

Electrochemical activation of carbon dioxide in ionic liquid: synthesis of cyclic carbonates at mild reaction conditions

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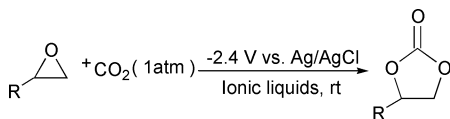
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Electrocatalytic cycloaddition of carbon dioxide to epoxides in room temperature ionic liquids as reaction media without any additional supporting electrolyte and catalyst could be conducted with high to excellent performances under mild conditions.

Room temperature ionic liquids as environmentally benign media for organic synthesis and catalytic reaction has been widely recognized and accepted.¹ Many reactions have been reported to occur in ionic liquids with good to excellent performance.² The combination of ionic liquid and supercritical carbon dioxide for achieving more convenient reaction and product recovery, reported recently,³ has further extended the research and application scope of ionic liquids. Other features possessed by ionic liquids, however, *i.e.* their high ionic conductivities and wide electrochemical windows, have not been explored as novel media for electrocatalytic organic synthesis.

On the other hand, much effort has been devoted to CO₂ as a carbon resource in organic synthesis,⁴ and one of ideal chemical fixations of CO₂ onto organic compounds is the addition of CO₂ to epoxides to produce five-membered cyclic carbonates, a kind of atom economy reaction. In the previous studies, the addition of CO₂ to epoxides for the preparation of cyclic carbonates was generally conducted at relatively high CO₂ pressures and reaction temperatures in the presence of metal halides,⁵ metal complexes⁶ or ionic liquids⁷ as the catalysts. Recently, Duñach *et al.*⁸ conducted the reaction of epoxides with CO₂ activated by an electrochemical method in the presence of nickel(II) complexes to afford the corresponding cyclic carbonates under very mild conditions. As in the conventional electrochemical activation of CO₂ for organic syntheses, a harmful organic solvent, supporting electrolyte, together with a catalyst, were necessarily employed, making a very complicated reaction system.

Within our continuing efforts in the application of room temperature ionic liquids⁹ as 'greener' reaction media, herein we report our results on the electrocatalytic cycloaddition of carbon dioxide to epoxides using pure ionic liquids based on 1-*n*-butyl-3-methylimidazolium (BMIM), 1-ethyl-3-methylimidazolium (EMIM) or *n*-butylpyridinium (BPy) ions such as [BMIM][BF₄] **1**, [EMIM][BF₄] **2**, [BMIM][PF₆] **3** and [BPy][BF₄] **4** as reaction media without any additional supporting electrolyte and catalyst:



Cyclic voltammetry of pure **1** showed that no reduction peak could be observed in sweeping the region +0.8—3.0 V, (Fig. 1, 1). After pure **1** was saturated with carbon dioxide at room temperature, a reduction peak of carbon dioxide appeared at about -2.4 V vs. Ag/AgCl (Fig. 1, 2) that should result from the one-electron reduction of CO₂, which generated an anion radical of CO₂.^{10,11} Because there was no corresponding

oxidation peak, it can be conjectured that the CO₂ anion radical reacted with itself and CO₂ in the absence of substrate.¹¹ In the presence of substrate, this anion radical, however, should react rapidly with the intermediate of the desired product, which was activated with the ionic liquid electrocatalytic system, rather than react with solvent or with itself or with any contaminants in the solvent, since FT-IR (Bruker, IFS 120HR) analysis of the ionic liquids after the reaction indicated that no carbonate compounds resulting from the anion radical of CO₂ were observed. Though it has been reported previously in the literature that the best electrochemical reduction temperature for CO₂ in aprotic solution is 0 °C,¹² the current at the reductive peak of CO₂ in pure **1** saturated with CO₂ at 0 °C (Fig. 1, 3) was smaller than that at room temperature. Similar results were also observed for **2** to **4** room temperature ionic liquids. Although CO₂ is more soluble in the ionic liquid at lower temperature,¹³ it is well known that the kinetic viscosity of imidazolium salts ionic liquids display essentially Arrhenius behavior.¹⁴ With the decrease of temperature, the viscosity increases remarkably, resulting in a lower reduction current at 0 °C.

The results of the incorporation of CO₂ into epoxides, *i.e.* propylene oxide **a**, epichlorohydrin **b** and styrene oxide **c**, in a series of ionic liquids consisting of BMIM⁺, EMIM⁺, BPy⁺ cations and BF₄⁻, PF₆⁻ anions are shown in Table 1. The conversion in Table 1 was based on the amount of epoxide converted after reaction. It can be seen that conversions of 54–92% with 69–100% selectivities were achieved when [BMIM][BF₄] was used (entry 1–3) and the best current efficiency was 87%. If [BMIM][BF₄] was replaced with [EMIM][BF₄] (entries 4, 5 and 6) or [BPy][BF₄] (entries 10, 11 and 12), the conversions were respectively decreased slightly and remarkably, while the selectivities were almost unchanged. Poor conversions, however, were obtained (entries 7, 8 and 9) when [BMIM][PF₆] was used. This indicates that in the ionic

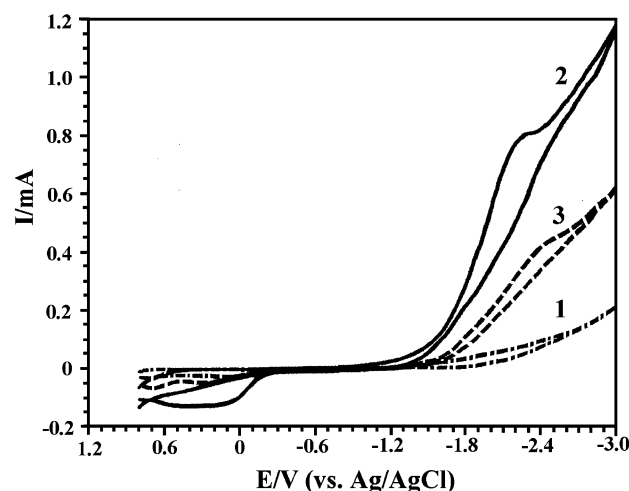


Fig. 1 Cyclic voltammograms of CO₂ in [BMIM][BF₄] (Cu working electrode (1.5 mm ϕ); Scan rate = 0.05 V s⁻¹) (1) pure [BMIM][BF₄]; (2) [BMIM][BF₄] saturated with CO₂ at room temperature; (3) [BMIM][BF₄] saturated with CO₂ at 0 °C.

Table 1 Synthesis of cyclic carbonates in different room temperature ionic liquids

Entry	Substrate	Ionic liquid	Charge (C)	C.E.(%) ^a	Conversion (%)	Selectivity (%)	Other products (selec.%)
1	a	1	1023	87	92	100	—
2	b	1	1011	52	54	100	—
3	c	1	989	53	78	69	Benzeneacetaldehyde (31)
4	a	2	1012	81	85	100	—
5	b	2	992	44	45	100	—
6	c	2	1002	48	75	67	Benzeneacetaldehyde (33)
7	a	3	989	52	53	100	—
8	b	3	945	28	27	100	—
9	c	3	980	28	45	63	Benzeneacetaldehyde (37)
10	a	4	1003	66	69	100	—
11	b	4	998	32	33	100	—
12	c	4	975	37	58	65	Benzeneacetaldehyde (35)
13 ^b	a	1	990	63	65	100	—
14 ^c	c	1	1015	49	77	67	—
15 ^d	a	1	1018	84	89	100	Benzeneacetaldehyde (33)
16 ^e	a	1	—	—	—	—	—

^a C.E. = theoretical charge based on the conversion and selectivity/charge passed during experiment. ^b Reacted at 0 °C. ^c Reacted at 50 °C. ^d Al rod as anode. ^e Reacted without current.

liquid both cation and anion have a relatively stronger impact on the addition reaction. The best performance was achieved with the ionic liquid consisting of BMIm⁺ and BF₄⁻. This result is also consistent with our previous work.⁷

It can be further seen that highest conversion, selectivity and current efficiency was achieved when using propylene oxide as substrate, though varied conversions to the desired cyclopropylene carbonate was obtained in different ionic liquids.

Substituent groups on the substrate molecule also have a strong impact on the epoxide conversion. For epichlorohydrin, the conversion to cyclic carbonate was decreased remarkably but no other by-product was detected. For styrene oxide, though the conversion was better than that of epichlorohydrin, the selectivity was relatively low and benzeneacetaldehyde was found. It should be noted that, although varied conversions were obtained for epichlorohydrin and styrene oxide, the selectivities to corresponding cyclic carbonates were almost unchanged in different ionic liquids.

The effect of temperature on the addition reaction was also investigated. When the experiment was carried out at 0 °C, in the case of propylene oxide and [BMIm][BF₄] as substrate and reaction medium respectively, the current was small, as cyclic voltammetry indicated in Fig. 1, and the conversion decreased remarkably in comparison with the results obtained at room temperature, though the selectivity was not changed. The results carried at 50 °C show that the conversion and selectivity were almost unchanged when styrene oxide was used as substrate (entry 14).

Also, the effect of sacrificed anode was studied, and the results suggested that no obvious differences could be observed between Mg and Al (entry 15). It indicates that the properties of the sacrificed anode may have less impact on the reaction. However, it can be seen that no reaction could be observed if a voltage was not applied (entry 16), indicating that electrochemical activation is necessary. After the reaction, Mg (*ca.* 6 mg ml⁻¹) and Al (*ca.* 4 mg ml⁻¹) were detected in the ionic liquid with an atomic absorption spectra instrument (Hitachi, 80–180), but their chemical states were not clear and the further characterization will continue in the next work.

In conclusion, we have reported the first use of pure room temperature ionic liquids as reaction media in the electrochemical activation of CO₂ for the synthesis of cyclic carbonates through cycloaddition of CO₂ to epoxides without additional supporting electrolyte and catalyst under mild conditions. Good to excellent results were obtained. The ionic liquid and electrochemistry reaction system and reaction conditions could be further optimized. This may start a new research field in the application of ionic liquids to catalysis and organic synthesis.

[EMIm][BF₄], [BMIm][BF₄], [BMIm][PF₆] and [BPy][BF₄] were prepared according to the synthesis outlined by Bonhôte *et al.*¹⁴ The ionic liquids were dried and degassed under vacuum at 100 °C for 4 h prior to use. Before the reaction, the CV result indicated that there was no detectable water and chlorion. Also, the FT-IR result showed that there was no absorption water peak between 3000–3600 cm⁻¹ in our ionic liquids and no other species were detected; the same result was also obtained after the reaction except that magnesium or aluminum was detected. Electrochemical experiments were performed using a CHI660A electrochemical workstation (CH instruments, USA). The undivided cell was fitted with a Cu plant as the cathode and a Mg or Al rod as the anode and a gas inlet and outlet. In a typical procedure, 15 ml of ionic liquid containing 10 mmol epoxide was charged into the cell and saturated with CO₂ by gentle bubbling (*ca.* 1–2 bubble s⁻¹) at normal pressure. The bubbling of CO₂ was continued throughout the reaction. The reaction was carried out at room temperature and at a constant potential (–2.4 V vs Ag/AgCl) until the consumption of substrate was neglectable. The reaction time was typically 24 h. The reacted mixture was extracted three times with diethyl ether and then the two phases were analyzed by an HP6890/5793 GC-MS (HP 5MS column) respectively.

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