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Synthesis of cyclic carbonates from epoxides and CO₂ in acetonitrile via the synergistic action of BMIMBr and electrogenerated magnesium

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ABSTRACT

Using 1-butyl-3-methyl-imidazolium bromide (BMIMBr) as the supporting electrolyte and magnesium as the sacrificial anode, a new and highly efficient electrochemically catalytic route was developed for the synthesis of cyclic carbonates from epoxides and CO₂. Based on the cooperative action of BMIMBr and an electrogenerated magnesium salt obtained under a N₂ atmosphere, CO₂ reacted with a wide range of epoxides to readily generate cyclic carbonates in moderate to excellent yields under mild conditions.

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1. Introduction

CO₂ is anticipated to have applications as a non-toxic, inexpensive, abundant and renewable C1 feedstock. For this reason, much effort has been devoted to developing effective processes for the synthesis of desirable, economically competitive products from CO₂. As an example, cyclic carbonates, which are used as raw materials for polycarbonates, as electrolytes in lithium-ion secondary batteries, and as polar aprotic solvents, have been synthesized from CO₂ and epoxides with high atom efficiency. However, the addition of CO₂ to epoxides for the preparation of cyclic carbonates in a typical synthesis procedure is generally conducted at relatively high pressures and reaction temperatures in the presence of metal halides or metal com-

plexes acting as catalysts [1–8]. Therefore, devising a simple and low energy alternative method for the preparation of cyclic carbonates from epoxides and CO₂ remains a challenge for organic chemists.

Recent studies have demonstrated that electrocatalysis is a promising method for the formation of cyclic carbonates from epoxides and CO₂, and that this technique can be performed at temperatures below 100 °C and at atmospheric pressure [9–16]. In electrochemical carboxylation systems reported to date, efforts have been focused on the electrochemical activation of CO₂ either by direct (at the electrode) or indirect (through heterogeneous or homogeneous catalysis) reduction. However, the electrogenerated CO₂^{•−} radicals acting as intermediates in the electrochemical carboxylation can be more

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readily converted into a number of side products (such as CO and CO₃²⁻) before diffusing from the electrode surface into the solution to react with epoxides. Indeed, the low Faradaic efficiency of these processes based on the electrochemical reduction of CO₂ has become the greatest obstacle to establishing industrial processes.

It has been reported that the synthesis of cyclic carbonates from epoxides and CO₂ involves three steps, consisting of ring-opening, CO₂ insertion and ring-closing reactions, and that the activation energy for each step is in the order ring-opening > ring-closing > insertion [17]. Based on this, the present work focused on lowering the activation energy of the ring-opening reaction by developing a catalytic system composed of two successive steps; an electrochemical reaction followed by carboxylation of the epoxide. Specifically, a magnesium salt acting as a Lewis acid catalyst for the ring-opening of epoxides was conveniently prepared in a N₂ atmosphere by the sacrificial metal anode method, after which the cooperative action of the electrogenerated magnesium (EGM) salt and 1-butyl-3-methyl-imidazolium bromide (BMIMBr) was used to promote the reaction of epoxides with CO₂ to effectively generate cyclic carbonates under atmospheric CO₂ pressure and at ambient temperature.

2. Experimental

2.1. Reagents

BMIMBr and 1-butyl-2,3-methyl-imidazolium bromide (BMMIMBr) were synthesized according to a previously reported procedure [18] and dried under vacuum at 80 °C for 24 h prior to use. Tetrabutylammonium bromide (TBABr) was obtained from the Aladdin Chemistry Co., Ltd. (China) and dried under vacuum at 80 °C for 12 h prior to use. Acetonitrile (MeCN, reagent grade) was purchased from the Shanghai Lingfeng Chemical Reagent Co., Ltd. (China) and dried over 4 Å molecular sieves before use. Other reagents were used as received.

2.2. General procedure for the synthesis of cyclic carbonates

Styrene oxide (**1a**) was used for catalytic studies. A typical galvanostatic electrolysis at a current density of 7.14 mA/cm² was carried out in a MeCN/BMIMBr (20 mL, 0.2 mol/L) solution under a N₂ atmosphere in a single compartment cell equipped with a sacrificial magnesium (Mg) rod anode and a 316 stainless steel (Ss) disk cathode (28 cm²) until an electric charge of 1 F per mole of the starting substrate had passed through the cell. The electrolyzed solution was subsequently transferred to a 50-mL three-neck round bottom flask fitted with a straight condenser tube, followed by the addition of 0.05 mol/L **1a**. The resulting mixture was stirred for 8 h at 50 °C under atmospheric pressure CO₂. Following the carboxylation reaction, the solvent was removed under reduced pressure and the residue was mixed with distilled water (20 mL) and then extracted with three 25-mL aliquots of diethyl ether, after which the combined organic layers were dried over anhydrous

MgSO₄. Subsequent to evaporation of the ether, the crude product was purified by chromatography on a silica gel column using light petroleum ether-ethyl acetate as the eluent. The **2a** yield was determined by gas chromatography with a flame ionization detector (GC-FID) and **2b–2e** yields are reported as isolated yields based on the starting epoxides.

The obtained products were characterized by Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) spectroscopy. FTIR spectra were acquired with a TENSOR27 spectrometer and NMR spectra were recorded with a Bruker DRX-400 spectrometer using CDCl₃ as the solvent and TMS as the internal standard.

4-Phenyl-1,3-dioxolan-2-one (**2a**). $\nu_{\max}$ (film)/cm⁻¹: 1794 (C=O); ¹H NMR (400 MHz, CDCl₃) δ : 7.27–7.48 (m, 5H), 5.61 (t, J = 8.0 Hz, 1H), 4.73 (t, J = 8.4 Hz, 1H), 4.27 (t, J = 8.3 Hz, 1H); ¹³C NMR (400 MHz, CDCl₃) δ : 71.21, 78.04, 125.92, 129.26, 129.77, 135.80, 154.90.

4-(Phenoxymethyl)-1,3-dioxolan-2-one (**2b**). $\nu_{\max}$ (film)/cm⁻¹: 1783 (C=O); ¹H NMR (400 MHz, CDCl₃) δ : 7.23 (m, 2H), 6.99–6.79 (m, 3H), 5.01–4.90 (m, 1H), 4.58–4.40 (m, 2H), 4.11 (m, 2H); ¹³C NMR (400 MHz, CDCl₃) δ : 66.25, 66.85, 74.19, 144.61, 121.99, 129.72, 154.78, 157.77.

4-Methyl-1,3-dioxolan-2-one (**2c**). $\nu_{\max}$ (film)/cm⁻¹: 1792 (C=O); ¹H NMR (400 MHz, CDCl₃) δ : 4.79–4.55 (m, 1H), 4.40 (d, J = 8.2 Hz, 1H), 3.98–3.67 (m, 1H), 1.29 (d, J = 6.3 Hz, 3H); ¹³C NMR (400 MHz, CDCl₃) δ : 19.20, 70.72, 73.76, 155.21.

4-Ethyl-1,3-dioxolan-2-one (**2d**). $\nu_{\max}$ (film)/cm⁻¹: 1798 (C=O); ¹H NMR (400 MHz, CDCl₃) δ : 1.04 (t, J = 8 Hz, 3H), 1.73–1.86 (m, 2H), 4.10 (t, J = 8 Hz, 1H), 4.54 (t, J = 8 Hz, 1H), 4.67 (q, J = 7 Hz, 1H); ¹³C NMR (400 MHz, CDCl₃) δ : 9.2, 27.6, 69.8, 78.8, 155.9.

4-Hexyl-1,3-dioxolan-2-one (**2e**). $\nu_{\max}$ (film)/cm⁻¹: 1801 (C=O); ¹H NMR (400 MHz, CDCl₃) δ : 4.61 (m, 1H), 4.44 (t, J = 8.1 Hz, 1H), 4.11–3.90 (m, 1H), 1.64–1.52 (m, 1H), 1.20 (t, J = 18.2 Hz, 8H), 0.79 (t, J = 6.7 Hz, 4H); ¹³C NMR (400 MHz, CDCl₃) δ : 13.99, 22.45, 24.32, 28.79, 29.68, 31.51, 33.85, 155.20.

3. Results and discussion

Styrene oxide (**1a**) was chosen as a model substrate to verify the effectiveness of the proposed catalytic system for the synthesis of cyclic carbonates. Experiments were conducted to investigate the effects of the catalysts (EGM and BMIMBr) as well as the carboxylation temperature on the yields of **2a**, with the carboxylation results summarized in Table 1.

EGM acting as a Lewis acid is capable of weakening the C–O bond of an epoxide to lower the activation energy of the rate-determining step in the carboxylation, which is the epoxide ring-opening. However, excess EGM can also strongly bind with the intermediate anion formed after the CO₂ insertion reaction to prevent the completion of the ring-closing reaction, which may decrease the selectivity of the carboxylation. To achieve a desirable yield of the cyclic carbonate, the effect of the EGM concentration was investigated, expressing the concentration using the charge (Q) passed through the cell during the electrolysis step. As shown in Table 1 (entries 1–5), the yield of **2a** increased significantly from 65.1% to 90.7%, as the

Table 1Effects of various factors on the synthesis of **2a** from **1a** and CO₂.

Entry	<i>Q</i> (F/mol)	<i>T</i> (°C)	Cocatalyst	Selectivity (%)	Yield (%)
1	0.5	50	BMIMBr	96.5	65.1
2	0.8	50	BMIMBr	94.8	79.5
3	1.0	50	BMIMBr	92.2	90.7
4	1.2	50	BMIMBr	90.3	88.6
5	1.5	50	BMIMBr	70.7	69.6
6	1.0	50	BMMIMBr	91.7	89.4
7 ^a	1.0	50	BMIMBr	98.1	5.4
8 ^b	0	50	BMIMBr	80.7	35.5
9 ^c	1.0	50	BMIMBr	78.4	54.2
10	1.0	50	TBABr	89.4	65.5
11	1.0	30	BMIMBr	96.2	58.4
12	1.0	40	BMIMBr	95.8	70.5
13	1.0	60	BMIMBr	90.8	86.5
14	1.0	70	BMIMBr	68.9	67.5

General conditions: **1a** 0.05 mol/L, acetonitrile 20 mL, Ss cathode, Mg anode, current density 7.14 mA/cm².^a No Lewis acid, Pt as anode.^b MgBr₂.^c EGM obtained under a CO₂ atmosphere.

charge increased from 0.5 to 1 F/mol, while the selectivity of the carboxylation was maintained at approximately 94%. Further increasing the charge improved the conversion of **1a** but dramatically lowered the selectivity. These results show that the concentration of EGM obtained after a charge consumption of 1 F/mol is adequate for the synthesis of cyclic carbonates from epoxides and CO₂.

It is noteworthy that a small amount of 1-butyl-3-methyl-imidazolium carbene (NHC) might be generated from the electrochemical reduction of the 1-butyl-3-methyl-imidazolium cation (BMIM⁺) during the preparation of the EGM. NHC has been reported to be an effective organic catalyst for the synthesis of cyclic carbonates from the coupling reaction of CO₂ and epoxides under a CO₂ pressure of 2 MPa and at 120 °C [19]. Therefore, it is necessary to ascertain whether NHC also catalyzes the synthesis of cyclic carbonates in the present reaction system. With this in mind, we replaced the BMIM⁺ cation with the 1-butyl-2,3-methyl-imidazolium cation (BMMIM⁺), which cannot generate NHC. Following this substitution, it was found that the yield of **2a** remained almost the same, at 89.4% (Table 1, entry 6). In addition, NHC was prepared in a two-compartment cell under a N₂ atmosphere to further identify the role of this compound in the carboxylation. It is important to note that, in the absence of EGM, we observed little cyclic carbonate formation (5.4%) and only recovered unreacted **1a** (Table 1, entry 7). These results clearly demonstrate that NHC has little influence on the synthesis of cyclic carbonates from epoxides and CO₂ in the current catalytic system.

To evaluate the advantage conferred by EGM, an equivalent amount of MgBr₂ was used as the Lewis acid catalyst for the carboxylation instead of EGM, in the absence of an applied current. Using this catalyst, only 35.5% of the **1a** could be trans-

formed to **2a** when the other reaction conditions remained unchanged (Table 1, entry 8). Based on this remarkable difference in catalytic activity between EGM and MgBr₂, we believe that the anions paired with the EGM in the acetonitrile solution may include species generated from the electrochemical reduction of the solvent or the cation of the supporting electrolyte, in addition to Br⁻. In general, reductive species with larger ionic radii will exert a weaker electrostatic attraction towards EGM than that of Br⁻, thus greatly improving the electrophilicity of the EGM and promoting the carboxylation of **1a**. To prove the importance of the reductive species, we also evaluated the catalytic activity of EGM obtained under a CO₂ atmosphere in a single compartment cell. The data show that the carboxylation yield dropped dramatically from 90.7% to 54.2% when the electrochemical reduction of the solvent or the cation of the supporting electrolyte was replaced by the reduction of CO₂ at the cathode (Table 1, entry 9). Based on the results shown above, it can be concluded that the use of EGM is essential for the carboxylation to proceed, and that the catalytic activity of EGM under a N₂ atmosphere is higher than that under a CO₂ atmosphere.

We subsequently examined the supporting electrolyte cation moiety, which can be expected to affect the strength of ion pairing between EGM and Br⁻. The carboxylation results showed that the catalytic activity in the presence of the imidazolium-based cation is superior to that obtained when using the tetrabutylammonium cation (Table 1, entry 10). Taking previously reported DFT calculations into account [20,21], these results can be explained by comparing the tetrahedral conformation of the quaternary ammonium cation with the planar geometry of the imidazolium cation. The imidazolium ion, having less steric hindrance, may form a tighter ion pair with Br⁻, thus decreasing the electrostatic attraction between EGM and Br⁻ and so increasing the catalytic activity of the EGM for the ring-opening reaction. Temperature also appears to be a crucial factor for the carboxylation of the epoxide. Increasing the temperature will be helpful in terms of obtaining the activation energy required for the carboxylation, although higher temperatures will also decrease the solubility of CO₂ in the acetonitrile. The effects of temperature on the carboxylation were investigated over the range 30 to 70 °C, and the results are presented in Table 1 (entries 3 and 11–14), showing that the optimal temperature is 50 °C.

Having identified the optimized conditions, we proceeded to screen the applicability of this system to a range of substrate types (Table 2). The corresponding cyclic carbonate was obtained from all substrates, including both electron rich and poor aromatic systems, and a range of aliphatic epoxides were also effectively converted to the corresponding cyclic carbonate. It should be noted that the lowest **2c** yield in the current catalytic system may have partly resulted from the volatilization of **1c** (b.p. 34 °C) during the carboxylation reaction.

4. Conclusions

EGM obtained under a N₂ atmosphere was found to exhibit excellent electrocatalytic activity for the synthesis of cyclic

Table 2

Electrochemically catalyzed synthesis of cyclic carbonates from epoxides and CO₂ in acetonitrile.

Entry	Epoxide	Cyclic carbonate	Yield (%)
1*			90.7
2			81.5
3			48.3
4			72.5
5			63.1

General conditions: epoxide 0.05 mol/L, acetonitrile 20 mL, BMIMBr 0.2 mol/L, Ss cathode, Mg anode, current density 7.14 mA/cm², electric charge 1 F/mol, *T* = 50 °C.

* This experiment was repeated here for clarity.

carbonates from epoxides and CO₂ in acetonitrile in the presence of BMIMBr as a cocatalyst. The results show that the concentration of EGM obtained after 1 F/mol charge consumption is adequate for the synthesis of cyclic carbonates from epoxides and CO₂. Comparison of the catalytic activity of three Lewis acids, EGM under a N₂ atmosphere, EGM under a CO₂ atmosphere and MgBr₂, indicates that the significant catalytic activity of EGM under a N₂ atmosphere may be related to the reductive species generated from the electrochemical reduction of the solvent or the supporting electrolyte cation. The stronger electrostatic attraction between the imidazolium cation and the bromine anion in acetonitrile solution will also enhance the catalytic activity of EGM. This study thus demonstrates a low energy alternative for the electrochemically catalyzed synthesis of cyclic carbonates from epoxides and CO₂ under mild conditions.

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Graphical Abstract

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Synthesis of cyclic carbonates from epoxides and CO₂ in acetonitrile via the synergistic action of BMIMBr and electrogenerated magnesium

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Epoxides were effectively transformed to cyclic carbonates by reaction with atmospheric pressure CO₂ at ambient temperature via the cooperative action of BMIMBr and an electrogenerated magnesium (EGM) salt.

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乙腈体系中咪唑溴盐和电制镁盐协同促进环氧化物与 CO₂ 羧化反应合成环状碳酸酯

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摘要: CO₂ 是一种储量丰富且廉价易得的可再生 C1 资源. 以 CO₂ 为原料的羧化反应可将 CO₂ 高效转化成羧酸及其衍生物等高附加值化学品. 例如, CO₂ 和环氧化物反应生成环状碳酸酯属于“原子经济”反应, 是有效利用 CO₂ 的方法之一, 其产物环状碳酸酯广泛用于极性有机溶剂、电池电解液和化妆品等. 由于 CO₂ 化学性质非常稳定, 不易活化, 制备环状碳酸酯的传统方法是以金属卤化物或金属配合物为催化剂在高温高压下进行反应. 因此, 开发出操作简便且能耗低的绿色技术用于合成环状碳酸酯面临巨大挑战.

最近研究表明, 电催化技术可使环氧化物和 CO₂ 在温和条件下转化为环状碳酸酯. 已报道的电催化反应研究重点都是如何通过多相或均相电催化还原 CO₂ 的方式使环氧化物能够在温和条件下进行羧化反应. 然而, CO₂ 电还原生成的 CO₂^{•-} 自由基非常活泼, 在其扩散到溶液中与环氧化物反应之前易在电极上直接转化为 CO 和碳酸盐等副产物, 从而导致羧化反应较低的电流效率.

Ema 课题组报道环氧化物与 CO₂ 羧化反应经历三个步骤, 即开环反应、CO₂ 插入反应和闭环反应, 其中开环反应活化能最大, 是羧化反应决速步骤. 与已报道的电催化途径不同, 本文通过建立一个由电化学反应和羧化反应组成的催化反应体系, 旨在通过降低开环反应活化能来促进环氧化物羧化反应. 在电化学反应过程中, 由牺牲阳极提供羧化反应必需的路易斯酸, 即电制镁盐; 在羧化反应过程中, 通过电制镁盐和咪唑溴盐的协同作用实现环氧化物和 CO₂ 在温和条件下高效率地转化为环状碳酸酯.

实验首先选取环氧苯乙烷为反应原料, 考察了电制镁盐、共催化剂的阳离子以及羧化反应温度对目标产物产率的影响. 如果羧化反应过程中没有镁盐或直接用等量溴化镁代替电制镁盐, 羧化产率仅为 5.4% 和 35.5%, 而电制镁盐条件下羧化反应产率高达 90.7%, 表明电制镁盐作为路易斯酸催化剂对提高羧化反应产率是必不可少的. 比较了在 N₂ 和 CO₂ 气氛中分别电解制备得到的镁盐的催化性能. N₂ 气氛中电制镁盐更高的催化性能可能与溶剂乙腈或支持电解质的阳离子在阴极发生电还原生成的物质有关. 该电还原产物可部分代替溴离子与电制镁盐配对, 由于其体积更大, 一定程度上提高了电制镁盐的亲电性, 有利于羧化反应进行. 如果用四丁基溴化铵代替咪唑溴盐作为共催化剂, 羧化反应产率从 90.7% 降为 65.5%. 羧化反应过程中溴离子对电制镁盐的配对能力受共催化剂阳离子静电引力的牵制而减弱, 共催化剂的阳离子对溴离子的静电引力越强, 溴离子对电制镁盐亲电性的影响就越弱. 前期研究成果表明, 在乙腈溶液中咪唑阳离子对阴离子的静电引力明显强于季铵阳离子, 由此可认为当咪唑溴盐作为共催化剂时提高了电制镁盐的亲电性, 促进了环氧化物的开环反应. 提高羧化反应温度虽然可以降低环氧化物开环反应的活化能, 但也会降低 CO₂ 在乙腈溶液中的溶解度, 50 °C 反应较为合适. 在最优反应条件下考察了该催化体系对其他环氧化物羧化反应的普适性, 所得环状碳酸酯产率为 48.3%–90.7%.

关键词: 电解制备镁盐; 咪唑溴盐; 二氧化碳; 环氧化物; 羧化反应; 环状碳酸酯

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