

Solvent-free Carboxylation of Styrene Oxide: Enhanced Reactivity of Quaternary Onium Salts in Ionic Liquid-CO₂ System

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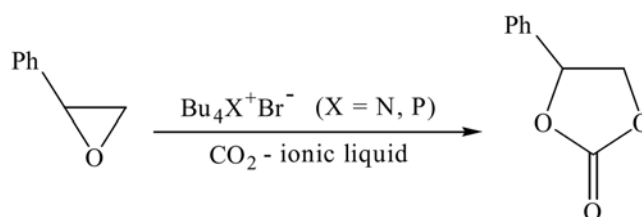
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The search for green process based on chemical fixation of carbon dioxide (CO₂) has attracted much attention in industrial chemistry from the standpoint of environmental protection and resource utilization.¹ The carboxylation of epoxides affording the cyclic carbonates *via* the cycloaddition of CO₂ with epoxides has emerged as one of the most promising methods in this area.² Five-membered cyclic carbonates are valuable as monomers, polar aprotic solvents, and intermediates for the synthesis of pharmaceuticals and fine chemicals.³ A variety of catalytic systems from simple alkali salts to organometallic complexes have been developed for conversion of CO₂ with epoxides to form the corresponding cyclic carbonates.⁴ Recently, we have reported the carboxylation of styrene oxide using quaternary onium salts such as tetraalkylammonium and phosphonium halides proceeds with full-atom-economy-type⁵ to convert styrene oxide into styrene carbonate. This process has advantages such as solvent-free reaction conditions, easy catalysts recovery by filtration, and simple product separation.⁶ Historically, quaternary onium salts have been frequently used as complexed with transition metal catalysts⁷ to promote the reactions of the coupling of CO₂ with epoxides and still remains as attractive catalysts due to their useful catalytic properties such as easy availability, high chemical stability against redox conditions and catalytic stability after use.

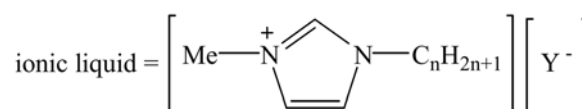
Ionic liquids have received a lot of interest recently because they possess some of the most important features, such as the negligible vapor pressure, unique solvation properties, good ion conductivity as well as catalytic activity and selectivity.^{8,9} Particularly, various ionic liquid-metal complexes such as metal imidazolium complexes have been used for improving reaction rate and effectiveness for the synthesis of cyclic carbonate by coupling CO₂ with epoxide.¹⁰

Herein, we report the use of ionic liquids in conjunction with quaternary onium salts accelerates the solvent-free carboxylation of styrene oxide (Scheme 1). Effectiveness of several ionic liquids (Figure 1) and effects of reaction parameters such as CO₂ pressure, temperature, and time have been investigated.

Influence of ionic liquids. Table 1 shows the results of the carboxylation of styrene oxide catalyzed by two representative quaternary onium salts (tetrabutylammonium bro-



Scheme 1



Y = BF₄, PF₆, OTf, NTF₂

Figure 1

midate and tetrabutylphosphonium bromide) (2 mol %) in ionic liquids-CO₂ system. The reactions depend greatly on the kind of alkyl chains and counter anions of imidazolium-based ionic liquids. The BF₄⁻ was found to be the most effective to promote the carboxylation. Thus, 1-Butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF₄] displayed the highest activity for the synthesis of styrene carbonate for both onium salts (99% conversion after 2 h). However, a longer reaction time (4 h) was necessary to obtain 96% conversion without [bmim][BF₄] under the optimized reaction condition. While the reaction is very sensitive to reaction temperature as discussed later, only a low conversion of styrene oxide into styrene carbonate was obtained when the carboxylation was performed without onium catalysts (< 20% conversion at 100 mol % concentration of [bmim][BF₄]) (entry 11, 12) even at an elevated temperature. The reaction was found to be also sensitive to the type of the anions of the onium catalysts. The bromide ion was the most effective for the tetraalkylammonium salts in the carboxylation of styrene oxide as discussed in the previous paper.⁵ Carboxylation with Bu₄NBF₄ gave a poor yield (entry 13) and the imidazolium compound with the bromide anion, [bmim]Br, showed only a modest conversion (entry 14). These facts show the intermediate species formed by ligand exchange in the reaction between the onium catalysts and

Table 1. Influence of ionic liquids on the carboxylation of styrene oxide

entry	ionic liquid (mol %) ^a	onium salt (2 mol %)	temperature (°C)	CO ₂ pressure (psi)	time (h)	yield (%) ^b
1	[hmim][NTf ₂] (20 mol%)	Bu ₄ PBr	120	2030	2	49.6
2	[hmim][PF ₆] (20 mol%)	Bu ₄ PBr	120	2030	2	62.4
3	[hmim][BF ₄] (20 mol%)	Bu ₄ PBr	120	2030	2	70.5
4	[bnmim][OTf] (20 mol%)	Bu ₄ PBr	120	2030	2	61.7
5	[bmim][BF ₄] (20 mol%)	Bu ₄ PBr	120	2030	2	99.4
6	[bnmim][BF ₄] (20 mol%)	Bu ₄ NBr	120	2030	2	63.6
7	[bmim][BF ₄] (20 mol%)	Bu ₄ NBr	120	2030	2	99.2
8	[emim][BF ₄] (20 mol%)	Bu ₄ NBr	120	2030	2	77.6
9	[moim][BF ₄] (20 mol%)	Bu ₄ NBr	120	2030	2	74.9
10	–	Bu ₄ NBr	120	2030	4	95.0
11	[bmim][BF ₄] (20 mol%)	–	120	2030	4	trace
12	[bmim][BF ₄] (100 mol%)	–	120	2030	4	17.0
13	–	Bu ₄ NBF ₄	120	2030	2	trace
14	[bmim]Br (20 mol%)	–	120	2030	2	69.0

^a[hmim]: 1-hexyl-3-methylimidazolium, [bnmim]: 1-benzyl-3-methylimidazolium, [emim]: 1-ethyl-3-methylimidazolium, [bmim]: 1-butyl-3-methylimidazolium, [moim]: 1-methyl-3-octylimidazolium, Tf: SO₂CF₃. ^bisolated yield

imidazolium salts, *i.e.*, Bu₄NBF₄ and [bmim]Br may be not much responsible for enhancing reactivity of the catalytic system. We believe some combinatory effect of onium salts and ionic liquids might involve here.

Influence of reaction temperature. It was found the yield of the styrene carbonate was strongly affected by the reaction temperature. As shown in Table 2, the yield of the styrene carbonate reached up to 99% at 120 °C (entry 9), however, the reactions at a lower reaction temperature (80 °C) usually gave a poor conversion, irrespective of varying the concentration of ionic liquids (entry 1-4), reaction time (entry 2-4, 7) and CO₂ pressure (entry 5, 6). Moderate yields were obtained at elevated temperature under low CO₂ pressure (560 psi) (entry 6, 8).

Influence of ionic liquids concentration and CO₂ pressure. The yield of the carbonate synthesis increases with the concentration of the ionic liquids and CO₂ pressure (Table 2 and 3). A typical conversion up to 99% was achieved with [bmim][BF₄] under supercritical condition

Table 2. Influence of reaction temperature on the carboxylation of styrene oxide

entry	ionic liquid (mol %)	onium salt (2 mol %)	temperature (°C)	CO ₂ pressure (psi)	time (h)	yield (%) ^a
1	[bmim][BF ₄] (20)	Bu ₄ PBr	80	560	2	12.5
2	[bmim][BF ₄] (20)	Bu ₄ PBr	80	560	4	30.8
3	[bmim][BF ₄] (40)	Bu ₄ PBr	80	560	4	30.0
4	[bmim][BF ₄] (60)	Bu ₄ PBr	80	560	4	28.7
5	[bmim][BF ₄] (20)	Bu ₄ PBr	80	2030	2	8.2
6	[bmim][BF ₄] (20)	Bu ₄ PBr	120	560	2	70.2
7	[bmim][BF ₄] (20)	Bu ₄ NBr	80	560	4	33.0
8	[bmim][BF ₄] (20)	Bu ₄ NBr	120	560	2	71.1
9	[bmim][BF ₄] (20)	Bu ₄ NBr	120	2030	2	99.2

^aisolated yield

(2,030 psi) at 120 °C (Table 2, entry 2 and 7). A longer reaction time (4h) was necessary to obtain the high conversion under low CO₂ pressure (560 psi) and 120 °C (entry 8) for the reaction with tetrabutylammonium bromide. The activity of tetrabutylammonium bromide/[bmim][BF₄] (20 mol%) under low CO₂ pressure (560 psi) for carboxylation of styrene is still higher than NaI/PPh₃/PhOH system¹¹ known as one of the most active catalytic systems (Table 3, entry 8 vs 14). The catalytic activity of the present catalytic system increases smoothly with CO₂ pressure (Table 3, entry 2-4 and 8-11). Effects of ionic liquid concentration and CO₂ pressure on this reaction can be explained in terms of the enhanced CO₂ solubility by imidazolium-based ionic liquids as reported elsewhere.¹² The increase of the effective CO₂ concentration in the reaction might be a key factor for

Table 3. Influence of ionic liquids concentration on the carboxylation of styrene oxide at 120 °C

entry	ionic liquid (mol %)	onium salt (2 mol %)	CO ₂ pressure (psi)	time (h)	yield (%) ^a
1	[bmim][BF ₄] (20)	Bu ₄ PBr	560	2	71.1
2	[bmim][BF ₄] (20)	Bu ₄ PBr	1010	2	78.0
3	[bmim][BF ₄] (20)	Bu ₄ PBr	1500	2	92.6
4	[bmim][BF ₄] (20)	Bu ₄ PBr	2030	2	99.4
5	[bmim][BF ₄] (40)	Bu ₄ PBr	560	2	87.1
6	[bmim][BF ₄] (60)	Bu ₄ PBr	560	2	96.3
7	[bmim][BF ₄] (20)	Bu ₄ NBr	560	2	70.2
8	[bmim][BF ₄] (20)	Bu ₄ NBr	560	4	99.8
9	[bmim][BF ₄] (20)	Bu ₄ NBr	1010	2	82.2
10	[bmim][BF ₄] (20)	Bu ₄ NBr	1500	2	94.4
11	[bmim][BF ₄] (20)	Bu ₄ NBr	2030	2	99.2
12	[bmim][BF ₄] (40)	Bu ₄ NBr	560	2	86.9
13	[bmim][BF ₄] (60)	Bu ₄ NBr	560	2	94.7
14	NaI/PPh ₃ /PhOH	–	560	4	85 ^b

^aisolated yield. ^bRef. 11.

promoting the catalytic efficiency of quaternary onium salts.

In summary, the carboxylation of styrene oxide catalyzed by several onium salts in the presence of the ionic liquid-supercritical CO₂ system accelerates the solvent-free carboxylation to produce styrene carbonate in an efficient and environmentally benign fashion. 1-Butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF₄] (20 mol%) displayed the highest activity for the synthesis of styrene carbonate for both onium salts under supercritical conditions. The yield of the styrene carbonate was strongly affected by the reaction temperature; the yield of the styrene carbonate reached up to 99% at 120 °C, however, the reactions at a lower reaction temperature (80 °C) usually gave a poor conversion, irrespective of the concentration of ionic liquids, reaction time, and CO₂ pressure. Formation of the styrene carbonate increases smoothly with the concentration of the ionic liquids. Also, the yield of the styrene carbonate significantly changes with variation of CO₂ pressure.

Experimental Section

A representative experimental procedure for the carboxylation of styrene oxide is as follows. Styrene oxide (262.2 mg, 2.18 mmol) was added to the mixture of [bmim][BF₄] (0.44 mmol, 20 mol %) and tetra *n*-butylammonium bromide (14 mg, 0.044 mmol) in a tubular stainless steel reactor of 24 mL capacity at room temperature. Then, CO₂ was introduced into the reactor and then the mixture was heated at 120 °C for 2 h with a magnetical stirring, at which time the pressure reached at 2,030 psi. The reaction mixture was cooled and CO₂ was vented. The residue was extracted from the ionic liquid with ethyl ether (5 mL × 5), leaving the catalyst recovered as a white solid, and the organic solvent was evaporated under reduced pressure to give the crude carbonate as a colorless oil. Further purification was done by column chromatography on silica gel (eluant:ethyl acetate/*n*-hexane = 1/4) to give a colorless solid; mp 54-55 °C (lit. 50-51 °C).¹¹ The purity of styrene carbonate obtained was analyzed to be >99.5% by HPLC (Shimadzu LC 10A, Phenomenex ODS column).

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