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Ionic Liquids in Green Carbonate Synthesis

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1. Introduction

Ionic liquids (ILs), made of relatively large organic cations and inorganic anions, could contribute as solvents and catalysts to green organic synthetic reactions [1-5]. The reaction systems using no organic solvents, dense phase carbon dioxide (supercritical and carbon dioxide-dissolved expanded liquid phases), and/or water are obviously advantageous from environmental viewpoints [1]. ILs would be one of attractive components for environment-friendly reaction and separation processes because of their physicochemical properties. But we should also note the possibility of negative effects caused by their toxicity on environment and products when we use ILs for practical applications.

There are a number of ILs using different cations and anions, and a few typical examples are shown in Fig. 1. It is evidenced that ILs act as good catalysts for several organic synthetic reactions, as noted in recent review articles [1-5], including Friedel-Crafts reactions, Diels-Alder reactions, hydrogenation, polymerization, and other reactions. Haumann and Riisager discuss various aspects (structure of substrates, type of ILs, form of ILs catalysts) in hydroformylation reactions using ILs [4]. Recently Baiker et al. have published a review on multiphase catalytic systems including ILs and carbon dioxide [5]. They point out the significance of the combination of ILs and carbon dioxide for chemical and separation processes. This review deals with physicochemical features of those multiphase reaction systems and catalytic reactions therein including those using carbon dioxide as a reactant.

After considering those previous reviews and other chapters of this book, we will concentrate our attention on the application of ILs to the synthesis of carbonate and related compounds using carbon dioxide. Those compounds are of practical importance as solvents, reagents, fuel additives, and intermediates in the production of pharmaceuticals and fine chemicals [6,7]. The authors previously reviewed the potential application of ILs for the synthesis of cyclic carbonates from carbon dioxide [8]. The present chapter will deal with the synthesis of cyclic carbonates, dialkyl carbonates, other related compounds, and polycarbonates using ILs as solvents and catalysts.

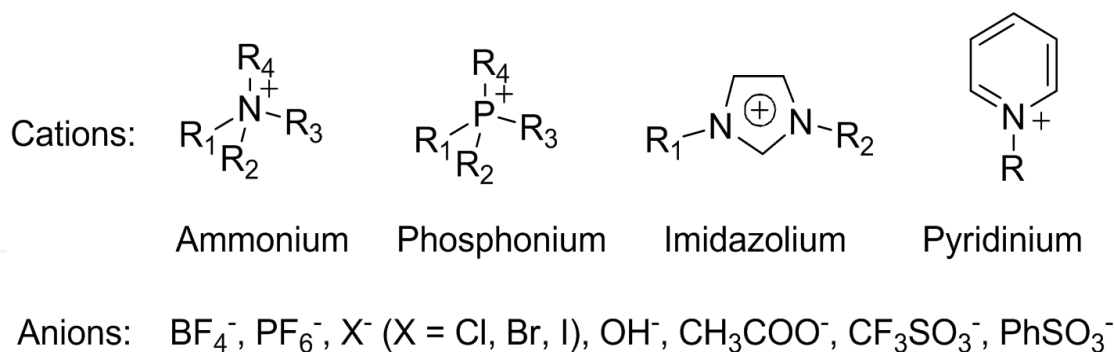


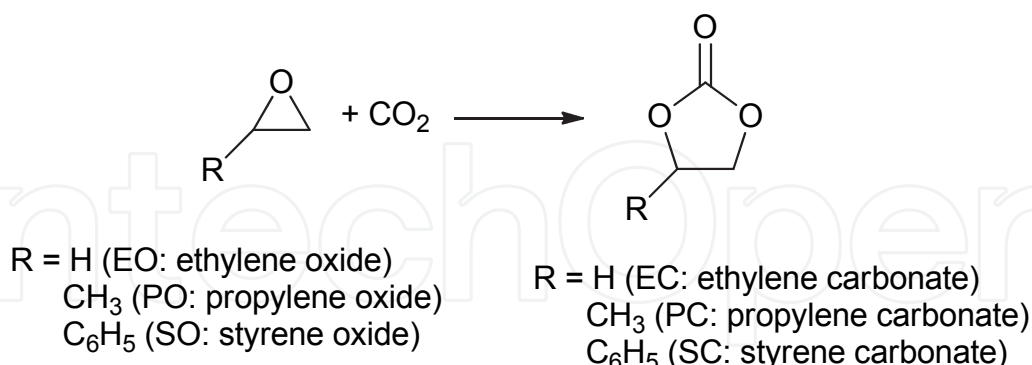
Fig. 1. Representative anions and cations of ILs.

2. Synthesis of cyclic carbonate in/by ILs

2.1 Synthesis of cyclic carbonate via CO₂ cycloaddition to epoxide

2.1.1 CO₂ cycloaddition catalyzed by ILs without additives

The synthesis of cyclic carbonates from epoxides and CO₂ (Scheme 1) is one of the major ways to transform CO₂ to valuable chemicals. The first successful synthesis of cyclic carbonate using room temperature ILs of imidazolium and pyridinium salts was reported by Peng and Deng in 2001 [9]. It has been shown that cycloaddition of CO₂ to propylene oxide (PO) producing propylene carbonate (PC) is effectively catalyzed by [BMIm]BF₄. PO was quantitatively converted to PC with 2.5 MPa of CO₂ at 110°C for 6 h in the presence of 2.5 mol% [BMIm]BF₄. After the reaction, PC was distilled from the reaction mixture and the catalyst was recycled up to four times with only a minor loss in activity. The ionic liquid catalyst is recyclable for the cycloaddition of CO₂ to PO. They also showed that the type of either cation or anion affect the activity of the ILs. The activity decreased in the orders of [BMIm]⁺ > [BPy]⁺ and of BF₄⁻ > Cl⁻ > PF₆⁻.



Scheme 1. Cycloaddition of CO₂ to epoxide. Abbreviations for some representative substrates and products are also given.

Kawanami and coworkers reported the PC synthesis from PO using various imidazolium salts under supercritical carbon dioxide (scCO₂) that is highly miscible with ILs [10]. The experimental results showed that both the type of anion and the length of alkyl chain in the cation have decisive effects on the conversion and selectivity. The performance of different ILs of 1-ethyl-3-methylimidazolium cation ([EMIm]⁺) with NO₃⁻, CF₃SO₃⁻, BF₄⁻ and PF₆⁻ was investigated, and BF₄⁻ was again found to be the most effective. In addition, the

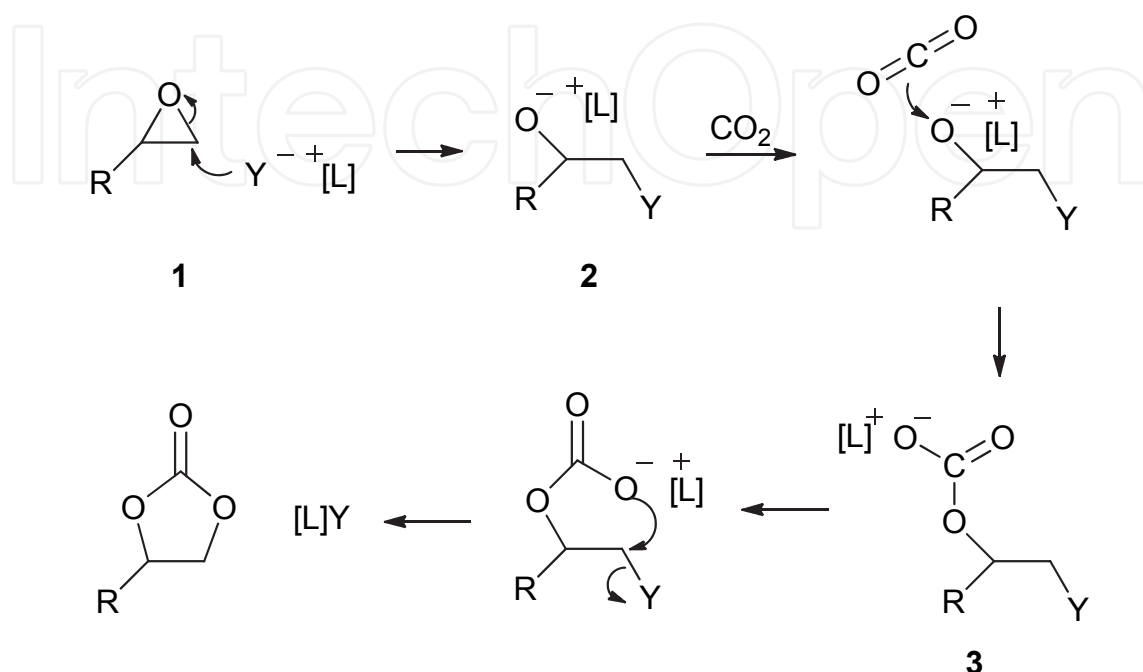
carbonate yield increased markedly with an increase of the alkyl chain length (from C₂ to C₈). In the presence of 1-octyl-3-methylimidazolium ([OMIm]BF₄), 98% yield and 100% selectivity for the production of PC from CO₂ and PO were achieved at 100°C and 14 MPa of CO₂ in a short reaction time of 5 min. On the other hand, the yield and the selectivity obtained with [EMIm]BF₄ were 61% and 87%, respectively, even for a longer reaction time of 2 h. This enhancement was attributed to higher solubility of both the epoxide and CO₂ in the IL having longer alkyl chain under the same pressure and temperature. Interestingly, because of the difference in the solubility, influence of CO₂ pressure on the yield also depends on the alkyl chain length. In the case of [OMIm]BF₄, when the CO₂ pressure was reduced from 14 MPa to a sub-critical pressure of 6 MPa, a remarkable decrease in the yield was observed. In contrast to this, [EMIm]BF₄ gave a higher yield at 6 MPa than 14 MPa. It was also shown that the [OMIm]BF₄-scCO₂ reaction media gave satisfactory yields for the synthesis of other carbonates.

As described above, imidazolium-based ILs containing BF₄⁻ such as [BMIm]BF₄ and [EMIm]BF₄ were more active than the ones containing another type anion of PF₆⁻, and [BMIm]BF₄ was more active than butylpyridinium IL [BPy]BF₄. Recently, Seki et al. studied the molecular interactions of pressurized CO₂ with imidazolium and pyridinium salts ([BMIm]BF₄, [BMIm]PF₆, [BMIm]Tf₂N, [BPy]BF₄) by in situ ATR infrared spectroscopy [11]. They suggested that Lewis acid-base interaction between CO₂ and BF₄⁻ leads to the formation of a new anion species, [BF₄-CO₂]⁻, which is more basic than the original anion of BF₄⁻. Similar new anion species were also produced from PF₆⁻ and Tf₂N⁻; however, they were less basic than [BF₄-CO₂]⁻ because of the difference in the interaction strength of CO₂ with the anion. It was also shown that the basicity of [BF₄-CO₂]⁻ was stronger for [BMIm]BF₄ than [BPy]BF₄, revealing that the interaction between CO₂ and BF₄⁻ also depends on the cation species of ILs. Thus, the basicity of the new anion species produced from CO₂ and the original anion of IL may explain the effectiveness orders of BF₄⁻ > PF₆⁻ and of [BMIm]⁺ > [BPy]⁺ for the cyclic carbonate synthesis observed in the previous studies.

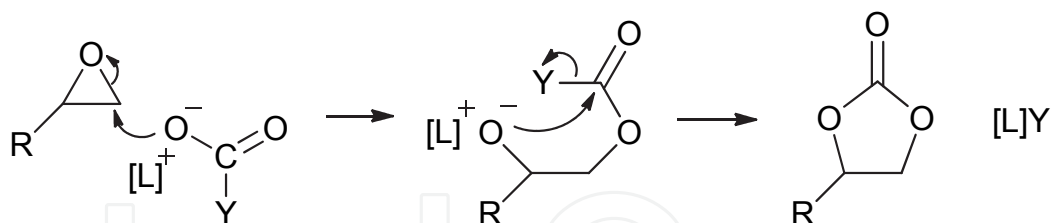
Quaternary ammonium salts can also catalyze CO₂ fixation into cyclic carbonate. Caló et al. reported that this reaction was effectively promoted by molten tetrabutylammonium bromide ([Bu₄N]Br) and/or tetrabutylammonium iodide ([Bu₄N]I) under atmospheric pressure of CO₂ at 120 or 60°C [12]. Using these salts as solvents and catalysts, a less active substrate (styrene oxide) and a polymerisation-sensitive oxirane (glycidyl methacrylate oxirane) were converted to the corresponding cyclic carbonates in satisfactory yields. [Bu₄N]I showed higher activity than [Bu₄N]Br because of the difference in the nucleophilicity of the halide ions. The reaction rate depended greatly on the structure of the cation as well as the nucleophilicity of anion. They also showed significant difference in the activity among [BMIm], N-methyl-pyridinium ([MPy]) and [Bu₄N] iodides. The first two salts indicated inefficient catalytic performance for the cyclic carbonate synthesis. They suggested that the effective activity of [Bu₄N]I comes from the bulkiness of the tetrahedral ammonium ion, which forces the halide ion away from the cation easier, resulting in less electrostatic interaction between anion and cation and consequently in more nucleophilicity of the anion. It was also shown that the ammonium salt was easily recyclable by vacuum distillation or extraction with ethyl acetate, in which the salt is insoluble.

A plausible reaction mechanism for CO₂ cycloaddition to epoxide catalyzed by IL is illustrated in Scheme 2. The reaction is initiated by the ring opening of epoxide that is made by a nucleophilic attack of the anion of IL to the less hindered carbon atom of the epoxide ring; then, an oxy anion species **2** is formed. The carbon atom of CO₂ interacts with the oxy

anion of complex **2**, producing an alkylcarbonate anion **3**. This species is further converted to the cyclic carbonate through the intermolecular cyclic elimination. Thus, the nucleophilic nature of the IL anion is significant for the reaction. Seki et al. who suggested the formation of the anion species of $[Y-CO_2]^-$ proposed a different mechanism [11], in which this new anion reacts with the epoxide, affording another intermediate (Scheme 3).



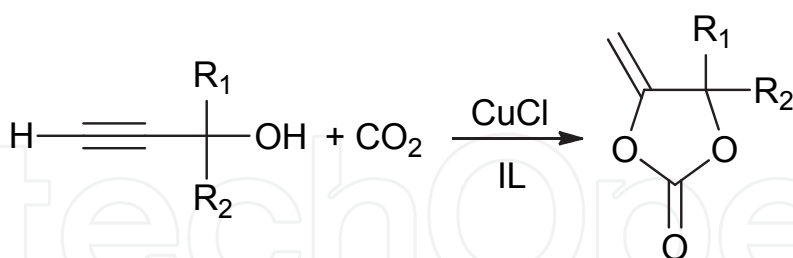
Scheme 2. A plausible mechanism for CO_2 cycloaddition to epoxide catalyzed by IL.



Scheme 3. A proposed mechanism involving an anion species of $[Y-CO_2]^-$ for CO_2 cycloaddition to epoxide [11].

The reaction of CO_2 and propargyl alcohol also produces a cyclic carbonate having a methylene group (Scheme 4). Gu et al. used the catalyst system of $\text{CuCl}/[\text{BMIm}][\text{PhSO}_3]$ for this reaction [13]. 2-Methyl-3-butyn-2-ol ($\text{R}_1, \text{R}_2 = \text{CH}_3$) was almost qualitatively converted to the corresponding cyclic carbonate at 100°C under 1 MPa of CO_2 for 8 h. Similar results were obtained with CuBr and CuI . CuCl_2 also gave a good yield of 84%. The activities of iron and cobalt salts were poor, and noble metal salts gave only polymeric products. Solvent screening showed that $[\text{BPy}][[\text{PhSO}_3]]$ gave a slightly lower yield of 80%, and moderate yields were obtained with $[\text{BPy}]\text{BF}_4$ and $[\text{BMIm}]\text{NO}_3$. Moderate product yields were obtained even in organic solvents. However, $[\text{BMIm}]\text{PF}_6$ gave only polymeric products. Thus, the IL seems to act as a solvent, but there would be some interactions between the IL

and CuCl and/or the alcohol. Interestingly, the reaction system was specific for tertiary alcohols; no desired products were detected from secondary and primary alcohols.



Scheme 4. Reaction of CO₂ with propargyl alcohol.

2.1.2 CO₂ cycloaddition catalyzed by ILs with Lewis acids

The presence of Lewis acidic compounds as co-catalysts greatly enhances the activity of ILs for the cyclic carbonate synthesis. In 1986, surprisingly, Kisch et al. already pointed out the significance of Lewis acid-base bi-functional system for the cyclic carbonate synthesis [14]. They showed that mixtures of ZnCl₂ and various ammonium and phosphonium halides can catalyze the PC synthesis even at room temperature with CO₂ at atmospheric pressure, although very long periods of reaction time were required to get high yields. This result was significant; however, it unfortunately did not attract attention of other researchers for a long time.

Lately, Kim et al. showed that the catalytic activities of ILs such as [BMIm]Cl and [BMIm]Br for the reactions of CO₂ with ethylene oxide (EO) and propylene oxide (PO) can surprisingly be improved by the combination of them with zinc bromide (ZnBr₂), although ZnBr₂ has no activity for the reactions [15]. For example, a TOF value of 37 h⁻¹ for PC production was obtained with [BMIm]Br alone at 100°C under CO₂ of 3.5 MPa; this value was increased to 1679 h⁻¹ by the co-presence of ZnBr₂. They concluded that the high activities are attributed to the in situ formation of [BMIm]₂ZnBr₂Cl₂ and [BMIm]₂ZnBr₄, because these tetrahalides separately prepared showed similar activities to the corresponding catalyst systems of [BMIm]Cl/ZnBr₂ and of [BMIm]Br/ZnBr₂. The catalytic activity of imidazolium zinc tetrahalide was greatly influenced by the nature of halide groups bonded to the zinc center. The activity was found in an order of [ZnBr₄]²⁻ > [ZnBr₂Cl₂]²⁻ >> [ZnCl₄]²⁻, suggesting the importance of the nucleophilicity of halide ligands. They propose that a halide ion is dissociated from the zinc tetrahalide and subsequently attacks the carbon atom of epoxide. On the contrary, the alkyl group attached on the imidazolium cation was found to have a negligible effect on the activity. It is also shown that the imidazolium zinc tetrahalide is stable and reusable. They also determined the structure of the tetrahalide catalyst of (1,3-dimethylimidazolium)₂ZnCl₂Br₂ by XRD [16]. A similar catalyst system of [BMIm]Br/ZnCl₂ was reported by Li et al. [17]. NMR measurements of the catalyst in D₂O suggested the formation of a ZnCl₂-[BMIm]Br complex through the coordination of ZnCl₂ with the hydrogen atom on C(2) of imidazolium ring. This catalyst system gave excellent yields for the cyclic carbonate synthesis with several types of epoxides at 100°C for 1 h under CO₂ of 1.5 MPa.

Shortly thereafter, our group used a series of metal halides together with [BMIm]Cl for the synthesis of styrene carbonate (SC) from styrene oxide (SO), which is less reactive as compared with PO and EO [18]. It was found that the catalyst system comprised of ZnBr₂ and [BMIm]Cl can afford 93% yield with 100% selectivity to styrene carbonate at a low

reaction temperature of 80°C for 1 h. No activity was observed with ZnBr₂ alone and [BMIm]Cl itself gave a very low SC yield (6%). However, the combination of ZnBr₂ and [BMIm]Cl can exhibit an appreciably high activity for the carbonate synthesis. The type of metal cations had strong effect on the carbonate yield, the order of activity being Zn²⁺ > Fe³⁺ > Fe²⁺ > Mg²⁺ > Li⁺ > Na⁺, which is the same order of Lewis acidity of the metal cations. When ZnI₂, ZnCl₂ or ZnO was used instead of ZnBr₂, the styrene carbonate yield was lowered. The influence of ILs showed that both the type of anion and the length of alkyl chain on the imidazolium cation had strong effects on the conversion and selectivity. Due to non-nucleophilic nature of BF₄⁻ and PF₆⁻ ions, when the [BMIm]BF₄ and [BMIm]PF₆ were used instead of [BMIm]Cl, low epoxide conversions were obtained. With these catalysts, selectivity for the styrene carbonate was also low because of the formation of oligomer of styrene oxide and/or styrene carbonate. When the IL having a longer alkyl chain, [OMIm]Cl, was used instead of [BMIm]Cl, the conversion was increased. Such an enhancement of the activity by lengthening the alkyl chain was also observed in the system of the imidazolium BF₄ under scCO₂, as described above. Interestingly, besides the influence of the types of metal halides and the ILs, the [BMIm]Cl/ZnBr₂ ratio also affected the carbonate yield, a ratio of 2 being optimum. The optimum CO₂ pressure was 4 MPa and elevated pressures had no positive effect on this SC synthesis. After the reaction, the catalyst phase of [BMIm]Cl and ZnBr₂ can be separated by an extraction with ethyl acetate and reused for another run without significant loss in activity.

Similar to the cases of the imidazolium salts, Lewis acid enhances the activities of ammonium salts. Our group also examined a series of metal halides together with [Bu₄N]Y (Y = Cl, Br, I) for the SC synthesis [19]. The co-presence of zinc halides again appreciably enhanced the activity of [Bu₄N]I by a factor of more than 25 times. The SC yield was in orders of ZnBr₂ > ZnI₂ > ZnCl₂ and of [Bu₄N]I > [Bu₄N]Br > [Bu₄N]Cl. The yield showed a maximum at a CO₂ pressure of 8 MPa. The most optimum ratio of [Bu₄N]I/ZnBr₂ was again 2. The activity of this catalyst system was very high; an almost quantitative yield was achieved even in a short reaction time of 30 min and at a mild reaction temperature of 80°C. It should be noted that, compared to the above mentioned catalyst system of [BMIm]Cl/ZnBr₂, the reaction time required to get the qualitative yield was half, although the types of halides were different.

As mentioned above, several bi-functional catalyst systems consisting of onium salts and zinc halides had been reported; however, direct comparison of their activities was difficult, because those catalysts were used for the reactions under different reaction conditions. Recently, our group has found that various zinc halide-based ILs whose general formula is [L]_nZnX₂Y_n where L is a onium cation and X and Y are halides can be prepared by a simple heat treatment of mixtures of zinc halides and corresponding onium halides [20]. Under these circumstances, we prepared zinc halide-based ILs containing [Bu₄N]⁺, [BPy]⁺, [BMIm]⁺, and [Chol]⁺, and used them for the SC synthesis [21]. The effectiveness of the onium cation as the active catalyst component was in the order of [Bu₄N]⁺ > [BPy]⁺ > [BMIm]⁺ >> [Chol]⁺ (choline). Interestingly, the halide originating from the Zn halide (X) was more influential on the activity than that originating from the IL used (Y). Influence of the ratio of IL cation to Zn was different by the type of the IL cation. For [Bu₄N]⁺, the activity increased linearly with the ratio up to 2; however, further increase in the ratio did not lead to the enhancement of the activity. For [BMIm]⁺, the activity increased linearly with the ratio at least up to 4. The explanation for these observations remained speculative. With the best catalyst, an almost quantitative yield was obtained even in a short reaction time of 30 min

and at 80°C under CO₂ of 5 MPa. On the other hand, the use of analogous physical mixtures of ZnBr₂ and the onium bromides for the reaction resulted in a similar order of [Bu₄N]⁺ ~ [BPy]⁺ > [BMIm]⁺, but the SC yields obtained with the mixtures were lower than those with the corresponding IL of [L]_nZnX₂Y_n.

The number of studies using mixtures of zinc halides and tetraalkylphosphonium halides as the catalysts for the CO₂ cycloaddition is limited [6,14,22,23]. Under the same conditions, the phosphonium catalysts showed lower activity compared with ammonium halide catalysts [14], but it was claimed that the former catalysts were more thermally stable than the latter ones [22].

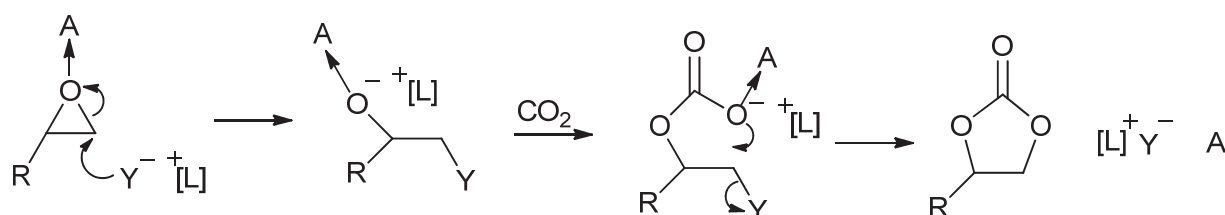
As well as zinc halides, CaCl₂ [24] and CoCl₂ [25] can also promote the CO₂ cycloaddition to epoxide catalyzed by tetraalkylammonium or phosphonium halides. The optimum ratio of CaCl₂/IL was again 2 [24]. Unfortunately, these catalyst systems required relatively higher temperature to achieve high cyclic carbonate yields. Interestingly, CoCl₂ gave higher cyclic carbonate yields than CoBr₂ [25], being different from the results obtained with zinc halides. Yokoyama and co-workers applied catalyst systems consisting of zinc salts and ILs for the PC synthesis under microwave radiation as heating source [26]. They employed zinc halides, zinc triflate (Zn(OTf)₂), and zinc phenosulfonate octahydrate (ZnPO), and five kinds of ILs. The PC yields under microwave were in the orders of [Bu₄N]Br > [HMIm]Br ~ [BMIm]Br ~ [EMIm]Br > [Bu₄N]I and of ZnPO > ZnI₂ > ZnBr₂ > Zn(OTf)₂. Those orders obtained under oil bath heating were slightly different, being [Bu₄N]Br > [BMIm]Br > [HMIm]Br > [Bu₄N]I > [EMIm]Br and ZnPO > ZnI₂ > Zn(OTf)₂ > ZnBr₂. It is interesting that rather unusual zinc salt of ZnPO was more effective than zinc halide conventionally used for the reaction. At optimum temperature of 120°C and CO₂ pressure of 5 MPa, a surprisingly high TOF of 20,371 h⁻¹ was achieved with ZnPO/[Bu₄N]Br. Analysis of the reaction kinetics led to the conclusion that activation energy was lowered by the use of microwave irradiation.

Sun et al. reported an interesting catalyst system of IL/water [27]. The presence of water significantly enhanced the activities of ILs for the PC synthesis. At the optimal molar ratio of water to IL around 0.3, the PC formation rate could be increased 7 times. Almost 100 % yield was obtained at 120°C and CO₂ pressure of 2 MPa for 30 min. Further increase of this water/IL ratio caused the decrease in the PC selectivity because of the formation of 1,2-propylene glycol, which is produced by the side reaction between water and PO. This catalyst system was applicable for other epoxides. Such promotional effects were also observed with organic compounds containing OH group(s) such as phenol, acetic acid, ethanol, propylene glycol, and 2-propanol.

Synergistic effect also occurs by the combination of metal complex and onium salt. Lu et al. employed coupled catalyst systems of a tetradentate Schiff-base aluminium complex (salenAlCl) and tetraalkylammonium halides for the reactions of CO₂ and epoxides [28–30]. It was reported that various cyclic carbonates are produced from corresponding epoxides even at room temperature with good yields, although the reaction time required is slightly long [30]. Various salen metal complexes were also used for the EC synthesis. The EC yield was in the order of AlCl ~ CrCl > Co >> Ni > Mg ~ Cu ~ Zn [28]. They proposed the reaction mechanism in which ring-opening insertion of epoxide into Al–Cl bond and subsequent insertion of CO₂ into Al–O bond of the resulting alkoxy complex are involved. The ammonium halide is supposed to contribute to the activation of epoxide [29]. Very recently, North and Pasquale analyzed the kinetics of the PC synthesis catalyzed by a similar system of [(salen)Al]₂O/[Bu₄N]Br [31]. The reaction was second-order on the

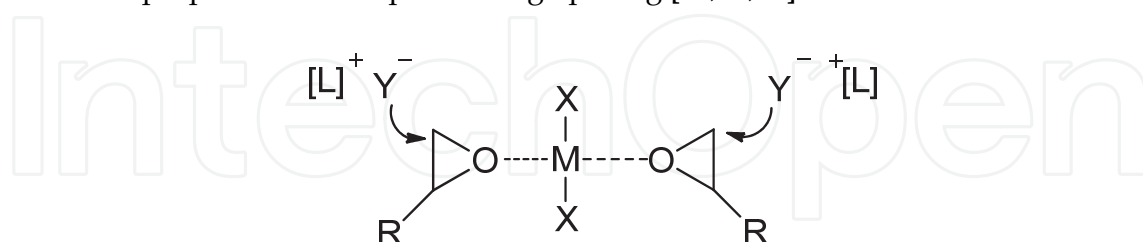
[Bu₄N]Br concentration, and induction periods were observed when the bromide concentration was very low. Furthermore, the formation of trace amounts of Bu₃N was detected after reaction runs. Based on these results, they proposed the involvement of a [Bu₃N-CO₂] complex in the catalytic cycle of the reaction, in which Bu₃N is produced from [Bu₄N]Br and interacts with CO₂, resulting in the formation of [Bu₃N-CO₂] that reacts with the ring opening product of hydroxyl anion species.

As described in this subsection, metal halides, metal complexes and water can improve the activities of ILs for the synthesis of cyclic carbonates from epoxides and CO₂. A generally accepted reaction mechanism for those bi-functional catalyst systems can be drawn as Scheme 5. Because these additives have Lewis acidic nature, they would interact with the oxygen atom of the epoxide. On the other hand, the basic anion of IL would attack the less hindered carbon atom of the epoxide ring. Such cooperative activation of the epoxide should make the ring opening easier, being the reason of the promotional effects of the additives. In some cases, the additives may have a role in the activation of CO₂.



Scheme 5. A generally accepted reaction mechanism for CO₂ cycloaddition to epoxide catalyzed by IL/Lewis acid bi-functional systems. A = metal halides, metal-salen complexes, water. [L] = dialkyl-imidazolium, tetraalkyl-ammonium, tetraalkyl-phosphonium, alkyl-pyridinium. Y = Cl, Br, I.

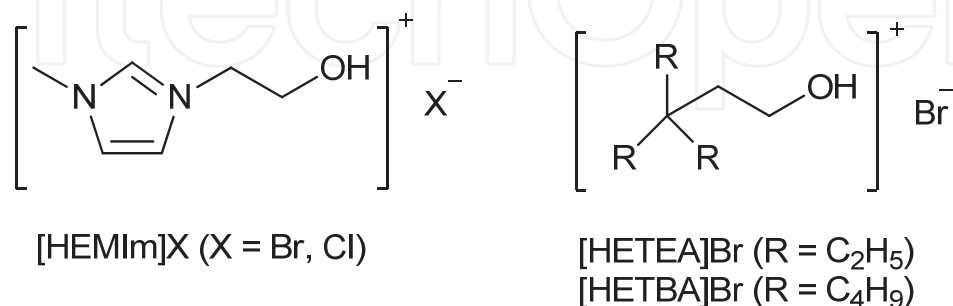
For the catalyst systems using metal halides, the optimum ratio of metal/IL was sometimes observed to be 2 [18,19,24]. This may be explained by simultaneous activation of two epoxide molecules by one metal halide molecule and two IL molecules (Scheme 6). Zinc tetrahalide ILs also showed notable activity for the reaction. Similar cooperative actions of the Zn center of [ZnX₂Y₂]²⁻ (Lewis acid) and a halide anion (Lewis base) liberated from the dianion were proposed for the epoxide ring opening [15,16,21].



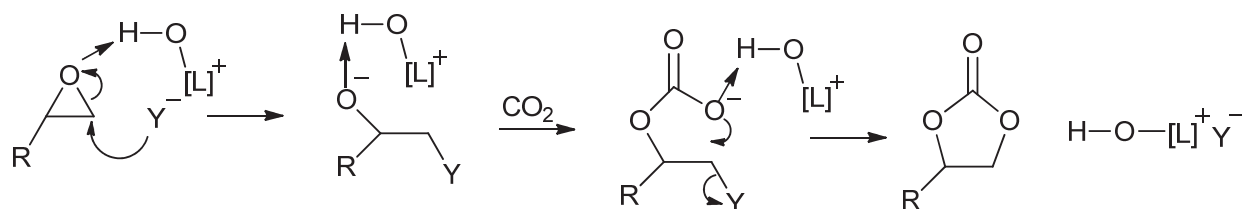
Scheme 6. Simultaneous activation of two epoxide molecules by one metal halide molecule and two IL molecules.

According to Scheme 5, if IL has hydroxyl-alkyl moiety, it can have high activity for CO₂ cycloaddition without additives, because of Lewis acidic nature of the OH group. Sun et al. [32] synthesized such task-specific ILs as hydroxyl-functionalized imidazolium and ammonium salts (Scheme 7). Among them, 1-(2-hydroxyethyl)-3-methylimidazolium bromide ([HEMIm]Br) had the highest activity. It gave almost quantitative yield for the PC synthesis at 120°C and CO₂ pressure of 2 MPa for 1 h, while non-modified IL of [EMIm]Br

gave a lower PC yield of 83%. Similar results were obtained with (2-hydroxyethyl)-tributylammonium bromide ([HETB]Br) and the analogous unmodified ammonium bromide of [Bu₄N]Br. Thus, introducing a functional group of OH shows promotional effects for the activities of the ILs. Based on these results, they proposed the reaction mechanism in which the epoxide is activated by cooperative actions of the OH group and the halide anion (Scheme 8). [HETB]Br was precipitated by cooling after the reaction, separated by simple filtration, and could be reused four times with minor loss in the activity.

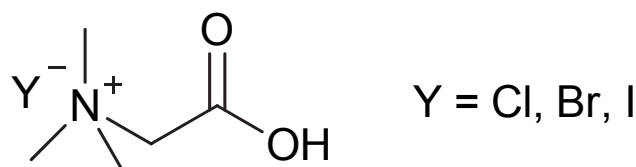


Scheme 7. Hydroxyl-functionalized ILs.



Scheme 8. CO₂ cycloaddition to epoxide with hydroxyl-functionalized IL. (H-O-[L] = [HEMIm], [HETB]. Y = Br, Cl.)

At almost the same time, Zhou et al. reported the PC synthesis using betaine-based ILs of [HBet]Y ([HBet] = 1-carboxy-N,N,N-trimethylammonium, Y = Cl, Br, I), which have a carboxylic group (Scheme 9) [33]. Carboxylic acid is supposed to be more acidic than hydroxyl group; however, the difference in the activity between [HBet]Cl (having carboxylic acid group) and [Chol]Cl (having hydroxyl group) was small. Furthermore, [HBet]Y catalysts required higher temperature and CO₂ pressure and longer reaction time to obtain good PC yields, compared with the above mentioned hydroxyl-functionalized ILs of [HEMIm]Y and [HETB]Y. The reason of this may be lower nucleophilicity of halide anion of [HBet]Y than [HETB]Y.



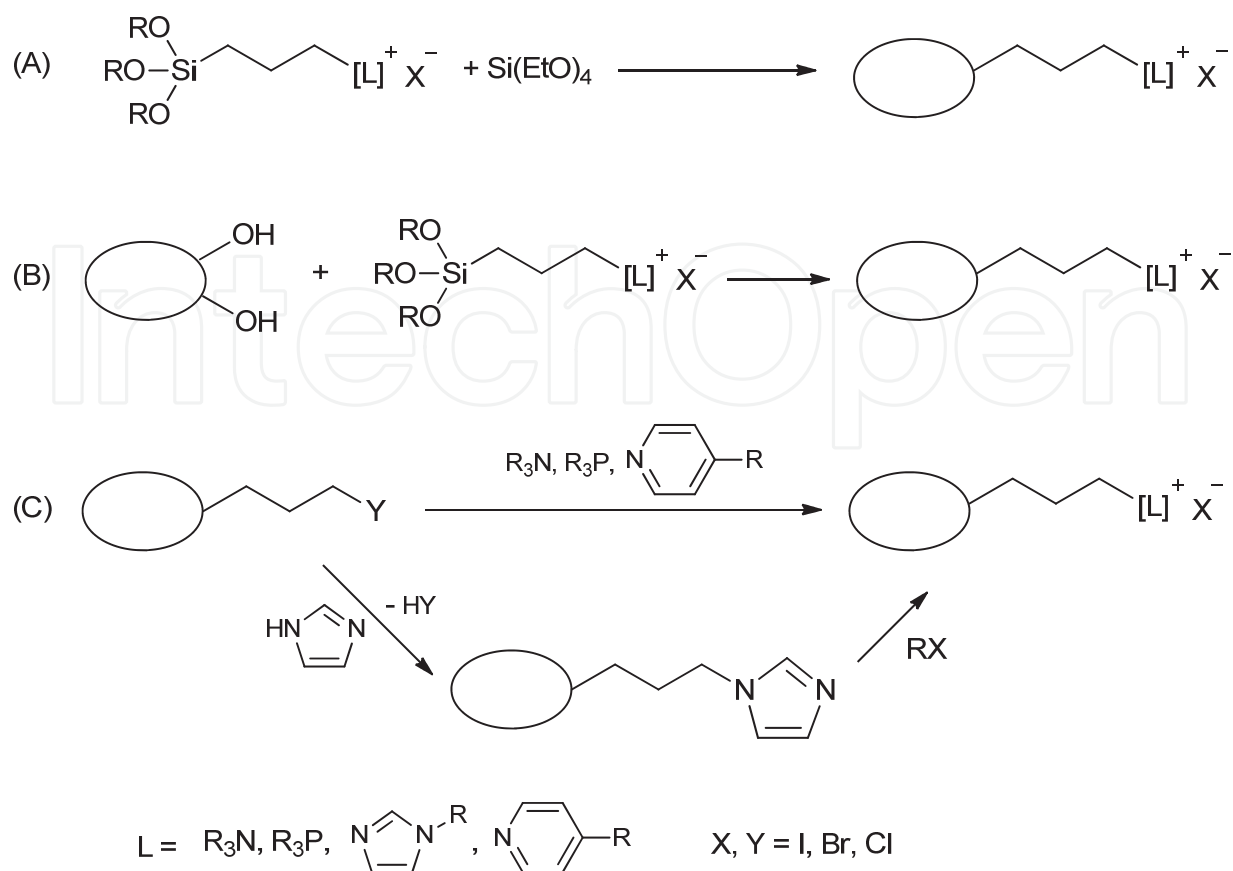
Scheme 9. Betaine-based ILs.

2.1.3 CO₂ cycloaddition catalyzed by immobilized ILs

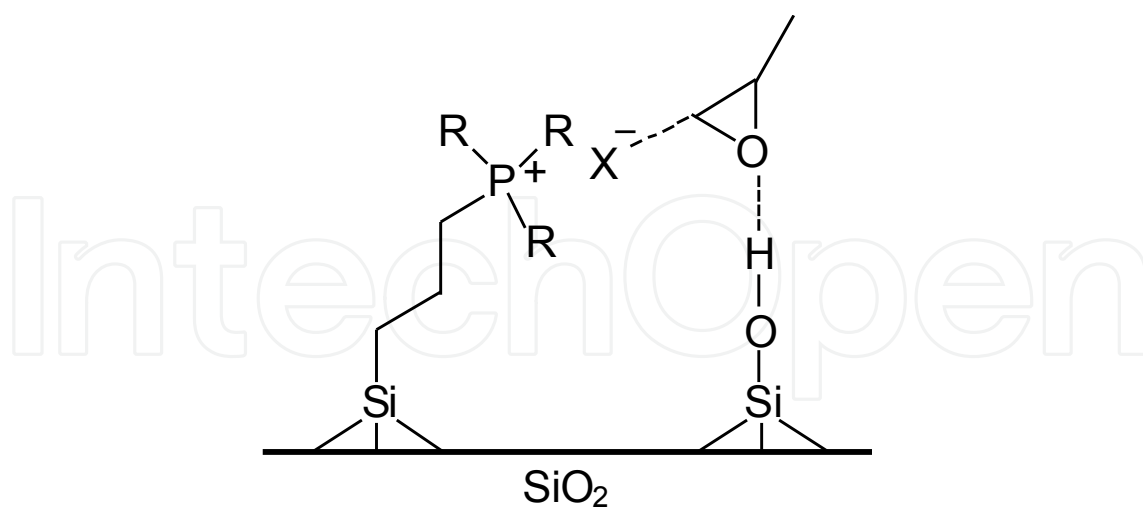
Heterogeneous catalysts are easily separated from reaction mixtures by simple filtration. This advantage can be added to IL catalysts by immobilization of them on solid materials. One easy way for the immobilization is the impregnation method. Wang et al. employed this method for the preparation of silica gel-supported ammonium and imidazolium IL catalysts [34,35]. Similarly, Zhu et al. prepared a molecular sieve-supported [Chol]Cl-urea IL catalyst [36]. In these preparations, the support materials were just dispersed in an acetone or methanol solution containing the IL, and the solvent was removed by evaporation. The activities of these catalysts for PC synthesis were almost the same with those of corresponding unsupported IL catalysts. These supported IL catalysts were easily separated from the reaction mixtures by simple filtration, and could be recycled several times without significant loss in the activity for the PC synthesis under solventless conditions, although, over these catalysts, the active component of IL was fixed on the surface of the support by weak physical adsorption.

ILs can also be covalently immobilized on inorganic materials of silica, mesoporous silicates, aluminosilicate, and alumina. For that three ways are known (Scheme 10). The first method is the co-condensation of a trialkoxysilylalkyl onium salt and triethoxysilane (Scheme 10-A) [37–39]. The second one is the immobilization by the reaction between surface hydroxyl groups of the solid and the alkoxy-silyl group (Scheme 10-B) [40,41]. For the last one (Scheme 10-C), the inorganic materials modified with alkyl halide (usually propylchloride) are used [42–46]; on them, corresponding amine, phosphine, or pyridine can be immobilized and quaternized. For the preparation of imidazolium-based immobilized IL, imidazole is fixed on the modified support in the presence of alkali compounds, followed by quaternization with alkyl halides.

The advantage of immobilizing ILs on solid materials is not only the easier separation of the catalyst, but also the usability of it for the continuous operation using a fixed-bed flow reactor. Takahashi et al. first reported the use of silica-immobilized phosphonium-based IL for a flow reactor [42]. They carried out the PC synthesis using 10 MPa of CO₂ for more than 1000 h. Unfortunately, the reaction temperature was required to be increased from the initial one of 90°C to 160°C for keeping the yield above 80%, suggesting that some leaching of IL from the support might occur; however, during the reaction run, the selectivity to PC was kept over 99.9%. In the same paper [42], they reported interesting synergistic effects of the immobilization of IL on silica. They also carried out the reaction runs in a batch reactor, and showed that the TOF of the immobilized IL was more than 300 times larger compared to that of corresponding phosphonium IL that was used homogeneously. However, the activity was not changed by the immobilization on polystyrene. The surprising enhancement of the activity by supporting on silica was ascribed to the co-operational activation of the epoxide by the acidic surface silanol groups and the halide anion of the immobilized phosphonium IL (Scheme 11). The enhancement of the activity by the immobilization was also observed with other ILs [44,46]. Thus, the activity of an inorganic solid-immobilized IL catalyst would be determined not only by its IL content, but also by the amount of surface hydroxyl group. This was pointed out by Udayakumar et al. [39] who prepared several silica-immobilized imidazolium IL catalysts for the reaction of CO₂ and allyl glycidyl ether. A higher TOF value was obtained with the catalyst containing a less amount of IL. This was ascribed to the presence of a larger amount of surface free silanol group on the catalyst.



Scheme 10. Methods for the immobilization of ILs on an inorganic solid.

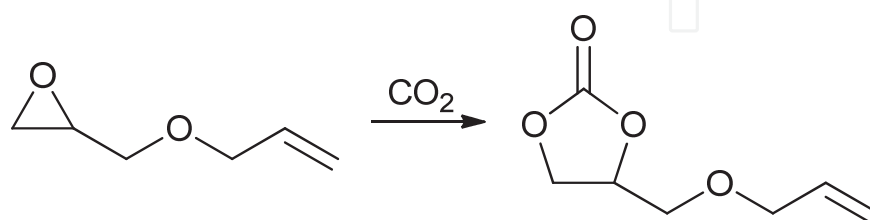


Scheme 11. Cooperative activation of an epoxide molecule on silica-immobilized IL.

Furthermore, the acidity of the OH group on the solid surface was also suggested to affect the activity of immobilized IL catalysts. Sakai et al. prepared immobilized phosphonium IL catalysts for the CO_2 addition to epoxyhexane using silica, aluminosilicate, and basic alumina as the support materials [40]. The conversion was in the order of silica > aluminosilicate > basic alumina. Because this order is the same with that of the acidity of the

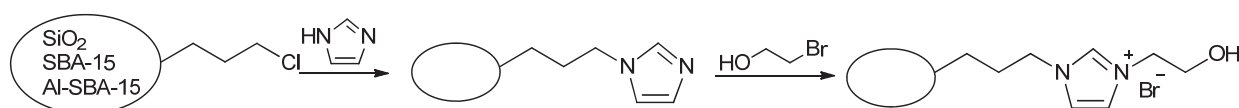
OH group on the support surface, they ascribed the differences in the activity among the catalysts to those in the acidity of the OH group of the supports used.

Udayalumar et al. reported a series of papers in which amorphous silica [38,39] and mesoporous silicate of MCM-41 [43,45] were used as the supports for immobilizing imidazolium-based ILs. They investigated the effects of pore structures, IL content, type of counter anion, and the length of the alkyl group attached to the IL on the catalyst activity for the CO₂ cycloaddition to allyl glycidyl ether producing allyl glycidyl carbonate (AGC) (Scheme 12). Based on the reaction results obtained, they suggested that free space around the immobilized IL molecule is significant for the reaction, because the substrate and the intermediates are rather bulky [45].



Scheme 12. Reaction of CO₂ and allyl glycidyl ether.

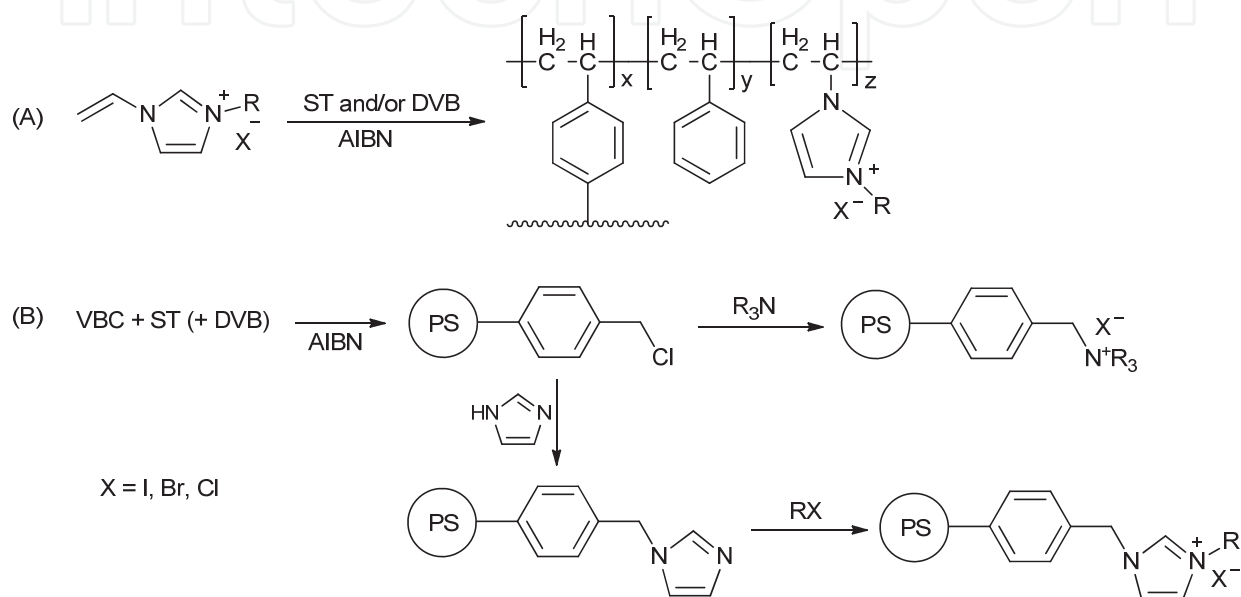
The same group also examined the influence of the co-presence of ZnBr₂ [38], which significantly improved the catalytic activity of un-immobilized imidazolium halides (see section 2.1.2.) [15,17,18]. ZnBr₂ also improved the activity of the immobilized IL catalyst, the AGC yield being increased from 52% to 78%. The promotional effect of ZnBr₂ for the immobilized IL catalyst was not drastic compared to those observed for the un-immobilized imidazolium catalysts whose activities were enhanced tens times by the co-presence of ZnBr₂. As mentioned in section 2.1.2., the hydroxyl-functionalized IL has enhanced activity because of the cooperative action of the hydroxyl group (Scheme 7). Dai et al. [46] immobilized 3-(2-hydroxyethyl)-1-propylimidazolium bromide ([HEPIm]Br) on silica and mesoporous materials of SBA-15 and Al-SBA-15 (Scheme 13). The activity for the PC synthesis was in the order of SBA-15 > Al-SBA-15 > SiO₂. One possible reason for this difference was proposed to be the difference in the surface area. The PC yield obtained with unsupported [HEPIm]Br was almost the half of that with the IL supported on SBA-15 ([HEPIm]Br-SBA-15). Thus, the synergistic effect resulting from the presence of silanol is again observed, even though [HEPIm]Br itself has the OH group. Recycling of [HEPIm]Br-SBA-15 was tested seven times. Although the PC yield declined in the first three recycling, the catalyst activity remained unchanged after the fourth run.



Scheme 13. Preparation of immobilized [HEPIm]Br.

ILs can also be immobilized on polystyrene (PS) including soluble and insoluble (cross-linked) ones. One method for the immobilization is the radical copolymerization of 1-vinyl-

3-alkylimidazolium halide with styrene (ST) and/or the cross-linker of divinylbenzene (DVB) using 2,2'-azobis(isobutyronitrile) (AIBN) (Scheme 14-A) [47,48]. Polymerization of vinylpyridine was also reported for the preparation of immobilized pyridinium-based IL (not shown) [49]. Another method to immobilize ILs on PS is the use of chloromethylated PS on which ILs can be immobilized by the reaction between the chloromethyl group and the IL precursor compound (Scheme 14-B) [50,51]. In this method, the quaternization with alkyl halide is also required for the preparation of immobilized imidazolium-based IL. The chloromethylated PS could be prepared by copolymerization of vinylbenzyl chloride (VBC) with ST and/or DVB.



Scheme 14. Methods for the immobilization of ILs on polystyrene.

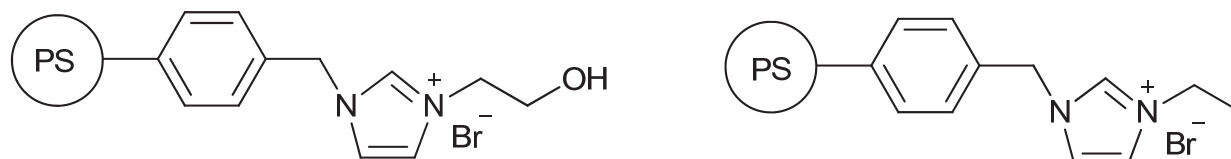
Xie et al. prepared a cross-linked PS supported imidazolium chloride catalyst by copolymerization of 1-vinyl-3-butylimidazolium chloride ([VBIm]Cl) and DVB [47]. This catalyst afforded 98% PC yield at 110°C and CO₂ pressure of 6 MPa for 7 h. The monomer of [VBIm]Cl gave the PC yield of 75%, and the polymer of [VBIm]Cl, which was prepared without the cross-linker DVB, gave 46% yield. The lower yield with [VBIm]Cl was ascribed to the immiscibility of the monomer with the substrate, because the copolymer of [VBIm]Cl and DVB was microparticles, and hence well dispersed in the substrate, resulting in the faster mass transfer. On the other hand, the lower yield of the [VBIm]Cl polymer was explained by insufficient use of the active IL site inside the polymer. Penetration of the substrates inside the polymer might be slow. Thus, using DVB for the mobilization is better to get more active catalyst.

In a similar way, Qiao et al. prepared soluble PS supported [VBIm] salt catalysts by copolymerization of ST and [VBIm] salts [48]. These PS supported IL catalysts were further reacted with ZnBr₂ (ZnBr₂/PS-[VBIm]X, X = Br, Cl, BF₄), to realize the high activity of zinc tetrahalide-base IL (see section 2.1.2.). ZnBr₂/PS-[VBIm]Br showed a high TOF of 3808 h⁻¹ for the reaction of CO₂ and less active epoxide of SO at 110°C and CO₂ pressure of 6 MPa. This value was much faster than those with ZnBr₂/PS-[VBIm]Cl and ZnBr₂/PS-[VBIm]BF₄. Furthermore, the activity of ZnBr₂/PS-[VBIm]Br was almost the same with that of un-immobilized ZnBr₂/[VBIm]Br, because the polymer catalyst was completely dissolved in the

substrate of SO and in the product of SC. Although the miscible nature of the catalyst is disadvantage from the viewpoint of its separation, $ZnBr_2/PS-[VBIm]Br$ was precipitated by addition of ethanol to the reaction mixture after completing the reaction and separated by centrifugation. The catalyst could be recycled without much loss in the activity for four times. Kim et al. also reported the modification of polyvinylpyridine with $ZnBr_2$ [49]. Unfortunately, this polymer catalyst was less effective than homogeneous analogue of $(pyridine)_2ZnBr_2$.

Park et al. investigated the influence of the structure of the polymer on the activity of PS-immobilized IL [50]. They immobilized ammonium-based IL on three types of chloromethylated PS (PS1, PS2, and PS3), and used the immobilized IL catalysts for the reaction of CO_2 and glycidyl methacrylate. PS1 is a soluble copolymer prepared from ST and VBC. Both PS2 and PS3 are the cross-linked (insoluble) copolymers prepared from ST, DVB, and VBC, but the latter had macropores which were generated by addition of isooctyl alcohol to the mixture of ST, DVB and VBC before the copolymerization and the consecutive extraction of the alcohol by methanol after the polymerization. The product yield depended on the structure of the support polymer. It was in the order of $PS1 > PS3 > PS2$, which could be expected by considering the accessibility of the substrates to the IL active site.

Sun et al. reported the use of polymer supported hydroxyl-functionalized IL catalyst for the PC synthesis [51]. They prepared hydroxyethyl imidazolium-based IL immobilized on PS (PS-[HEIm]Br), and the corresponding un-functionalized immobilized IL (PS-[EIm]Br) for comparison (Scheme 15). An excellent PC yield of 98% was obtained with PS-[HEIm]Br at $120^\circ C$ and CO_2 pressure of 2.5 MPa for 4 h, while that with PS-[EIm]Br was a lower value of 64%. Thus, introducing the OH group is effective for the CO_2 cycloaddition reaction even for the polymer immobilized IL system.

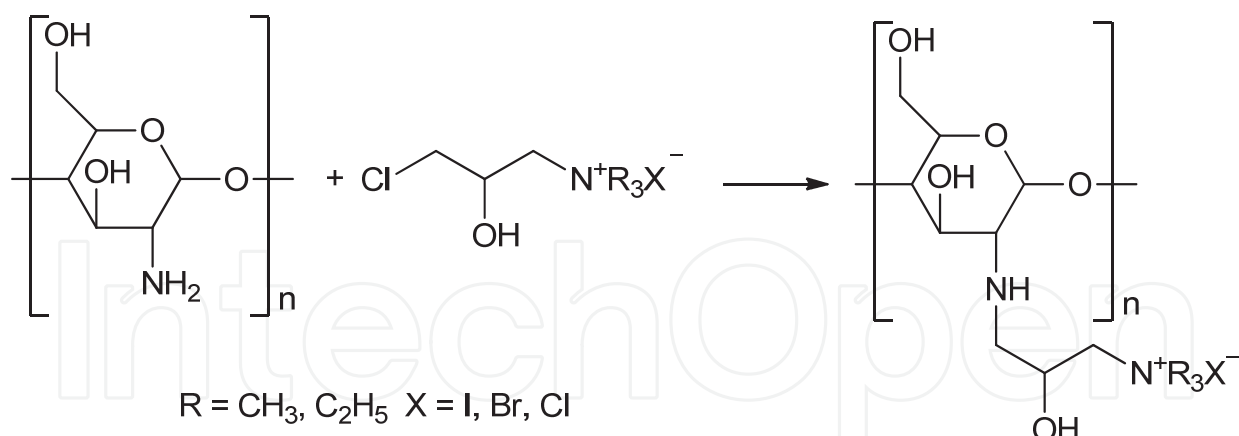


Scheme 15. Hydroxyl-functionalized and un-functionalized ILs immobilized on PS.

Zhao et al. first reported that a biopolymer of chitosan can also be employed for the immobilization of IL [52]. They immobilized ammonium salts on chitosan (CS-[R_3N]X) via the reaction between the amino group attached to the six-membered ring of chitosan and corresponding chloroisopropyl-trialkyl ammonium salts (Scheme 16). Interestingly, CS-[Me_3N]Cl revealed high activity for the PC synthesis, although the corresponding homogenous ammonium salt of [Me_4N]Cl produced only a trace amount of PC. This promotional effect by the immobilization was ascribed to the presence of the OH group of the ring; however, such effect was absent, when triethyl ammonium chloride was used instead of trimethyl one. Thus, the reason of the synergetic effect was still unknown.

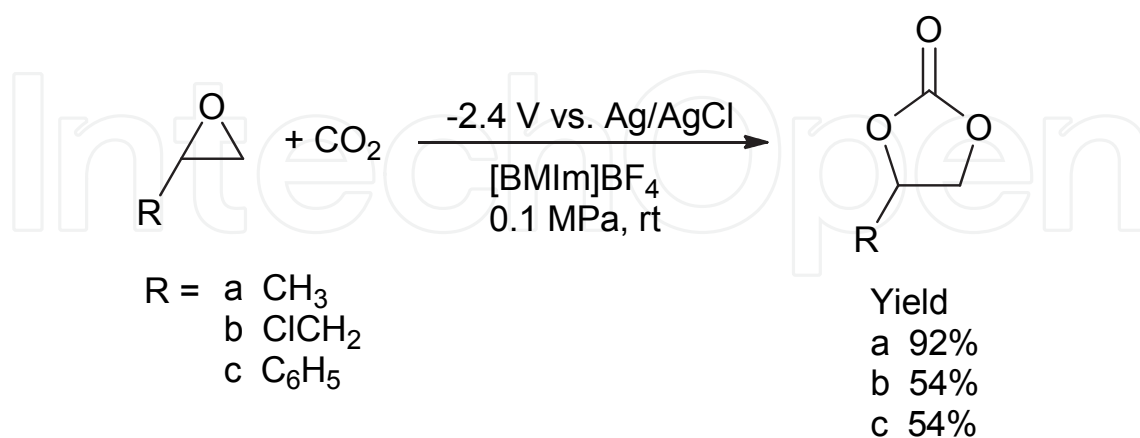
2.2 Electrochemical synthesis of cyclic carbonates

Electrochemical synthesis of cyclic carbonates from CO_2 with epoxides, anilines, alcohols, and glycols was reported [53–60]. For example, Duñach et al. [54] conducted the reaction of epoxides with CO_2 to the corresponding cyclic carbonates by an electrochemical method in the presence of nickel(II) complexes. In these methods, harmful organic solvents, supporting



Scheme 16. Preparation of chitosan-immobilized ammonium ILs.

electrolytes, and/or catalysts were necessarily used, making the reaction systems complicated. Ionic liquids, because of their high ionic conductivities, wide electrochemical windows, and miscibility with many gaseous substrates, should be an effective medium for electrocatalytic organic synthesis from CO₂. Deng et al. [61,62] reported the first use of pure ILs as reaction media in the electrochemical activation of CO₂ for the synthesis of cyclic carbonates from several epoxides under mild conditions (Scheme 17). They tested different kinds of ILs including cations of [BMIm]⁺, [EMIm]⁺, [BPy]⁺ and anions of BF₄⁻, PF₆⁻. [BMIm]BF₄ was the best catalyst, giving conversions of 92% and 54% with 100% selectivity for PO and epichlorohydrin, respectively, at room temperature. For SO, a high conversion of 78% was obtained but the selectivity was 69% with a byproduct of benzylacetaldehyde. [EMIm]BF₄ and [BMim]PF₆ showed lower total conversions but the selectivity values remained almost unchanged. These results indicate that the activity of ILs depends on both cation and anion and the rate of conversion and the product selectivity also change with the structure of epoxide. It is noted that harmful organic solvent, additional supporting electrolyte, and catalyst were not used in these electrochemical reaction systems.



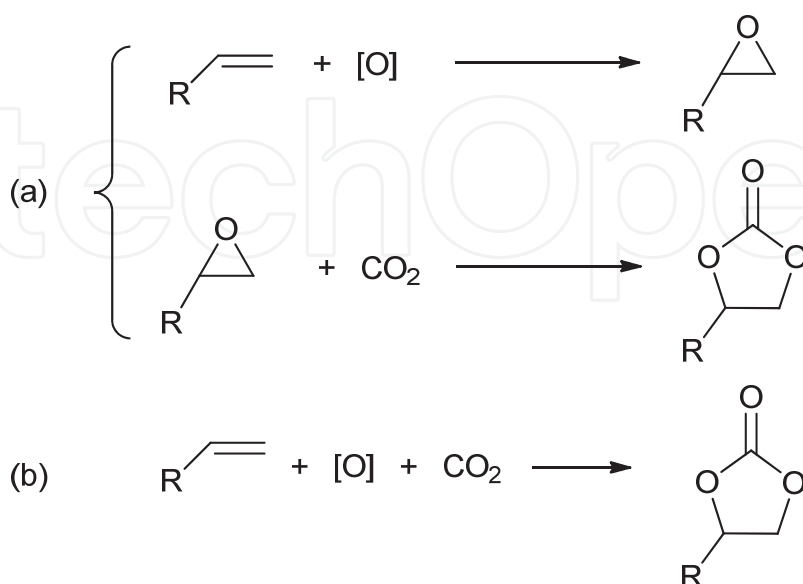
Scheme 17. Electrochemical cycloaddition of CO₂ to epoxides forming cyclic carbonates in the presence of IL.

Jiang et al. used a 0.05 M solution of [Bu₄N]Br in dimethylformamide (DMF) as electrolyte for the synthesis of cyclic carbonates at ambient temperature and at 4.0 MPa CO₂ [63]. The

effects of such key factors as electrode materials, supporting electrolyte, CO₂ pressure, and solvent on the electrochemical synthesis of cyclic carbonates were investigated. The best results with PO were obtained with an aluminium anode and a platinum cathode (98% yield) or a zinc anode with a platinum cathode (95%). Lower, but still reasonable, yields were obtained when the aluminium anode was used with either copper, nickel or brass cathode (67–77%). Other terminal epoxides also showed moderate to high yields of 65–98% to the corresponding cyclic carbonates under the same conditions. In those reactions [Bu₄N]Br acts as supporting electrolyte and catalyst. Similar work on electrocatalytic synthesis of PC was reported using ILs/DMF mixed solvents with Mg as a sacrificial anode [64]. It was also confirmed that the ILs including Br⁻ showing higher nucleophilicity were the best supporting electrolytes.

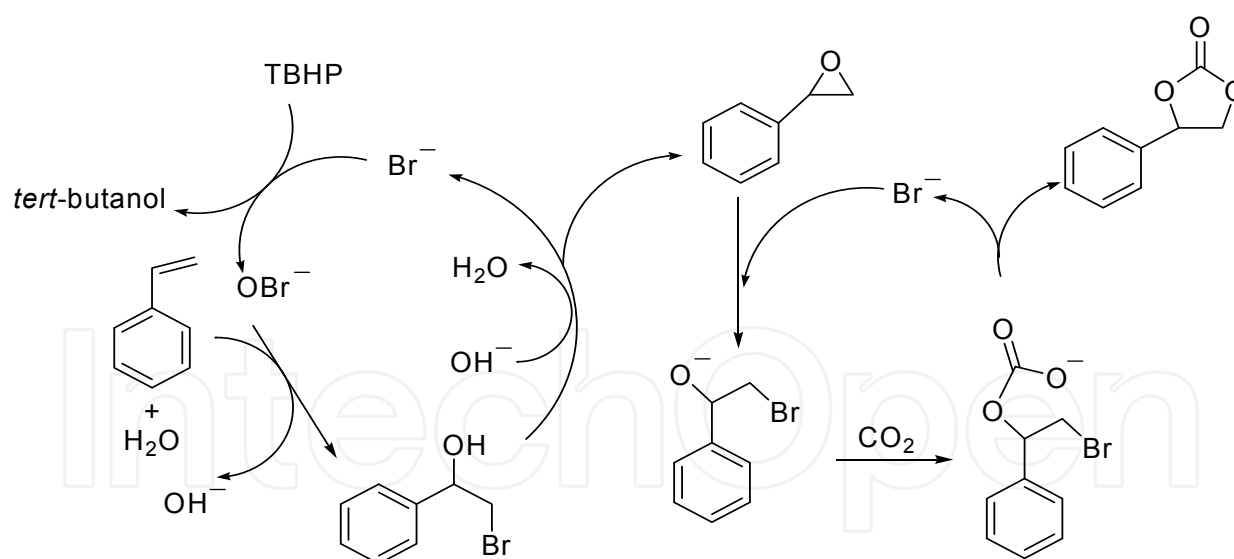
2.3 Synthesis of cyclic carbonates by oxidative carboxylation

Currently cyclic carbonates are extensively synthesized by CO₂ cycloaddition to epoxides, which has been commercialized. Although the above synthetic approach is quite atom-efficient, such a reaction usually requires the initial synthesis of epoxides; an additional step sometimes involves the use of expensive or toxic reagents and requires chemical separations [65]. Therefore, the direct synthesis of cyclic carbonates from olefins instead of epoxides, a so-called one-pot “oxidative carboxylation” of olefins, would be appealing. The oxidative carboxylation synthesis from olefins can be roughly viewed as the coupling of two sequential processes of epoxidation of olefins and CO₂ cycloaddition to epoxides formed (Scheme 18). The reaction uses easily available and low-priced chemicals of olefins as substrates and, moreover, preliminary synthesis and separation of epoxides would be avoided. So, the oxidative carboxylation would be a simpler and cheaper carbonate synthesis process with industrial potential from environmental and economic points of view. Although the three-component couplings have been known at least since 1962 [66], up to date, only a few works have been made on these reactions in contrast to extensive studies on the addition reactions of CO₂ to epoxides in ILs as catalyst/or solvent.



Scheme 18. (a) Two-steps and (b) one-step synthesis of cyclic carbonates from olefins. [O] = oxidant.

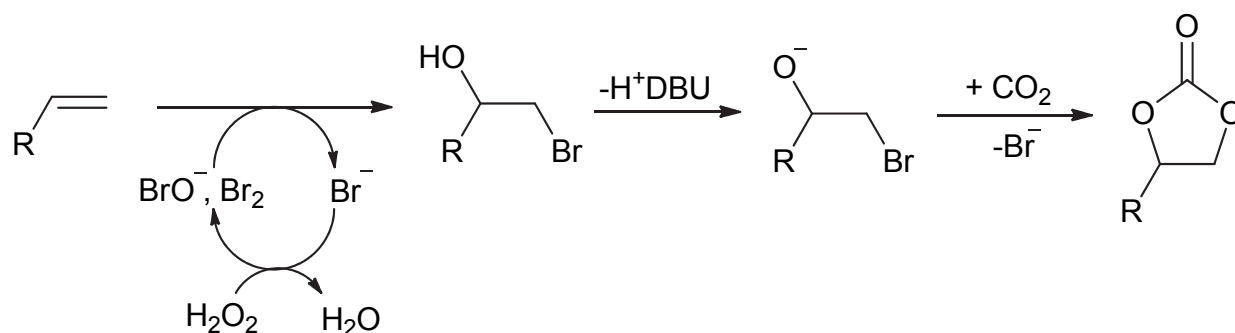
Our group reported the first example of direct oxidative carboxylation of styrene (ST) to SC in the presence of ionic liquid catalyst and an aqueous solution of *tert*-butyl hydroperoxide (TBHP) as an oxidant [67–69]. In this reaction system, ILs acted both as catalyst and solvent and no additional solvent was used. It was found that the structure of ILs and the nucleophilicity of anions strongly affected the yield of SC. [BMIm]BF₄, [BMIm]PF₆, and [EMIm]BF₄ were inactive, whereas [Bu₄N]X (X = Cl, Br, I) was effective to the synthesis of SC, which could be ascribed to the differences in the structure and solubility of ILs [67]. With quaternary ammonium salt catalysts, the carbonate yield was improved with the increase in alkyl chain lengths [69]. For example, the yield of SC was only 10% with a large amount of styrene oxide intermediates in the presence of [Me₄N]Br catalyst. However, the SC yield was improved to 38% with [Bu₄N]Br having a longer alkyl chain. Moreover, the effectiveness of counter anion appeared in the order of [Bu₄N]Br > [Bu₄N]I > [Bu₄N]Cl. Although the nucleophilicity of iodide anion was stronger than that of bromide anion, the stronger reductive property of iodine anion led to its decrease in activity in the presence of the oxidant. Furthermore, CO₂ pressure played a crucial role in obtaining the high yield of SC. The change of the SC yield with the pressure was complicated; it was maximized at 1 MPa, 8 MPa and 15 MPa, which was discussed on the basis of the phase behavior of the multiphase reaction system [68]. Under mild reaction conditions (1 MPa CO₂, 80°C, 6 h), SC was obtained in a yield of 38%. Scheme 19 illustrates the proposed reaction mechanism, in which hypobromite (OBr⁻) and bromide ion (Br⁻) catalyze the epoxidation reaction and CO₂ cycloaddition reaction, respectively. The formation of SO intermediate was observed in this catalytic system.



Scheme 19. A proposed reaction mechanism for one-pot synthesis of SC from styrene in the presence of Bu₄NBr.

Later on, Eghbali and Li investigated the direct conversion of alkenes and CO₂ into cyclic carbonates with hydrogen peroxide catalyzed by [Bu₄N]Br in water [70]. They used a certain amount of such an organic base as 1,8-diazabicyclo[5.4.0] undec-7-ene (DBU) as a “CO₂ activator”, which was considered to deprotonate the weakly acidic alcohol and neutralized hydrobromic acid formed. For ST, a good SC yield of 70% was obtained at a total olefin

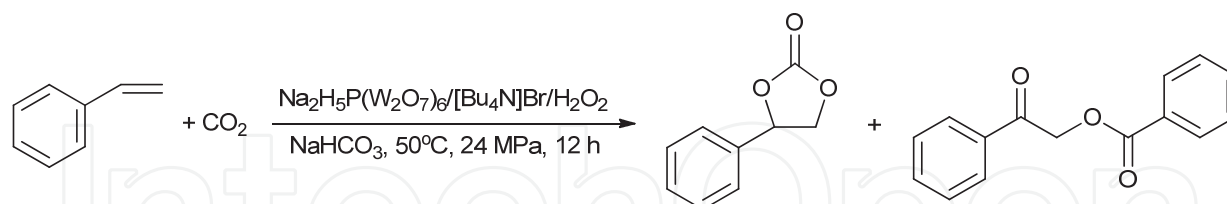
conversion of 89% in the presence of $[\text{Bu}_4\text{N}]\text{Br}$ and DBU at about 50°C and around 20 MPa CO_2 for 15 h. A water-soluble substrate, $4\text{-SO}_3\text{C}_6\text{H}_5\text{-CHCH}_2$, gave a better yield of the desired carbonate product of 89% at a total conversion of 98% under the same conditions. Because catalytic amounts of *N*-bromosuccinimide and NaBr (both are bromide ion sources) also gave moderate SC yields, the presence of bromide ions were suggested to be important for the reaction. It was speculated that the bromide ion could be readily oxidized to bromine or hypobromous acid, a reagent known to react with olefins in water to form the bromohydrin [71]. Indeed, styrene bromohydrin was formed with 8% yield in the case of SC synthesis under the conditions described above. After the formation of the bromohydrin intermediate and its subsequent reaction with CO_2 , the bromide ions were regenerated, leaving water as the only byproduct. Bromohydrin would be assumed to be a crucial intermediate from an olefin, thereby leading to the formation of cyclic carbonate. After the in situ generation of the “bromohydrin” intermediate, the product was formed by attacking by base and the reaction with CO_2 (Scheme 20), which could avoid the preparation of epoxide. This method was also applicable for other alkenes; for example, 1-hexene and 1-octene were also effectively converted to the corresponding carbonates in 47% and 27% yields at temperatures of $45\text{--}55^\circ\text{C}$ in 20 h. The ratio of reagents, particularly $\text{Br}^-/\text{H}_2\text{O}_2$, was found to be important for the reaction because bromide ion can catalyze the unwanted and non-productive decomposition of hydrogen peroxide to generate O_2 and water. An aqueous solution of sodium persulfate was also used as the oxidant but less effective compared to hydrogen peroxide.



Scheme 20. Bromine-catalyzed direct conversion of alkenes to cyclic carbonates with H_2O_2 .

Following the “bromohydrin” intermediate principle for the synthesis of cyclic carbonates via oxidative carboxylation [70], He and coworkers [72] developed a binary catalyst system composed of sodium phosphotungstate and $[\text{Bu}_4\text{N}]\text{Br}$ for facile synthesis of cyclic carbonates in a single operation from alkenes and CO_2 with an inorganic base (Scheme 21). The direct synthesis of cyclic carbonate was conducted through in situ generation of “bromohydrin” intermediate with Bu_4NBr and H_2O_2 catalyzed by the phosphotungstate, followed by its subsequent reaction with CO_2 in the presence of the base acting as a “deprotonation reagent”. Indeed, the key intermediate 2-bromo-1-phenylethanol was isolated in 16% yield in the absence of any base. The presence of a base as “deprotonation reagent” markedly improved the formation of SC; a SC yield of 57% was achieved with phenacyl benzoate in 14% yield under mild reaction conditions (50°C , 2.4 MPa, in aqueous medium). Interestingly, by subtly tuning the quantities of CO_2 and H_2O_2 , the selective formation of phenacyl benzoate and cyclic carbonate could be controlled. Phenacyl benzoate, which is also an important intermediate and reagent in organic synthesis, could be

obtained in good yields directly from ST in the absence of CO₂. This methodology was also applicable to several styrene derivatives producing the corresponding cyclic carbonates.



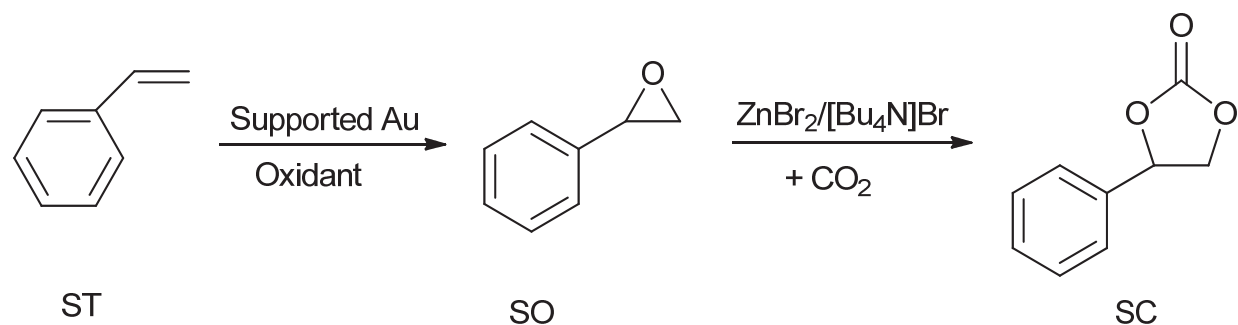
Scheme 21. A direct synthesis of SC from ST and CO₂ through “oxybromine” in situ generated.

The oxidative carboxylation of olefins to cyclic carbonates can proceed through the first step of epoxidation of olefins and the subsequent cycloaddition of CO₂ to epoxides formed (Scheme 18). Thus it is supposed that a system of combining catalysts effective for the first step and for the second one would be effective for the direct synthesis of cyclic carbonates via the oxidative carboxylation of olefins. Indeed the direct preparation of carbonates was successfully achieved with a few catalyst systems including ILs coupled with oxidation catalysts. One patent [66] reported that the cyclic carbonate was formed from an olefin, CO₂, and oxygen in the presence of dual catalysts. The catalyst system includes a heavy metal compound and a quaternary ammonium hydroxide or halide. However, the heavy metal compounds would easily induce the corrosion of equipments and result in the undesired reduction of activity and selectivity.

Our group reported that ZnBr₂/[Bu₄N]X catalysts showed excellent activity and selectivity for CO₂ coupling with SO, as mentioned in section 2-1 [18,19]. By combining ZnBr₂/[Bu₄N]X with such an epoxidation catalyst as Au/SiO₂, the resultant three-component catalysts were efficiently applied for the direct oxidative carboxylation of ST to SC [73]. With Au/SiO₂-ZnBr₂/Bu₄NBr catalyst, the highest carbonate yield of 45% was obtained at 80°C and at 1 MPa CO₂ for 4 h with cumene hydroperoxide (CHP) as an oxidant. The influence of oxidants used was obvious and anhydrous TBHP and CHP were more active than aqueous TBHP, indicating that the water contained in the oxidant was detrimental to the carbonate synthesis. The lower activity with aqueous TBHP was possibly due to hydrolysis of epoxide to phenyl glycol, which would decrease the quantity of the starting material for the second step of carbonate synthesis. One of the authors further studied the influence of the support on the catalytic performance of Au nanoparticles [74]. With Au/Fe(OH)₃ and the ZnBr₂/Bu₄NBr catalyst, a SC yield of 53% was obtained at 80°C and at 4 MPa CO₂ in 10 h. The reaction pathways were postulated as illustrated in Scheme 22 in which the supported Au was active for the epoxidation step, while ZnBr₂/Bu₄NBr cooperatively catalyzed the subsequent step of CO₂ cycloaddition to epoxide formed. Furthermore, the epoxidation reaction was the rate-determining step in the one-pot oxidative carboxylation synthesis of cyclic carbonate, and the efficiency of the one-pot carbonate synthesis would be determined by the catalytic performance of the epoxidation catalyst. Hence, if we could explore more active and selective catalysts for the epoxidation reaction, more effective catalyst systems would be realized for the direct one-pot carbonate synthesis via the oxidative carboxylation from olefins.

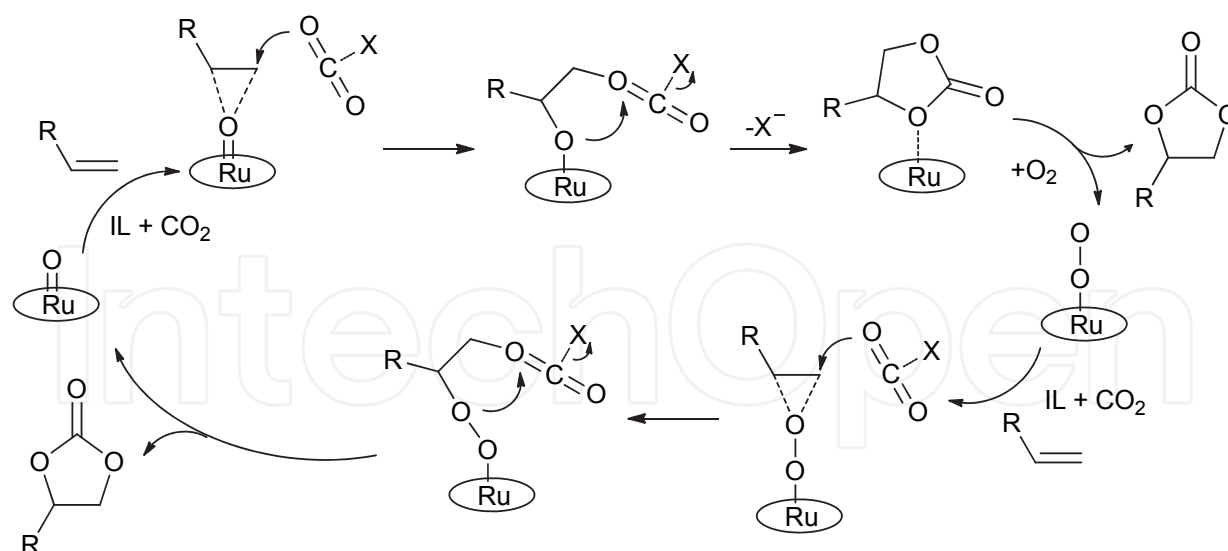
Yokoyama et al. [75] further examined the combination of an epoxidation catalyst system of MTO/UHP/[BMIm]BF₄ (MTO, methyltrioxorhenium; UHP, urea hydrogen peroxide) [76]

and a CO₂ cycloaddition catalyst of [EMIm]₂ZnBr₄ [15] for the one-pot synthesis of SC from ST. The epoxidation catalyst system of MTO/UHP/[BMIm]BF₄ offered a high SO yield of 93% at a ST conversion of 95% at 30°C in 2 h with a UHP/ST ratio of 1.1 in the absence of CO₂. This PO yield was decreased to 71% by the presence of 3 MPa CO₂, revealing the negative effect of CO₂ on the epoxidation reaction. It was also found that, in the presence of peroxide, Zn[EMIm]₂Br₄ was instable and hence not effective for the CO₂ cycloaddition, although it was reported to be very active for this reaction in the absence of peroxide. Based on these results, they employed multistep protocol for the one-pot synthesis of SC. In this method, after the epoxidation reaction was completed with MTO/UHP/[BMIm]BF₄ at 30°C in 2 h, CO₂ and Zn[EMIm]₂Br₄ were charged into the same reactor, and then the CO₂ cycloaddition to SO produced was carried out for 2 h at an elevated temperature (80 or 110°C). This change in the operation improved the SC yield to 83% (at 110°C and 3 MPa CO₂ for the second step), being much higher than previously reported results. Other improvements such as better utilization of oxidant, easy separation of the product, and reusability of reaction medium could also be achieved through this method.



Scheme 22. Reaction pathways for the direct synthesis of SC from ST.

From the viewpoint of the cost, the use of molecular oxygen for the oxidative carboxylation is more preferable than hydrogen peroxide and organic peroxides. Aresta et al. [77,78] first reported the use of molecular oxygen for the one-pot synthesis of SC from ST with Rh complexes, which, however, suffered from short lifetime and low SC yields. Recently, Bai and Jiang [79] developed a catalyst system of Ru(TPP)(O)₂ (dioxo(tetraphenylporphyrinato)ruthenium) and [Bu₄N]I for the carbonate formation from olefin, O₂ and CO₂, following the result that ruthenium porphyrin complexes can catalyze the epoxidation. SC was obtained in 76% yield with 100% selectivity using 4 mol% of Ru(TPP)(O)₂/[Bu₄N]I at 30°C and low pressure (0.5 MPa O₂ and 1.1 MPa CO₂) for 48 h, which was the first example of 100% selectivity to SC with homogeneous catalyst. The molar ratio of Ru(TPP)(O)₂/[Bu₄N]I was an important factor determining the catalyst activity. An SC yield of 76% was obtained at the ratio of 2. Larger or smaller ratio decreased the SC yield. The reactions of other olefins were also tested using [Bu₄N]I or PTAT (phenyltrimethylammonium tribromide). Interestingly, [Bu₄N]I gave a good yield of cyclic carbonate from chloropropylene, but poor yields from hexane, octane, cyclohexene, and cyclooctene. In contrast, PTAT gave good yields from the latter four olefins, but poor yield from the first olefin. Scheme 23 depicts the possible mechanism proposed by those authors in which the participation of two-type oxoruthenium complexes and the activation of CO₂ by the anion of IL are involved.



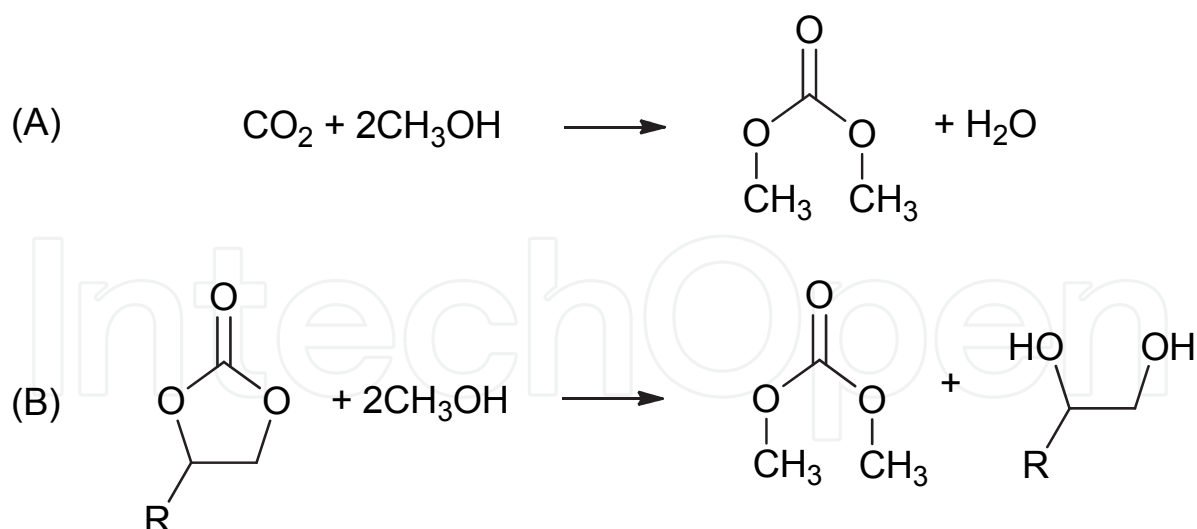
Scheme 23. Proposed mechanism of aerobic oxidative carboxylation of olefins catalyzed by $\text{Ru}(\text{TPP})(\text{O})_2/\text{IL}$. $\text{X} = \text{I}^-, \text{Br}^-$

3. Synthesis of dimethyl carbonate (DMC) in/by IL

Dimethyl carbonate (DMC) has been drawing much attention as a safe, non-corrosive, and environmentally friendly building block for the production of polycarbonate as well as useful methylating and methoxycarbonylating agents replacing toxic phosgene, dimethyl sulfate, and methyl iodide [80,81]. And DMC is also of interest as an additive to fuel oil replacing methyl *tert*-butyl ether to meet the oxygenate specifications, owing to a high octane number, reducing particulate emission from diesel engines [81–83]. In addition, it has been used as an electrolyte in lithium batteries due to its high dielectric constant [81,84]. DMC is industrially synthesized by the phosgenation of methanol, by the oxidative carbonylation of methanol using CO and O₂ with copper (II) and/or palladium (II) as catalyst, and by the reaction of CO and methyl nitrite [80,85,86]. These routes suffer from a low production rate, need for corrosion resistant reactors, and toxicity of phosgene and CO, and potential explosive hazard in the case of oxidative carbonylation. As the requirement of green chemistry, the utilization of CO₂ as a readily available, inexpensive, nonflammable, and environmentally acceptable starting material for DMC synthesis has been attempted. For this, two reactions are known. One is (A) direct synthesis of DMC from CO₂ and methanol, and the other one is (B) the transesterification of cyclic carbonate with methanol (Scheme 24). The latter can be called as an indirect synthesis of DMC from CO₂, because the cyclic carbonate can be produced from CO₂ and epoxide, as described in the earlier section. Some examples of these reactions using ILs will be given in this section.

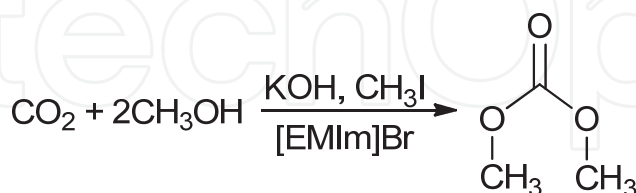
3.1 Direct synthesis of DMC from methanol and CO₂

For the synthesis of DMC from methanol and CO₂, several metal complexes, metal oxides, and metal halides are known as effective catalysts. These catalysts generally require reaction temperatures around 150°C or higher [81]. Alkali salts can also catalyze the reaction in the presence of CH₃I as a reaction promoter [87,88]. With these catalysts, the required reaction temperatures were rather lower.



Scheme 24. Synthesis of DMC (A) from CO_2 and methanol, and (B) by the transesterification of cyclic carbonate with methanol.

To our knowledge, there is only one paper reporting the use of IL for the direct synthesis of DMC, which was published by Wang et al. [89]. They studied the effects of the presence of [EMIm]Br on the synthesis of DMC using the catalyst of KOH and the promoter of CH_3I (Scheme 25). Without [EMIm]Br, the DMC yield was 8.5% in the presence of 55 mmol KOH and 48 mmol CH_3I (methanol 850 mmol) at CO_2 pressure of 2 MPa. The yield was gradually increased to 11% by adding [EMIm]Br into the reaction system up to 21 mmol. With further increase of the IL amount, however, the DMC yield remained unchanged. They proposed that the promotional effect of the IL may be ascribed to the strong polarity and electrostatic field of the IL, which may stabilize the charged intermediate. Effects of the amounts of KOH and CH_3I and of CO_2 pressure were also investigated. Interestingly, as the CO_2 pressure was raised, the DMC formation showed two maxima near 2.0 MPa and 7.3 MPa. This trend is similar to that reported in our previous work [88], in which two maxima of the DMC yield were observed near 4.5 and 8.0 MPa in the presence of K_2CO_3 as the catalyst. Thus, the high CO_2 pressures were not required for the DMC formation and supercritical conditions were detrimental for the reaction.

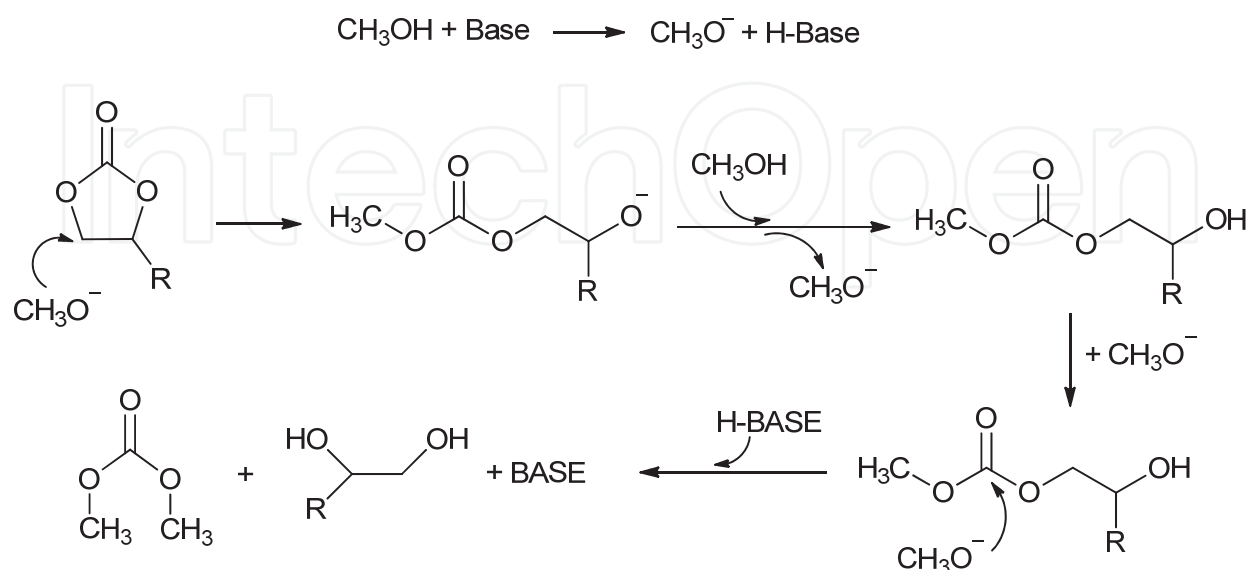


Scheme 25. Direct synthesis of DMC from CO_2 and methanol catalyzed by KOH.

3.2 DMC synthesis via transesterification of cyclic carbonate with methanol

The above mentioned direct synthesis of DMC requires organic or inorganic dehydration reagents to get high DMC yields because of the reaction equilibrium. On the other hand, the transesterification of cyclic carbonate with methanol relatively easily gives high DMC yields. ILs can also be used as the catalysts for this reaction. Scheme 26 illustrates the generally accepted reaction mechanism for the base catalyzed transesterification of

methanol with cyclic carbonate. A methoxy anion produced from methanol reacts with the cyclic carbonate, producing an intermediate species of methyl-hydroxyalkyl carbonate. This species further reacts with another methoxy anion molecule, producing DMC and glycol.



Scheme 26. Generally accepted reaction mechanism for the base catalyzed transesterification of methanol with cyclic carbonate.

Park's group did thorough investigation of the synthesis of DMC through transesterification using homogenous and heterogeneous IL catalysts [90–96]. At first, they used several tetraalkyl ammonium salts of $[(\text{C}_n\text{H}_{2n+1})_4\text{N}]\text{X}$ ($n = 3, 4, 6, 8, 12$; $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-$) for the reaction of methanol and PC ($\text{R} = \text{CH}_3$ in Scheme 24-B) in the presence of pressurized CO_2 [90]. The presence of CO_2 was required to prevent the undesired decomposition of PC to PO and CO_2 . The PC conversion increases with the increase of alkyl chain length of IL, resulting from that bulkier ammonium ion makes the halide ion away from the cation easier, and, hence, more nucleophilic. The type of the halide anion also affected the activity of IL. The PC conversion was in the order of $\text{Cl}^- > \text{Br}^- > \text{I}^-$. This order is different from that observed for the cycloaddition of CO_2 to epoxide (see the section 2). The selectivity to DMC was slightly changed by the IL catalysts. Those values were around 75 %, although the authors did not mention what was the by-product, and the highest one was obtained with $[\text{Bu}_4\text{N}]\text{Cl}$. Consequently, this IL gave the highest DMC yield of 48% at 140°C for 6 h.

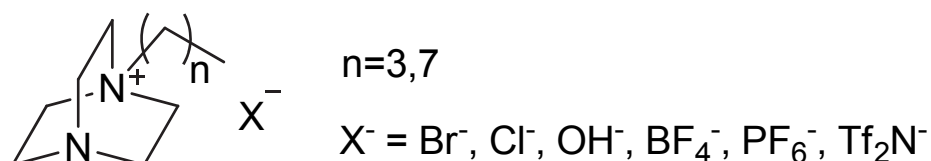
They also examined the use of a series of imidazolium-based ILs consisting of cations of $[\text{EMIm}]^+$, $[\text{BMIm}]^+$, $[\text{HMIm}]^+$ and $[\text{OMIm}]^+$, and of anions of Cl^- , BF_4^- and PF_6^- [91,92]. The DMC yield from the reaction of methanol and EC ($\text{R} = \text{H}$ in Scheme 24-B) was in the orders of $[\text{EMIm}]^+ > [\text{BMIm}]^+ > [\text{HMIm}]^+ > [\text{OMIm}]^+$, and of $\text{Cl}^- > \text{BF}_4^- > \text{PF}_6^-$ [91]. The most active IL of $[\text{EMIm}]\text{Cl}$ gave the largest DMC yield of 76% at 140°C for 6 h. The difference in the DMC yield by the alkyl chain length was ascribed to that in the solubility of ILs. IL having shorter alkyl chain is more soluble to methanol. The same orders of the DMC yield were observed for the reaction of methanol and PC [92]. However, the selectivity to DMC was significantly different by the type of the cyclic carbonate used. The selectivity values for DMC from EC were higher than 90%, while those from PC were in a range between 21 and 67%. Furthermore, the latter values were lower than those obtained with the above mentioned ammonium ILs. The conversions of PC obtained with the imidazolium ILs were

also lower than those with the ammonium ILs. Thus, the imidazolium ILs were less effective than the ammonium ILs; however, the authors claimed that the former ILs are more thermally stable than the latter ones at high reaction temperatures. Kinetic studies indicated that the reaction rate was pseudo first order with respect to the concentration of EC or PC.

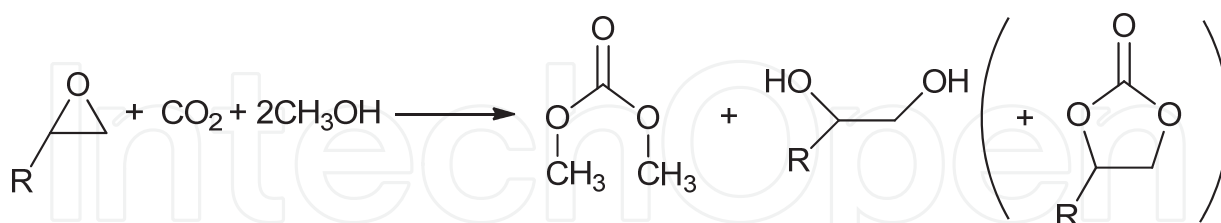
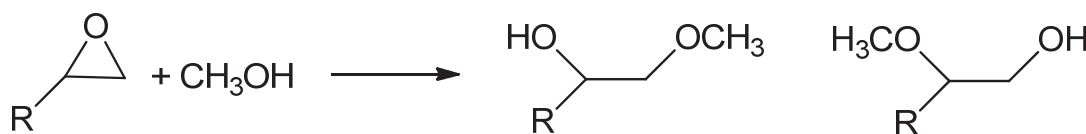
They further investigated the reaction of EC and methanol under microwave heating using the catalysts of imidazolium-based and ammonium-based ILs [93]. Reaction experiments carried out for various periods of reaction time revealed that a high DMC yield with high selectivity was achieved in a short reaction time of 15 min. After that, the increase in the DMC yield was marginal, while the EC conversion increased gradually because of its decomposition. The optimum microwave power was in a range between 200 and 300 W. Under microwave irradiation at 500 W, the DMC yield was significantly decreased. The EC conversion was in the order of $[\text{HMIm}]^+ > [\text{BMIm}]^+ > [\text{OMIm}]^+ > [\text{EMIm}]^+$, being different from the order observed with the conventional heating. On the other hand, when the ammonium ILs were used for the reaction, the EC conversion increased with increasing the alkyl chain length of the ammonium IL up to C_6 , being consistent with the result obtained under the conventional heating. Thus, the influence of the catalyst structure on the reaction is different by the heating mode only for the imidazolium ILs. In most cases, the temperature of the reaction mixture reached around 120°C within 5 min under the microwave irradiation at 100 W. Under this irradiation condition, $[\text{BMIm}]\text{Br}$ gave a DMC yield of 57%. Under the conventional heating, however, the same IL catalyst required a longer reaction time than 6 h to get the same yield. Thus, the activity of the IL is much better under the microwave irradiation. The reason of this was proposed to be rapid polarization of ionic species (the catalyst, the substrate, and the intermediates).

The same group also carried out the reaction of EC and methanol using imidazolium-based ILs and ammonium-based ILs covalently immobilized on amorphous silica [94,95] and on MCM-41, respectively (see section 2.1.3.) [96]. To get similar conversion levels, the immobilized IL needed slightly higher reaction temperatures than corresponding homogeneous ILs. The immobilized IL catalysts could be reused up to three consecutive runs without any considerable loss of their initial activity or with only a slight loss in the activity and the selectivity to DMC.

Another example of the DMC synthesis by the transesterification reaction of EC with methanol was recently reported by He and co-workers [97]. They developed DABCO-based (1,4-diazabicyclo[2.2.2]octane) Lewis basic ILs (Scheme 27). The prepared DABCO-based ILs were active under mild conditions. They could catalyze the reaction even at 80°C , which was much lower than the temperatures required for the above mentioned ammonium- and imidazolium-based ILs. The catalytic efficiency increased in the order of $\text{Cl}^- < \text{Br}^- < \text{OH}^-$ ($n=3$). $[\text{C}_4\text{DABCO}]\text{OH}$ gave a DMC yield of 81% with 90% selectivity at 80°C for 6 h. This IL catalyst could be recovered after separation of DMC and ethylene glycol (EG) from the reaction mixture by distillation and reused for four times without loss in either DMC yield or selectivity. Furthermore, in comparison with the common basic catalysts, $[\text{C}_4\text{DABCO}]\text{OH}$ showed higher activity than $\text{N}^+(\text{CH}_3)_3\text{HO}$ -functionalized PS, $[\text{BMIm}]\text{Br}$ and $[\text{Me}_4\text{N}]\text{Br}$. Although DABCO itself and NaOH showed higher catalytic activity for the reaction, but these catalysts were hardly recyclable. The authors suggested that it could effectively activate methanol through tertiary nitrogen in the cation part of the IL in combination with hydroxide anion, producing methoxy anion.

Scheme 27. DABCO-based IL of $[C_{n+1}DABCO]$.

By combining the CO_2 cycloaddition to epoxide and the transesterification of cyclic carbonate with methanol, one-pot synthesis of DMC from epoxide, CO_2 and methanol is possible (Scheme 28). He and co-workers conducted the one-pot synthesis of DMC from SO ($R = C_6H_5$ in Scheme 28), CO_2 and methanol using a mixed catalyst system of $[Bu_4N]Br/Bu_3N$ [98]. This catalyst system gave an SO conversion of 98% and a DMC yield of 84% at $150^\circ C$ and 15 MPa CO_2 for 8 h. It should be noted that the selectivity for the methanolysis of epoxide (Scheme 29), which is sometimes problematic for the one-pot synthesis [99,100], was very low with this catalyst. The time course of the reaction clearly showed that DMC was formed through the formation of SC. The optimum CO_2 pressure was 15 MPa for this catalyst system. At lower pressures, the SO conversions were lower probably because of slower rate of the CO_2 cycloaddition step. At higher pressures, the conversion of SO was high, but the selectivity to DMC was lower because of the suppression of the transesterification of SC formed. The activities of either $[Bu_4N]Br$ or Bu_3N were evaluated for the CO_2 cycloaddition, the transesterification reaction, and the one-pot reaction. $[Bu_4N]Br$ was very active for the CO_2 cycloaddition, but inactive for the transesterification. On the other hand, Bu_3N had low activity for the former reaction, while significant activity for the latter one. Based on these results, the authors proposed a reaction mechanism, in which the CO_2 cycloaddition and the transesterification are catalyzed by $[Bu_4N]Br$ and Bu_3N , respectively. They also suggested that the interaction of CO_2 with the amine caused the suppression of the transesterification at higher pressure than 15 MPa. Probably, CO_2 converted the amine to inactive carbamate species, although it was not stated.

Scheme 28. One-pot synthesis of DMC from epoxide, CO_2 and methanol.

Scheme 29. Methanolysis of epoxide.

At almost the same time, Chen et al. reported a similar catalyst system of $[BMIm]BF_4/CH_3ONa$ for the reaction of PO ($R = CH_3$ in Scheme 6), CO_2 and methanol [101].

This catalyst system gave PO conversion and DMC yield of 96% and 53%, respectively, under the conditions of 4 MPa, 150°C, and 5 h. Unfortunately, the selectivity for the methanolysis products was 19% with this reaction system, probably because of the nature of both the catalyst and the epoxide. When only CH₃ONa was used, the PO conversion, the DMC yield, and the selectivity for the methanolysis were changed to 96%, 30%, and 29%, respectively. Thus, there is some synergistic effect between [BMIm]BF₄/CH₃ONa. The ratio of [BMIm]BF₄/CH₃ONa was also important. With the ratio of 1:1 by weight, the DMC yield was 56%. Increasing only the amount of [BMIm]BF₄ three times resulted in the improvement of the DMC yield to 68%. However, further increase in this amount caused decrease of the DMC yield to below 20%. The amount of [BMIm]BF₄ had little effect on the conversion of PO. It was also observed that the DMC yield increased with the increase in CO₂ pressure, reached a maximum at 4 MPa, and then decreased when the CO₂ pressure was further increased. Too high CO₂ pressure again suppressed the transesterification reaction.

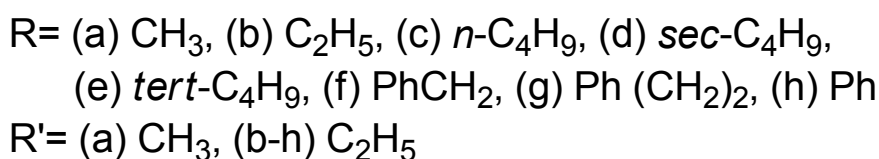
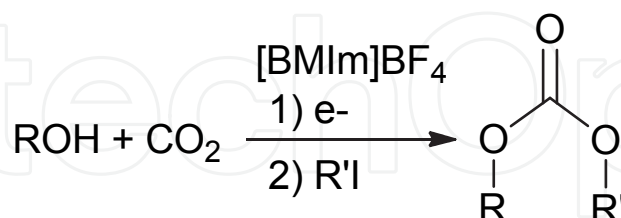
3.3 Electrochemical synthesis of DMC

Section 2.2. mentioned electrochemical synthesis of cyclic carbonate from CO₂ and epoxide. Electrochemical synthesis of DMC from CO₂ and methanol is also possible. Lu et al. used an electrochemical procedure for the synthesis of various dialkyl carbonates from CO₂ and alcohols in CO₂-saturated [BMIm]BF₄ solution (Scheme 30) [102]. Cyclic voltammetry of CO₂ in [BMIm]BF₄ with a Ti, Cu, Ni or Ag cathode and a Mg anode showed that [BMIm]BF₄ could act as a medium for CO₂ reduction, and the CO₂ reduction was the easiest on the Cu cathode. It was also found that the reduction of CO₂ in the IL was easier than that in organic solvents. The easiness of the CO₂ reduction was suggested to result from stabilization of CO₂ anion radical by the ion-pairing with [BMIm] cation. For the synthesis of dialkyl carbonate, the electrolyses in the IL using the Cu cathode and the Mg anode was first performed under an atmospheric CO₂ stream. At the end of the electrolyses, alcohol was added to the IL and the solution was kept for 1 h under stirring. Then, alkyl iodide was further added to the solution and the mixture was stirred for 5 h. By this protocol, the primary and secondary alcohols were converted to dialkyl carbonates in good yields, whereas tertiary alcohol and phenol were unreactive. Effects of temperature, alcohol concentration, and the charge passed on the DMC yield were also investigated. At the optimum conditions, DMC was obtained with 75% yield. The IL could easily be separated from DMC and alcohol by simple distillation after the reaction and used directly for the next run. The reuse of the IL was tested for 5 times. After the second reuse, the DMC yield was decreased from 75% to about 50%, and then maintained at this level. After that, they further investigated the use of mixtures of [BMIm]BF₄/MeCN as the solvent for the DMC synthesis [103]. It was shown that the [BMIm]BF₄/MeCN mixture was better than the pure IL as the solvent, and the highest DMC yield was obtained at the volumetric ratio of 7/3.

Liu et al. employed the same system of [BMIm]BF₄-CH₃I for the electrochemical DMC synthesis but using a silver-coated nanoporous copper (NPC-Ag) cathode [104]. NPC-Ag showed much higher yields of DMC compared with silver and NPC cathode materials, and the highest yield of DMC was reached up to 80% under the optimal reaction conditions.

Yuan et al. conducted the electrochemical synthesis of DMC with two Pt electrodes in dialkyl imidazolium ILs–basic compounds–methanol solutions [105]. It is important to note that their system required neither alkyl iodide nor organic solvents, resulting in the greener reaction system. In it, IL served as electrolytes, and the base acted as a co-catalyst. The solution was saturated with CO₂ bubbling at ambient pressure, and the reaction was carried

out for 48 h under a 5.5 V potential. The yield of DMC increased from 0.2% to 3.9% as following the order of $[\text{EMIm}]\text{BF}_4 < [\text{BMIm}]\text{BF}_4 < [\text{BMIm}]\text{OH} < [\text{BMIm}]\text{Cl} < [\text{BMIm}]\text{Cl} < [\text{EMIm}]\text{Br} < [\text{BMIm}]\text{Br}$. These findings indicated that the effect of the anions on the reaction was very significant, while the dialkylimidazolium cations had a negligible impact on the electrolysis.

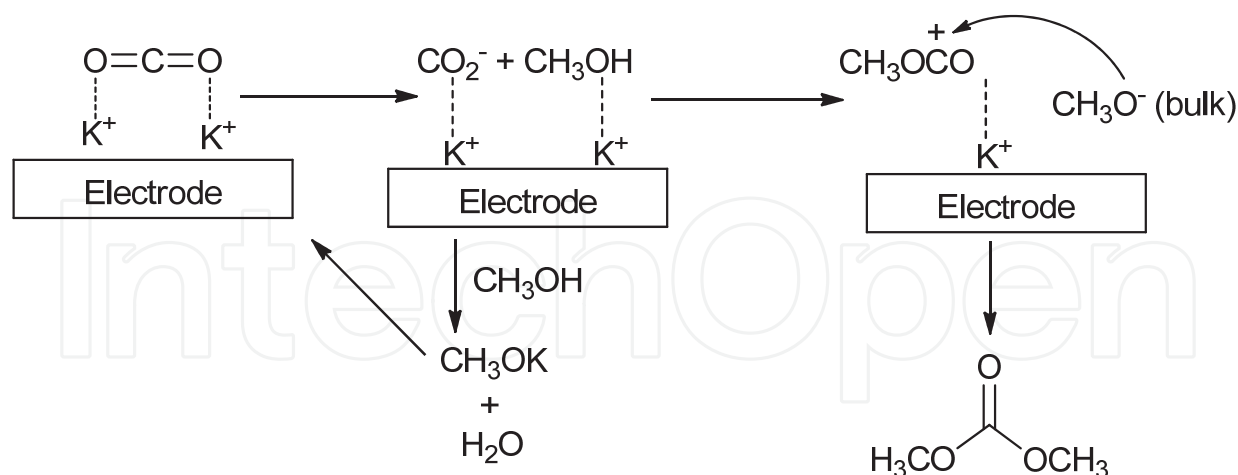


Scheme 30. Electrochemical synthesis of dialkyl carbonates from CO₂ and alcohols in CO₂-saturated [BMIm]BF₄ in the presence of alkylating agent.

The type of the basic compounds was also significant for the reaction. The DMC yield was in the order of CH₃OK > K₂CO₃ > KOH > NaOH >> CH₃ONa. CH₃ONa was almost completely inactive. Thus the type of alkali cation was very important for the reaction. They suggested that the small cation Na⁺ is hardly adsorbed at the electrode surface because it is strongly solvated with the solvent. Conversely, the less solvated and bulky cation K⁺ is preferentially adsorbed on the cathode. The specifically adsorbed K⁺ at the electrode surface can directly interact with nucleophilic sites of CO₂ and methanol. Reaction runs for the optimization of the reaction conditions were performed. Among the results obtained, an interesting one was that the DMC yield showed a maximum value of 3.9% at the reaction time of 50 h. Further increasing the reaction time, the yield gradually decreased to 0.2% because of further transformation of DMC to trimethoxyl methane and tetramethoxyl orthocarbonate. Unlike CH₃OK, the addition of CH₃I to the system has basically no impact on the reaction. It is indicated that CH₃I does not participate as a methylating agent in the electrochemical reaction. They proposed a reaction mechanism as Scheme 31. CO₂ is adsorbed on the cathode via interaction with previously adsorbed K⁺ on the cathode and, then, it is reduced into CO₂⁻(ad) when it accepts an electron from the electrode surface. This species interacts with CH₃OH(ad), which is adsorbed on the electrode, generating a CH₃OCO⁺ cation and K OH(ad). The cation successively reacts with methoxide CH₃O⁻ in the bulk to give DMC. The K OH(ad) formed in the course of the elemental step further reacts with bulk CH₃OH, producing CH₃OK. Thus, the catalyst is recyclable.

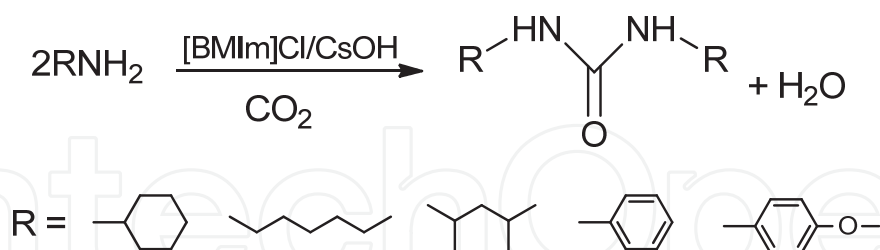
4. Synthesis of nitrogen containing carbonyl compounds from CO₂ using ILs

CO₂ can be one of the substrates for the synthesis of dialkyl urea and cyclic urethane compounds that have found extensive applications as dyes, antioxidants, and intermediates for the preparation of pharmaceuticals and agricultural chemicals. In this section, some examples where ILs could successfully be used for these reactions will be described.



Scheme 31. A mechanism for electrosynthesis of DMC from CO₂ and methanol with Pt electrodes in the IL-CH₃OK-methanol system.

Deng and co-workers [106] reported the synthesis of symmetric urea derivatives from CO₂ with aliphatic and aromatic amines using a catalyst system consisting of [BMIm]Cl and CsOH (Scheme 32). This catalyst system gave excellent yields of dialkyl ureas at 170°C under 6 MPa CO₂ for 4–6 h without dehydration reagents. Although longer time was needed, good yields were also obtained with less reactive aniline compounds which were not directly carbonylated with CO₂ so far. For this catalyst system, the presence of the IL was indispensable, because no urea was obtained only with CsOH. KOH was less effective for the reaction than CsOH. After the reaction, the product was precipitated by adding water to the reaction mixture and separated by filtration. The IL and the base in the filtrate were recovered by removing water by distillation and could be reused three times with small loss in the activity.

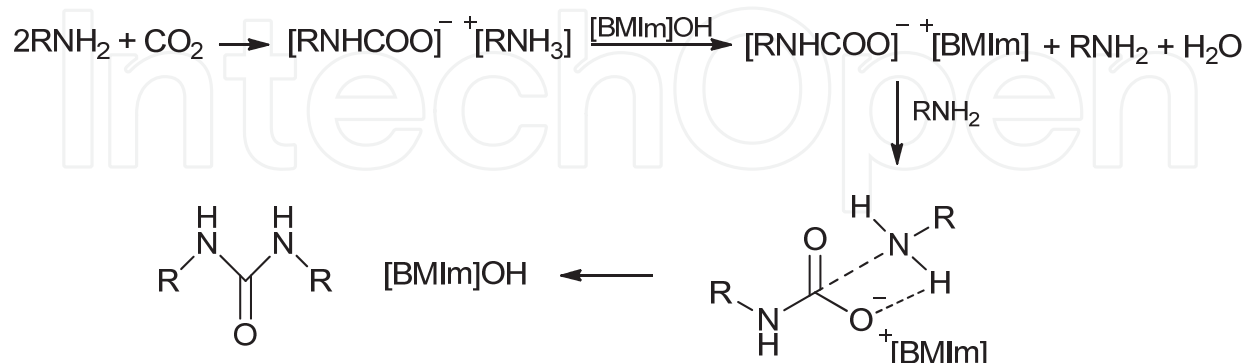


Scheme 32. Synthesis of dialkyl urea from amine and CO₂.

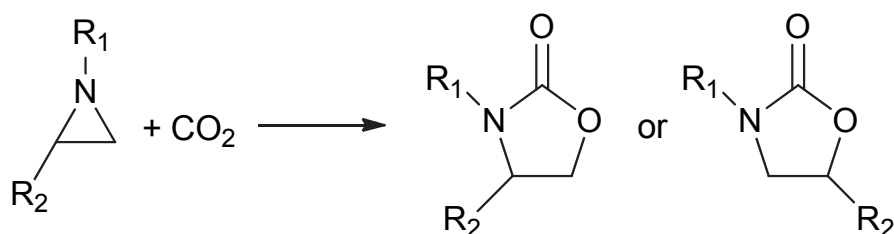
Lately, Jiang et al. [107] used [BMIm]OH for the dialkyl ureas under conditions similar to those employed by Deng et al. This catalyst also gave good yields of dialkyl ureas, although slightly longer reaction time was required. Unfortunately, no urea was obtained from aniline, which could afford *N,N'*-diphenyl urea with CO₂ by [BMIm]OH/CsOH. No ureas were produced from dibutyl amine and from tributyl amine. Scheme 33 illustrates a reaction mechanism proposed by the authors.

The reaction of CO₂ with aziridine producing 2-oxazolidinone is analogous one to the cyclic carbonate synthesis from CO₂ and epoxide. If an alkyl or aryl group is attached to the aziridine ring, two oxazolidinone products could come from the ring opening across N-CH₂

and across N-CH (Scheme 34). Nomura et al. reported the reactions of CO₂ with 1-phenyl-2-methyl (R₁ = C₆H₅, R₂ = CH₃) and 1-phenyl-2-ethyl (R₁ = C₆H₅, R₂ = C₂H₅) azilidines using [Bu₄N]Br in an organic solvent of acetonitrile at 60°C under 5 MPa CO₂ [108]. The obtained products were nearly equimolar mixtures of 3,4-disubstituted and 3,5-disubstituted oxiazolidinones.



Scheme 33. A proposed mechanism for the synthesis of dialkyl urea from amine and CO₂ catalyzed by [BMIm]OH [107].

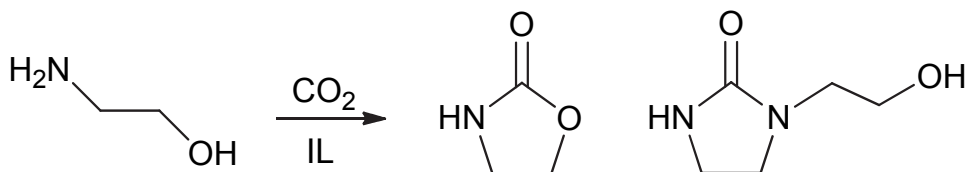


Scheme 34. Synthesis of 2-oxazolidinone from CO₂ and aziridine.

Kawanami et al. employed I₂/IL systems for the reaction of CO₂ and 2-methyl aziridine (R₁ = H, R₂ = CH₃) [109]. Surprisingly, the reaction system of [Oc₄N][TFSI] (tetraoctylammonium bis(trifluoromethylsulfonyl)imide) regioselectively and almost quantitatively gave 4-methyl-oxiazolidinone at 60°C under 5 MPa CO₂ for a very short reaction time of 5 min, although the reason for the high selectivity to the 4-substituted product was unknown. [EMIm][TFSI] was less effective for the reaction than [Oc₄N][TFSI]. The optimum pressure of CO₂ was around 10 MPa. This was discussed by the solubility of CO₂ in IL and that of the aziridine to scCO₂. At lower pressures, the lower concentration of CO₂ in the IL phase limited the reaction, while the lower yield at higher pressures was ascribed to the lower concentration of the substrate in the IL because of its dissolution into scCO₂ phase. When ethanol was used as the solvent instead of [Oc₄N][TFSI], the selectivity to 4-methyl-2-oxazolidinone was lower (70%) because of the formation of the regioisomer of 5-methyl-2-oxazolidinone, and a long period of reaction time was required to get a reasonable conversion. The TOF value obtained in [Oc₄N][TFSI] was 116 times larger than that in ethanol.

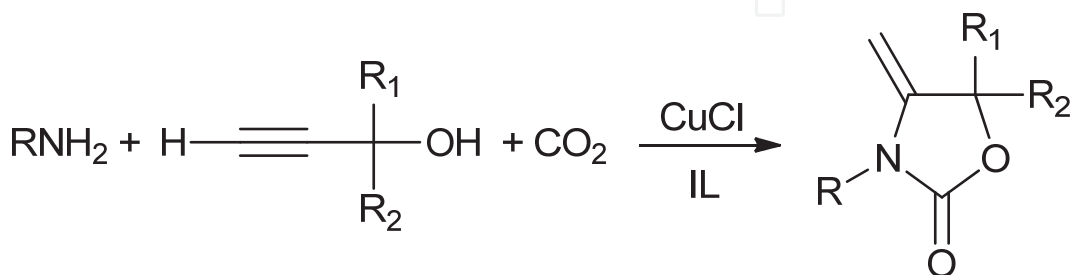
Another way to produce cyclic urethane is the reaction of CO₂ and aminoethanol. Aminoethanols are much cheaper than aziridines, so this reaction is preferable for large scale synthesis of cyclic urethane. Our group examined the use of [BMIm]-based ILs,

[Bu₄N]Br and [Bu₄P]Br for this reaction at 150°C under 10 MPa CO₂ [110]. The reaction yielded not only 2-oxazolidinone but also 1-(2-hydroxyethyl)-2-imidazolidinone and oligomeric products (Scheme 35). Among the ILs used, [Bu₄N]Br gave the highest conversion of aminoethanol, and [BMIm]BF₄ produced almost only the substituted imidazolidinone with a high yield. On the basis of the work by Deng et al. [106] described above, effects of adding alkali metal carbonates or hydroxides on the reaction with [Bu₄N]Br were further investigated. Among the alkali salts tested, K₂CO₃ inhibited the formation of the oligomers. Other alkali additives did not show beneficial influence. The reaction runs for different periods of reaction time revealed that the oxiazolidione formed is consecutively converted to the substituted imidazolidinone by the reaction with aminoethanol. On combining this result with those of reaction runs using several types of amino alcohols, the reaction mechanisms for the oxazoilidionone and the substituted imidazolidione were proposed. In these mechanisms, IL was considered to be Lewis acid on the basis of reported IR and NMR studies, which showed the Lewis acidic nature of the hydrogen atom on the C(2) of the imidazolium ring [111, 112].



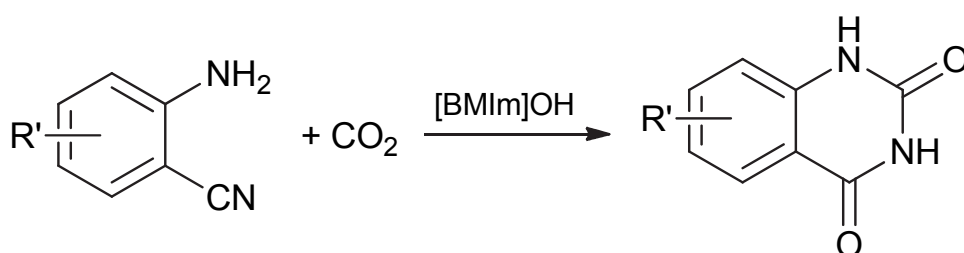
Scheme 35. Reaction of CO₂ with aminoethanol in the presence of ILs.

Deng's group who carried out the reaction of CO₂ and propargylic alcohol (see section 2.1.1.) also reported a similar reaction of the synthesis of methylene oxazolidinone from amine, propargylic alcohol, and CO₂ using the reaction system of CuCl/[BMIm]BF₄ (Scheme 36) [113]. Various methylene oxazolidinones could be obtained from the corresponding amines and propargylic alcohols with excellent yields at 100°C under 2.5 MPa of CO₂ for 10–15 h. Only a small amount of the product was obtained in the absence of CuCl, and good product yields were obtained even in organic solvents. Thus, the IL again seems to simply act as a solvent. Catalyst and IL screening revealed that the yield was in the orders of CuCl > CuI ~ CuBr > CuCl₂ and of [BMIm]BF₄ > [BMIm]PF₆ > [BPy]BF₄. It should be noted that [BMIm]PF₆ gave only polymeric products for the reaction of CO₂ and propargylic alcohol, i.e. in the absence of amine. The reaction system was again specific for tertiary alcohols; no desired products were detected from secondary and primary alcohols. The same results were obtained for the reaction of CO₂ and propargylic alcohol.

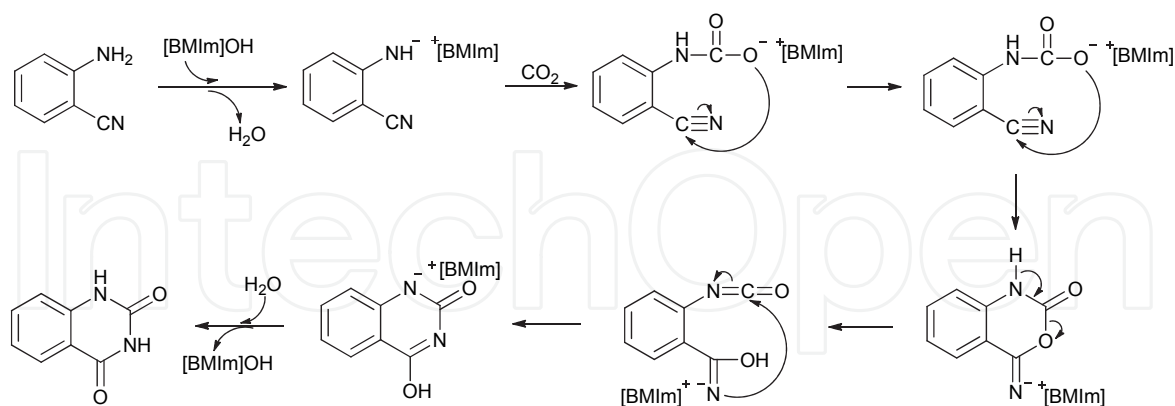


Scheme 36. Synthesis of methylene oxazolidinone from amine, propargylic alcohol and CO₂.

Recently, Bhanage's group reported another interesting example of using IL for a reaction converting CO₂ to useful chemicals [114]. They used a basic IL of [BMIm]OH for the reactions of CO₂ and aminobenzonitriles to produce rather complex compounds of quinazoline-2,4(1H,3H)-diones (Scheme 37), which are important because of their biological activity and widely used as key structures in medical drugs. [BMIm]OH gave good to excellent product yields from a broad range of aminobenzonitriles at 120°C and 3 MPa CO₂ for 18 h. This protocol was also applicable for five/six membered *N*-heterocyclic carbonitriles. [BMIm]OH was much more effective for the reaction than organic and inorganic bases of Et₃N and Cs₂CO₃. Other ILs of [BMIm]BF₄ and [BMIm]HSO₄ showed no activity. After the reaction, the product was precipitated by pouring the reaction mixture to water and filtered out. The catalyst in the filtrate was recovered by removing water under vacuum. The catalyst was recycled four times. Unfortunately, gradual decreases in the yield on the recycling was observed; however, no structural change of [BMIm]OH was observed. Loss of the catalyst during the recycling might be the reason for the decrease in the yield. Scheme 38 represents the proposed reaction mechanism in which the deprotonation of the amino group by the OH anion of the IL, the formation of [BMIm] carbamate ester, intermolecular cyclization, and the rearrangement of the resulting cyclic intermediate are involved.



Scheme 37. Synthesis of quinazoline-2,4(1H,3H)-diones from CO₂ and aminobenzonitriles.



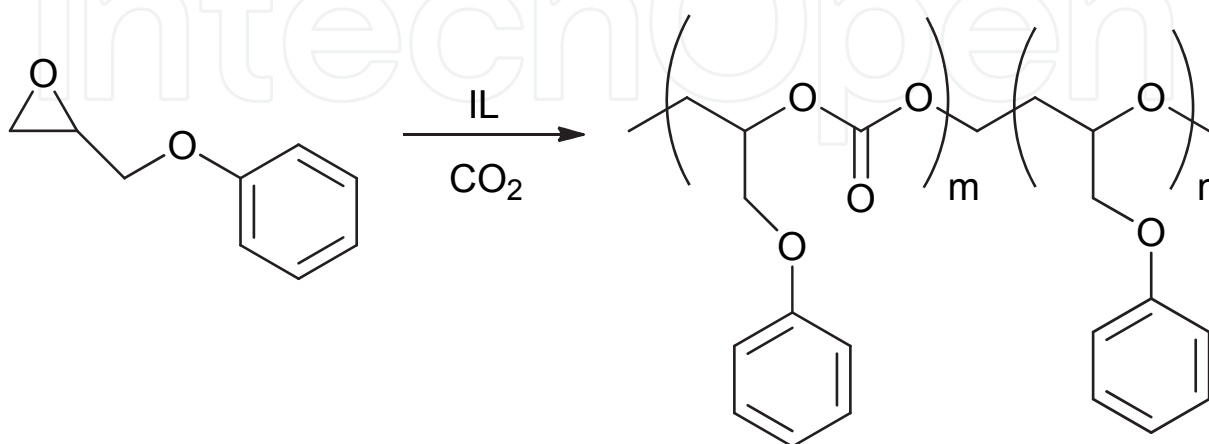
Scheme 38. A proposed mechanism for quinazoline-2,4(1H,3H)-dione from CO₂ and aminobenzonitrile catalyzed by [BMIm]OH [114].

5. Polycarbonate synthesis in/by IL

Polycarbonates, with such features as high ductility, good transparency, high heat and impact resistance, and high biocompatibility, are considered as specialty polymers and find

increasing uses in engineering thermoplastics and many different fields [115]. The copolymerization of CO₂ and epoxides to produce polycarbonates is the most promising area of CO₂ utilization as a direct material, which may lead to a solution for resource, energy, and environmental problems. Inoue et al. first reported the synthesis of high molecular weight polycarbonates by alternating copolymerization of CO₂ and epoxides using a catalyst derived from diethyl zinc and water [116]. Since then, several excellent reviews [117–121] have appeared on this interesting topic. It is demonstrated that coordination compounds based on zinc, aluminum, cadmium, chromium, manganese, cobalt, and rare-earth metals are promising candidates for highly active catalytic systems for the copolymerization of epoxides with CO₂. In the following, we will deal with the polycarbonate synthesis from CO₂ and epoxides with ILs as catalysts or cocatalysts.

Park et al. used several imidazolium-based ILs of different alkyl groups (C₂–C₈) and anions as catalysts in the copolymerization of CO₂ with a substituted epoxide of phenyl glycidyl ether (PGE) in a batch or semi-batch reactor without any solvent (Scheme 39) [122–124]. In the presence of the ILs, CO₂ could be effectively added to the epoxide ring of PGE to produce the polycarbonate whose polydispersity was close to unity, i.e. a narrow molecular weight distribution. The activity of IL containing Cl⁻ was in the order of [BMIm]⁺ > [EMIm]⁺ ≈ [HMIm]⁺ ≈ [OMIm]⁺. This was ascribed to the steric hindrance effect and/or the differences in the hydrophobicity and the viscosity. The order of the activity for the different anions in imidazolium-based ILs decreased as Cl⁻ > BF₄⁻ >> PF₆⁻, which was proposed to result from the difference in the solubility of IL in PGE. [EMIm]PF₆ had no activity. Every Cl-containing ILs produced polycarbonates with the carbonate content, *f*(CO₂), of 100% by the copolymerization at 80°C. For the copolymerization at 120°C, the high *f*(CO₂) value of the polycarbonate was maintained with [BMIm]Cl, whereas those value were about 70% with the other ILs. Higher CO₂ pressure was favorable for the PGE conversion and *f*(CO₂) [124]. The reaction mode (batch or semi-batch) also affected *f*(CO₂) [122,123]. The polycarbonates produced in the batch reactor sometimes had lower *f*(CO₂) than those produced in the semi-batch reactor (under continuous pressurized CO₂ flow) depending on the polymerization conditions (temperature, CO₂ pressure, reaction time). For comparison, [Bu₄N]Cl, and [BPy]Cl were also used for the copolymerization [123,124]. Compared to [BMIm]Cl, [Bu₄N]Cl, and [BPy]Cl showed lower activities, average molecular weight (*M_n*), and *f*(CO₂).



Scheme 39. Copolymerization of PGE and CO₂ in the presence of IL.

As mentioned in section 2.1., there can be some synergistic effect by the combination of IL and zinc halide for the CO₂ cycloaddition to epoxide. Park et al. also investigated the influence of the co-presence of ZnBr₂ on the copolymerization of CO₂ and PGE with [BMIm]Cl [124]. ZnBr₂ alone showed a low activity and a low Mn, but enhanced the activity of [BMIm]Cl. By the co-presence of ZnBr₂, Mn of the copolymer produced was also increased; however, its f(CO₂) was smaller than that of the copolymer produced with the IL alone. For the enhancement of the activity, they proposed the cooperative activation of epoxide by Zn and halide anion of the IL, which was very similar to that proposed for the CO₂ cycloaddition reaction (Scheme 6 in section 2.1.2.).

They also prepared silica-immobilized imidazolium ILs of different alkyl groups and used them as the catalysts for the same copolymerization [125]. Although the immobilized IL catalysts were easily separated by filtration after the polymerization, they produced copolymers whose Mn and f(CO₂) were smaller than those of the copolymers prepared with the corresponding homogeneous IL catalysts. Effects of the alkyl chain length of IL and the reaction conditions on the nature of the copolymer synthesized showed similar trends to those observed with the homogeneous ILs. The immobilized ILs could be reused up to four consecutive runs without considerable loss of activity and f(CO₂).

Several research groups reported that various ILs could be effective cocatalysts in the copolymerization of CO₂ and epoxides with metal salen or metal porphyrin complexes [126–130]. In some cases, it was shown that the activities of these metal complexes were drastically enhanced by the co-presence of IL, although they had no or a very low activity for the copolymerization in the absence of IL.

Inoue and co-workers reported the successful alternating copolymerization of CO₂ with EO, PO, or CHO (cyclohexene oxide) by the use of Al porphyrin complexes in combination with quaternary phosphonium or ammonium salts [126]. The copolymerization of CO₂ and PO or CHO was conducted at room temperature and 5 MPa CO₂, producing polycarbonates with the perfect alternating structure (f(CO₂) = 100%) and a very narrow molecular weight distribution (Mw/Mn < 1.1). For the polycarbonate produced from EO, f(CO₂) was 70%. When one reaction run with PO was completed, the next run was carried out by just adding CO₂ and PO to the reactor. The molecular weight distribution measurements of the starting and the final copolymers revealed that the average molecular weight was increased, while keeping the narrow distribution. This indicated the “living” nature of the copolymerization with this catalyst system. They also achieved the synthesis of block copolymers.

The same group also used the system of Al salen complex and [Et₄N]OAc for the copolymerization of CO₂ and CHO [127]. This catalyst system required a higher reaction temperature of 80°C to obtain the copolymer with a high yield and high f(CO₂), compared to the above mentioned catalyst system using Al porphyrin complex. In the absence of the IL, the salen Al complex was less active and yielded the polymer mostly containing ether linkage (f(CO₂) = 2%). The lower activity and a very lower f(CO₂) value without IL were also reported by Jung et al. [128] for the copolymerization with Al salen/[Et₄N]Br. Thus, one can say that the cocatalyst of IL enhances not only the polymerization activity of the metal complex catalyst, but also its ability for the CO₂ insertion.

Lu and Wang reported the CO₂ and PO copolymerization over the binary catalysts of (salen)Co^{III}X/[Bu₄N]Y at 25°C and 2 MPa CO₂ for 3 h [129]. All the polycarbonate synthesized with these catalysts had f(CO₂) values more than 99%. However, the selectivity to polycarbonate and cyclic carbonate could be drastically affected by adjusting axial group X of (salen)Co^{III}X and the anion Y of [Bu₄N]Y. It was found that the use of a cobalt complex

with an electron-withdrawing axial group X and a quaternary ammonium salt with poor leaving ability anion, increased the selectivity for poly(propylene carbonate). For example, in the presence of the [Bu₄N]Br cocatalyst, a change in the axial group X of chiral [salenCo^{III}X] from acetate to dinitrophenoxy improved the selectivity to polycarbonate from 3 to 78%. On the other hand, with the Co complex of dinitrophenoxy as the catalyst, a change in the anion Y of [Bu₄N]Y from Br⁻ to Cl⁻ or CH₃COO⁻ resulted in an increase in the selectivity for polycarbonate from 78 to 99%. Besides, the catalyst system was found to be applicable to other aliphatic epoxides, providing the corresponding polycarbonates with > 99% carbonate linkages.

Imidazolium salts ILs had also been proved to be effective cocatalysts in the copolymerization of CO₂ with cyclohexene oxide (CHO) catalyzed by (salen)Cr^{III}Cl complex [130]. The loading of ILs had great effect on the copolymerization. Although the Cr complex alone showed no activity, it produced the polycarbonate in the presence of 2.25 equivalent [OMIm]Br with a TOF value of 219 h⁻¹ (based on Cr) and f(CO₂) of 98%. The TOF value was slightly increased to 286 h⁻¹ by using 13.5 equivalent IL, while keeping the high f(CO₂). However, the co-presence of 20 equivalent IL decreased the TOF to 86 h⁻¹ and f(CO₂) to 56%. These results strongly suggest that the activity of [OMIm]Br was low, and there is the synergistic effect for the activity and f(CO₂) in the (salen)Cr^{III}Cl/[OMIm]Br system with appropriate ratios, although the authors did not point out these issues. Anions of imidazolium salts with higher nucleophilicity and better leaving ability, such as Cl⁻ and Br⁻, were beneficial for improving the activity, f(CO₂), and Mn than BF₄⁻ and PF₆⁻. In addition, the activity was increased with the alkyl chain length of the IL cation. Dodecylmethylimidazolium bromide ([DDMIm]Br) displayed an enhanced TOF of 242.5 h⁻¹, f(CO₂) > 99%, and, and a lower polydispersity index of 1.1. The enhanced activity might come from the increased nucleophilicity of an anion, the hydrophobicity, and solubility of CO₂ with increasing alkyl chain length.

6. Concluding remarks

This chapter reviews the application of ILs to the chemical and electrochemical synthesis of carbonates and related compounds using CO₂ as a direct or indirect reactant. Several types of ILs are active catalysts and active components in multi-component catalysts for these synthetic reactions, depending on the kind and chemical nature of cations and anions involved. The above-reviewed reactions may proceed under relatively mild conditions, which is one of practical merits of using ILs. In some cases, however, a long reaction time is needed. For one-step reactions such as the synthesis of a cyclic carbonate from an epoxide and CO₂, the selection of active ILs is important and the separation and recycling of ILs are also an issue of practical importance. The ILs may be dispersed and immobilized on the surfaces of suitable solids in order to change the homogeneous catalytic reactions into the heterogeneous ones, in which the post-reaction catalyst separation and recycling would be easier. A few interesting attempts are to conduct multi-step reactions such as the synthesis of a cyclic carbonate from an olefin and CO₂, including the first formation of an epoxide and the second addition of CO₂ to this product, in a single reactor. Multi-component catalysts containing a few different types of ILs should be required, which are respectively and selectively active for certain reactions involved. In addition, if possible, these active components should be effective under the same or very similar reaction conditions, which, however, is not an easy requirement at present. A possible way to cope with these difficulties is the use of different reaction conditions, which are switched at a certain stage of reactions. For this, careful kinetics analysis of the reactions is required in advance.

Note again that ILs are interesting and effective components of catalysts for organic synthetic reactions, as demonstrated with many examples. For the industrial application of ILs in order to realize eco-friendly and effective processes including chemical/catalytic and post-reaction chemical/physical procedures, further work is still of significance to clarify their catalytic, physicochemical, and biological features in more detail.

7. Acknowledgements

One of the authors (JMS) acknowledges the financial support from National Natural Science Foundation of China (21073049), State Key Lab of Urban Water Resource and Environment of Harbin Institute of Technology (HIT2010DX15). This work was supported in part by Japan Society for the Promotion of Science with Grant-in-Aid for Scientific Research (B) 22360327.

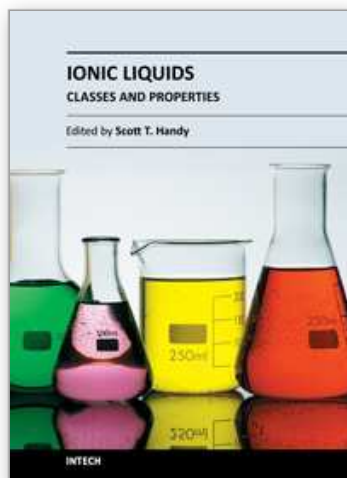
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Ionic Liquids - Classes and Properties

Edited by Prof. Scott Handy

ISBN 978-953-307-634-8

Hard cover, 344 pages

Publisher InTech

Published online 10, October, 2011

Published in print edition October, 2011

Room temperature ionic liquids (RTILs) are an interesting and valuable family of compounds. Although they are all salts, their components can vary considerably, including imidazolium, pyridinium, ammonium, phosphonium, thiazolium, and triazolium cations. In general, these cations have been combined with weakly coordinating anions. Common examples include tetrafluoroborate, hexafluorophosphate, triflate, triflimide, and dicyanamide. The list of possible anionic components continues to grow at a rapid rate. Besides exploring new anionic and cation components, another active and important area of research is the determination and prediction of their physical properties, particularly since their unusual and tunable properties are so often mentioned as being one of the key advantages of RTILs over conventional solvents. Despite impressive progress, much work remains before the true power of RTILs as designer solvents (i.e. predictable selection of a particular RTIL for any given application) can be effectively harnessed.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Jianmin Sun, Ruixia Liu, Shin-ichiro Fujita and Masahiko Arai (2011). Ionic Liquids in Green Carbonate Synthesis, *Ionic Liquids - Classes and Properties*, Prof. Scott Handy (Ed.), ISBN: 978-953-307-634-8, InTech, Available from: <http://www.intechopen.com/books/ionic-liquids-classes-and-properties/ionic-liquids-in-green-carbonate-synthesis>

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