chiral aluminum, manganese, chromium and cobalt salen complexes [7–10]. However, to our knowledge, there is no paper which focuses on the electrosynthesis of enantiomerically pure cyclic carbonates so far. As our researches continue on asymmetric electrochemical fixation of CO_2 [11–13], herein we report our results on the electrosynthesis of enantiomerically pure cyclic carbonates from CO_2 and chiral epoxides under atmospheric CO_2 pressure and at ambient temperatures without any additional catalyst in one-step. The effects of synthesis conditions, such as solvents, supporting electrolytes (SE), current densities (j), electricity quantity (Q) and temperatures (T) have been studied.

2. Experimental

N, N-dimethylformamide (DMF) and acetonitrile (MeCN) were dried over 4 A molecular sieves prior to use. Other reagents were used as received.

A typical galvanostatic electrolysis, performed using a direct current-regulated power supply (HY3002D, HYelec®, China), was carried out in a mixture of R-styrene oxide (0.067 M), supporting electrolyte (0.1 M) and 15 mL MeCN saturated with CO_2 (0.1 MPa) in an undivided glass cell equipped with a sacrificial magnesium (Mg) rod anode and a 316 stainless steel (SS) cathode (18 cm^2). Continuous CO_2 flow was maintained throughout the duration of the whole electrolysis process. Finally, the product was extracted with diethyl ether and detected by HPLC (Daicel Chiralcel OD-H). Propene carbonate was detected by GC (HP-CHIRAL-20B).

3. Results and discussion

3.1. Electrosynthesis of enantiomerically pure cyclic carbonates from CO_2 and chiral epoxides

This investigation aimed to establish a green and mild procedure for the one-step electrosynthesis of R-styrene carbonate from CO_2 with R-

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* Corresponding author. Tel.: +86 21 52134935.
** Corresponding author. Tel.: +86 21 62233491.
E-mail addresses: hwang@chem.ecnu.edu.cn (H. Wang), jxlu@chem.ecnu.edu.cn (J.-X. Lu).

http://dx.doi.org/10.1016/j.elecom.2014.03.012
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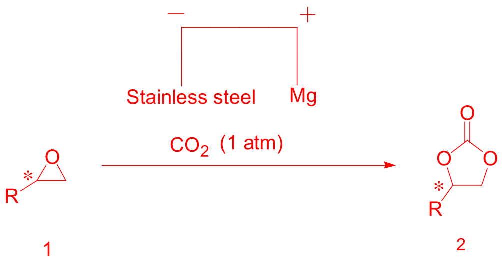
Table 1
Effects of various factors on the electrosynthesis of enantiomerically pure cyclic carbonates[a].



R= (a) R-Ph; (b) S-Ph; (c) R-Me; (d) S-Me

Entry	SE	Q (F·mol^{-1})	j (mA·cm^{-2})	T (°C)	Conv. (%)	Selec. (%)	ee (%)
1[b]	TEAI	1.5	2.88	25	38	21	90 (R)
2	TEAI	1.5	2.88	25	60	87	91 (R)
3	TEABr	1.5	2.88	25	54	82	84 (R)
4	TEACl	1.5	2.88	25	40	41	83 (R)
5	TEABF$_4$	1.5	2.88	25	35	6	43 (R)
6	TEABF$_4$[c]	1.5	2.88	25	56	82	96 (R)
7	TEABF$_4$[d]	1.5	2.88	25	33	75	93 (R)
8	TEAI	1.5	1.79	25	38	71	87 (R)
9	TEAI	1.5	2.34	25	47	82	91 (R)
10	TEAI	1.5	2.72	25	58	86	91 (R)
11	TEAI	1.5	3.42	25	23	55	84 (R)
12	TEAI	1.5	3.97	25	14	8	53 (R)
13	TEAI	0.5	2.88	25	25	82	84 (R)
14	TEAI	1.0	2.88	25	53	88	91 (R)
15	TEAI	1.3	2.88	25	59	93	91 (R)
16	TEAI	2.0	2.88	25	68	38	83 (R)
17	TEAI	2.5	2.88	25	73	4	46 (R)
18	TEAI	1.3	2.88	−10	25	93	96 (R)
19	TEAI	1.3	2.88	0	67	96	99 (R)
20	TEAI	1.3	2.88	10	60	94	95 (R)
21	TEAI	1.3	2.88	20	58	91	92 (R)
22[e]	TEAI	1.3	2.88	0	67	95	98 (S)
23[f]	TEAI	1.3	2.88	0	70	95	97 (R)
24[g]	TEAI	1.3	2.88	0	72	94	97 (S)

[a] Cathode: Ss, anode: Mg, solvent: MeCN (15 mL), SE: 0.1 M, R-styrene oxide: 0.067 M, CO$_2$: 0.1 MPa.
[b] Solvent: DMF.
[c] Add KI (0.1 M).
[d] Add KBr (0.1 M).
[e] S-styrene oxide (0.067 M).
[f] R-propene oxide (0.067 M).
[g] S-propene oxide (0.067 M).

styrene oxide. To optimize the procedure, the effects of different parameters were investigated. The electrolysis results are summarized in Table 1.

Quite good conversion, selectivity and ee value were achieved using MeCN as solvent rather than DMF (Table 1, entries 1–2). The solubility of CO$_2$ (1 atm, rt) in the DMF (0.196 M) is lower than that in MeCN (0.282 M) [14], which will affect the conversion and selectivity of the target product. Some other factors may also influence the reaction.

In the case of supporting electrolyte, highest conversion, selectivity and ee value to cyclic carbonate were achieved by using TEAI (Table 1, entries 2–5). Halide anions are superior to BF$_4^-$, which was approved by the addition of KBr or KI (Table 1, entries 5–7). During the reaction, the anions may help open the ring of the oxide, so that the influence order is identical with their nucleophilicity [15] (BF$_4^-$ < Cl$^-$ < Br$^-$ < I$^-$).

Then the influence of the electricity quantity and current density was investigated (Table 1, entries 8–17). The optimized conversion of 59% with 93% selectivity and an ee value of 91% (R) was achieved under 1.3 F·mol^{-1} and 2.88 mA·cm^{-2} (Table 1, entry 15). When the electricity quantity was above 1.3 F·mol^{-1}, the target product would unceasingly be adsorbed on the electrode and was further reduced to the by-products [16]. The temperature can be a crucial factor for this reaction (Table 1, entries 18–21). When the temperature was lowered to 0 °C, the conversion was up to 67% with 96% selectivity and an ee value of 99% (R) which was higher than that at room temperature, however the conversion dropped to 25% at −10 °C. With increasing the temperature, the conversion, selectivity and ee value all decreased, which may be caused by the effect of temperature on both the CO$_2$ solubility in MeCN and the activation energy of electrolysis.

To test the effectiveness and generality of this methodology, the investigation was extended to other chiral epoxides (Table 1, entries 22–24). S-styrene oxide, R-propene oxide and S-propene oxide could afford the corresponding chiral cyclic carbonates in good conversion (67%, 70%, 72%, respectively), excellent selectivity (94–95%) and ee values (97–98%), be similar to that of R-styrene oxide.

3.2. Proposed mechanism

To deeply understand the reaction, eight contrast experiments were carried out and summarized in Table 2. If the anode is Pt instead of Mg (Table 2, entries 1–2), no cyclic carbonate could be detected. In order to further prove the effect of Mg^{2+} ion, MgBr$_2$ was added with Pt as the anode (Table 2, entry 3). 48% of styrene oxide was converted, while the selectivity of styrene–carbonate can be achieved in 86% with 80% ee value. Obviously, Mg^{2+} ion was necessary to this reaction. When R-styrene oxide was added after the electrolysis (Table 2, entry 4), good selectivity and ee value could also be obtained, indicating that the ring opening of R-styrene oxide didn't rely on the electrolysis, which may be caused by Mg^{2+} ions and halide ions as reported in the literature [1,17]. Instead, no reaction occurred when CO$_2$ was added after the electrolysis (Table 2, entry 5). This indicates that electrolysis is a must for CO$_2$ to react here. During the galvanostatic electrolysis, the cathodic potential is ca. −1.5 V vs Ag/AgI/I$^-$. According to the cyclic voltammograms, the reduction potentials of both R-styrene oxide and TEAI are much more negative than −1.5 V. Therefore CO$_2$ (Ep = −1.38 V) was the only material that could be electroreduced here. If Mg^{2+} ion is only for the ring-opening step, MgBr$_2$ could be added after the electrolysis with R-styrene oxide. Surprisingly, no target product was obtained (Table 2, entry 6). To avoid the effect of anodic reaction, a divided electrolytic cell was used (Table 2, entry 8). No target reaction occurs again. Once MgBr$_2$ was added before the electrolysis (Table 2, entry 7), styrene carbonate could be acquired. The result shows that the electrochemically activated CO$_2$ may need to combine with Mg^{2+} ion to form a stable intermediate so that styrene carbonate could be acquired.

Under high pressure together with suitable catalysts, CO$_2$ molecule could insert into R(+)-styrene-oxide leading to the formation of cyclic carbonate [18,19]. However, it cannot be achieved under normal pressure without any catalyst, as indicated in Table 2 entry 5. According to the electrosynthesis results, we proposed that the reaction initiated with forming an anion radical electroreduced from CO$_2$ (Scheme 1, A). The anion radical could be stabilized via the coordination of oxygen atom of the free anion radical to Mg^{2+} and Br$^-$ leading to the formation of intermediate **I**. **I** further reacted with R(+)-styrene-oxide **II** to generate **III**. Due to the electrophilic effect of Mg^{2+} and the fact that the C$_\beta$–O bond energy (1816.63 kJ·mol^{-1}) was 22.77 kJ·mol^{-1} less than that of C –O bond (1839.40 kJ·mol^{-1}) by density functional theory (DFT) calculation, it was easy for the bromine anion to attack C$_\beta$ rather than C , resulting in the C$_\beta$–O bond breaking with retention of C -configuration of the epoxide to generate **IV**. Therefore a good retention of configuration at the C can be proposed to explain the excellent ee value of styrene carbonate.

The following nucleophilic attack of oxygen atom on epoxide to carbon atom, leading to the formation of intermediate **V**, which possibly transferred an electron to CO$_2$ to generate **VI** along with the regeneration of the stabilized intermediate **I** or go through some sequence reactions [20,21]. The product **VII** could be generated through intramolecular nucleophilic replacement of bromine atom by a