

Cycloaddition of carbon dioxide to propylene oxide catalyzed by ionic liquids

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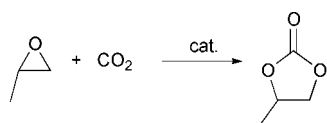
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In room temperature ionic liquids based on 1-*n*-butyl-3-methylimidazolium and *n*-butylpyridinium salts, cycloaddition of carbon dioxide to propylene oxide without any additional organic solvents has been investigated. It was found that 1-*n*-butyl-3-methylimidazolium tetrafluoroborate was the most active catalyst with almost 100% selectivity, and a suitable CO₂-propylene oxide molar ratio was needed for high conversion. The ionic liquid used as catalyst for the reaction was recyclable.

Five-membered cyclic carbonates are excellent aprotic polar solvents and are used extensively as intermediates in the production of drugs and pesticides. The formation of cyclic carbonates *via* cycloaddition of epoxides and carbon dioxide, which is one of the routes for carbon dioxide chemical fixation,¹ has received much attention as regards the utilization of carbon resources and the reduction of CO₂ pollution.

Cycloaddition between epoxides and carbon dioxide using organic and inorganic compounds such as metal halides,^{2,3} onium halides, metal complexes^{4–6} and MgO,⁷ Mg–Al mixed oxides,⁸ KI–ZnO,⁹ *etc.* as catalysts generally occur at low rates unless high temperature, high carbon dioxide pressure, long reaction time and/or high catalyst/substrate ratios are used. More recently, propylene carbonate has also been synthesized from supercritical carbon dioxide (sc-CO₂)-propylene oxide mixture with phthalocyaninatoaluminium chloride-tetrabutylammonium bromide as catalyst, which necessitates a higher reaction pressure and larger CO₂/propylene oxide molar ratio.¹⁰



Recently, the use of room temperature ionic liquids as environmentally benign media for catalytic processes or chemical extractions has become widely recognized and accepted.^{11,12} Room temperature ionic liquids have negligible vapor pressure, excellent thermal stability and special characteristics in comparison with conventional organic and inorganic solvents. Many reactions catalyzed with ionic liquids and showing high performance have been reported.^{13–17} This offered some new clues that using ionic liquids as catalysts for those traditionally acid–base synthetic reactions may be not only possible but also practical and even highly efficient. Our new approach, reported herein, involves the use of room temperature ionic liquids based on 1-*n*-butyl-3-methylimidazolium (BMIm) and *n*-butylpyridinium (BPy) salts as catalytic media for the cycloaddition of carbon dioxide to propylene oxide, and the possibility of recycling the ionic liquids.

Results and discussion

Effect of the ionic liquid and its amount on the cycloaddition

The results of the cycloaddition of CO₂ to propylene oxide in a series of ionic liquids consisting of BMIm⁺ or BPy⁺ and Cl[–], BF₄[–], PF₆[–] (Table 1) indicated that both the cations and anions have a strong impact on the catalytic activities, entries 1–4. BMImPF₆ and BPyBF₄, used as catalysts, showed the lowest catalytic activities with that of BMImPF₆ being the worst. The conversion of propylene oxide could, however, be greatly increased if BMImCl catalyst was employed, and even better catalytic performance was achieved with the ionic liquid consisting of the BMIm⁺ cation and BF₄[–] anion (entry 4).

The effect of the amount of BMImBF₄ catalyst on the cycloaddition was examined. The conversion of propylene oxide increased with increasing amount of BMImBF₄ under the same reaction conditions, entries 5–7, although the TONs decreased correspondingly. There was no detectable conversion of propylene oxide if no ionic liquid catalyst was used.

The catalytic performances of combined ionic liquids were also tested. Only a moderate improvement in catalytic activity was obtained when a small amount of BMImCl was added to BMImBF₄, entry 8; however, the activity was greatly enhanced if a small amount of BMImCl was added to BMImPF₆, entry 9. This indicates that the PF₆[–] anion is not a favorable component for the BMIm⁺ cation-containing ionic liquid as the catalyst towards cycloaddition, while some synergism may exist between BF₄[–] and Cl[–], which could enhance the catalytic performance of BMImBF₄ ionic liquid as the catalyst if the results of entries 5 or 6 are compared with that of entry 8.

Although varied conversions of propylene oxide were obtained with different ionic liquids, it is worth noting that the selectivity for the desired propylene carbonate product was essentially 100%, since GC-MS analysis showed that there were no other detectable products.

Effect of the amount of added CO₂ and temperature on the cycloaddition

Since the best catalytic activity was obtained with BMImBF₄ ionic liquid, the effect of the amount of carbon dioxide added

Table 1 Effect of the ionic liquid and its amount on the cycloaddition reaction^a

Entry	Ionic liquid	Amount added/mmol	P(CO ₂)/MPa	Conversion (%)	Selectivity (%)	TON ^b
1	BMImPF ₆	(1.5)	2.0	11.3	100	7.8
2	BPyBF ₄	(1.5)	2.0	25.3	100	16.8
3	BMImCl	(1.0)	2.0	63.8	100	63.8
4	BMImBF ₄	(0.75)	2.5	67.4	100	89.9
5	BMImBF ₄	(1.5)	2.5	80.2	100	53.5
6	BMImBF ₄	(2.0)	2.5	90.3	100	45.2
7	BMImBF ₄	(2.5)	2.5	100	100	40.0
8	BMImBF ₄ + BMImCl	(1.5 + 0.2)	2.0	90.5	100	53.2
9	BMImPF ₆ + BMImCl	(1.5 + 0.2)	2.0	45.3	100	26.6

^a Reaction conditions: 110 °C, 6 h. ^b TON: mol propylene carbonate converted per mol of ionic liquid.

Table 2 Effect of the amount of CO₂ added and the temperature on the cycloaddition reaction^a

Entry	BMImBF ₄ /mmol	P(CO ₂)/MPa	CO ₂ added/g	CO ₂ /propylene oxide molar ratio	T/°C	Conversion (%)	TON
1	1.5	1.5	4.1	0.93	110	80.7	53.8
2	1.5	2.0	5.8	1.32	110	90.1	60.1
3	1.5	2.5	8.0	1.82	110	80.2	53.5
4	1.5	3.5	11.7	2.66	110	74.3	49.5
5	1.5	4.5	16.5	3.75	110	69.4	46.3
6	2.5	2.5	8.0	1.82	rt	24.1	9.6
7	2.5	2.0	5.8	1.32	rt	35.8	14.3
8	2.5	2.5	8.0	1.82	65	55.2	22.1
9	2.5	2.5	8.0	1.82	90	77.5	31.0
10	2.5	2.5	8.0	1.82	100	96.8	38.7
11	2.5	2.5	8.0	1.82	110	100	40.0
12	2.0	2.5	8.0	1.82	110	90.3	45.2
13	0.75	2.5	8.0	1.82	110	67.4	89.9
14	0.4	2.0	5.8	1.32	130	97.7	244.3
15	0.2	2.5	8.0	1.82	140	82.3	411.5
16	0.2	2.0	5.8	1.32	140	89.9	449.5

^a Reaction: 6 h.

and the reaction temperatures was further examined using the BMImBF₄ ionic liquid system. From the results in Table 2, entries 1–5, it can be seen that insufficient or excessive amounts of CO₂ result in relatively lower conversions, that is there exists an optimum CO₂–propylene oxide molar ratio for high conversion, *ca.* 1.3, which seems to have little relation to the amount of ionic liquid used. Since the amount of ionic liquid used in this work was 0.02–0.3 ml and since only a very small portion of CO₂ may be dissolved in the ionic liquid, it can be conjectured that the CO₂ introduced was dissolved in the propylene oxide or ‘liquified’ through the formation of a CO₂–propylene oxide complex, which has been postulated on the basis of the appearance of a new absorption band in the UV spectrum of a saturated solution of CO₂ in propylene oxide.¹⁸ Too much CO₂ may retard the interaction between propylene oxide and the ionic liquid catalyst, thus resulting in a lower conversion.

As expected, the reaction temperature has a strong impact on the reaction rate. It is worth noting that the BMImBF₄ ionic liquid exhibited some activity even at room temperature, entries 6 and 7. When the amount of ionic liquid was fixed at 2.5 mmol, conversion of propylene oxide increased with increasing temperature, with 110 °C being high enough for complete conversion of propylene oxide, entry 11. If the reaction temperature was further increased to 130 or 140 °C, the amount of the ionic liquid catalyst could be greatly reduced and high TONs could be achieved, entries 14–16.

The possibility of recycling the BMImBF₄ ionic liquid catalyst

In order to investigate the possibility of recycling the BMImBF₄ ionic liquid catalyst, a recycle experiment was conducted. BMImBF₄ (12.5 mmol) was placed in the autoclave, then 0.5 mol propylene oxide and CO₂ with an initial pressure of 4.0 MPa at room temperature were introduced into the

autoclave successively and reacted at 110 °C for 6 h. After this time, the resulting mixture was distilled at 83–86 °C/2 mmHg to give the desired propylene carbonate product of 100% purity, as analyzed by GC-MS. The reactor containing the used ionic liquid after distillation was charged with propylene oxide and CO₂ again. This procedure was repeated for 5 cycles. The conversion and yield results are listed in Table 3. Since the ionic liquid is non-volatile and thermally stable, the desired product could be easily separated from the ionic liquid by simple distillation, and satisfactory yields could be obtained. After the ionic liquid catalyst had been used 5 times, the catalytic activity was only slightly decreased. This indicates that the ionic liquid catalyst for the cycloaddition of CO₂ to propylene oxide is recyclable.

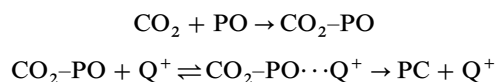
Although the reaction mechanism for the cycloaddition of CO₂ to propylene oxide is not clear at this stage, it can be conjectured, based on the experimental results, that BMIm⁺ may act as the main active site for the activation of the CO₂–propylene oxide complex mentioned above, since the non-nucleophilic BF₄[−] and PF₆[−] ions cannot form covalent bonds with the epoxide.¹⁹ The nature of the anion, BF₄[−], PF₆[−], Cl[−], *etc.*, has a strong impact on the physicochemical

Table 3 Stability of the ionic liquid catalyst^a

Cycle number	PO conv. (%) ^b	PC yield (%) ^b	TON
1	100	90.7	40
2	100	91.8	40
3	98.2	90.5	39.3
4	97.5	89.2	39.0
5	96.1	86.9	38.4

^a Reaction conditions: 110 °C, 6 h. ^b PO = propylene oxide; PC = propylene carbonate.

properties of BMIm⁺; for example, BMImBF₄ is soluble in water while BMImPF₆ is insoluble in water and much less ionic than BMImBF₄. Such an impact or modulation caused or controlled by the anions would result in an enhancement or inhibition of the interaction between the BMIm⁺ active sites and CO₂-propylene oxide complex. Thus, the following reaction pathway is tentatively proposed:



where PO = propylene oxide; PC = propylene carbonate; CO₂-PO = CO₂-propylene oxide complex; Q⁺ = BMIm⁺.

In conclusion, BMImBF₄ room temperature ionic liquid is an effective catalyst for the cycloaddition of CO₂ to propylene oxide with excellent selectivity and relatively short reaction time. The resulting product can be separated from the ionic liquid by simple distillation, while the ionic liquid catalyst is recyclable.

Experimental

1-*n*-Butyl-3-methylimidazolium tetrafluoroborate (BMImBF₄) and hexafluorophosphate (BMImPF₆) were synthesized according to the procedures reported in the literature.^{20,21} *n*-Butylpyridinium tetrafluoroborate (BPyBF₄) was synthesized using the same procedure. BMImBF₄, BMImPF₆, BPyBF₄ and BMImCl were used as the only catalyst without any other additives.

All cycloaddition reactions were performed in a 90 cm³ stainless steel autoclave equipped with a magnetic stirrer. For each typical reaction, ionic liquid (0.2–2.5 mmol) and propylene oxide (100 mmol) were successively charged into the reactor without any additional solvent, and then CO₂ was introduced at room temperature. Since the autoclave could be conveniently and precisely weighed in a balance, the amount of CO₂ added was also measured by weight. The autoclave was heated up to the desired temperature with stirring for 6 h. After cooling, the resulting liquid mixture was analyzed with a Hewlett-Packard 6890/5793 GC-MS equipped with a HP 5MS column (30 m long, 0.25 mm i.d., and 0.25 μm film thickness). The concentration of reactant and product was directly given by the GC-MS Chemstation

system according to the area of each chromatograph peak. Isolated yields of propylene carbonate were based on the propylene oxide added.

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