

Chemical Fixation of Carbon Dioxide to Propylene Carbonate in Ionic Liquids

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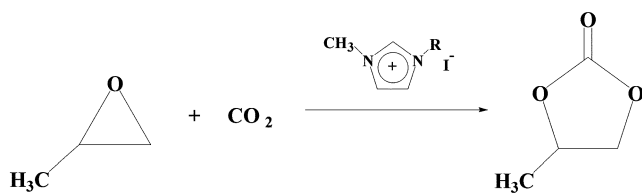
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The efficient transformation of harmful wastes such as CO₂ into useful chemicals is an important contribution to the preservation of the earth. Chemical fixation of CO₂ onto organic compounds is interesting because of a synthetic merit; one carbon atom and two oxygen can be incorporated in one step with a high atom efficiency. The conversion of CO₂ into carbonates has been carried out in conventional organic solvents using catalysts such as dialkyltin methoxide,¹ organoantimony halide,² alkali metal salts,³ Mg-Al mixed metal oxide⁴ and Cr(III) salen complex.⁵ In particular, the addition reaction of CO₂ to epoxide is a powerful candidate for CO₂ fixation to produce five-membered cyclic carbonate which can be used as valuable raw materials for engineering plastics and highly polar solvents.⁶ However, these reactions using metallic catalysts have disadvantages, such as poor solubility of the catalyst,³ difficulties in catalyst recycling,² air sensitivity, the need for co-solvent, or the requirement for high temperatures.

Many organic solvents evaporate into the atmosphere with detrimental effects on the environment and human health. But room-temperature ionic liquids, with low viscosity and no measurable vapour pressure,⁷ can be used as environmentally benign media for a range of industrially important chemical processes,⁸⁻¹² despite uncertainties about thermal stability and sensitivity to oxygen and water. Here, we found that using ionic liquids as solvents as well as catalysts can improve the reaction rate significantly at low temperatures (Scheme 1).

Numerous low-melting ionic salts are known, including alkylphosphonium, *N*-alkylpyridinium, alkylammonium, and *N,N'*-alkylimidazolium cations with various anions.¹³ We chose to use the 1-alkyl-3-methylimidazolium cation because: (i) their synthesis is facile,¹⁴ and (ii) it is neither oxygen nor water sensitive (but is hygroscopic). With iodide as the counteranion, whose role has been extensively studied in our previous studies,¹⁵ they can act as solvents as well as catalysts.

A typical experimental procedure for the carboxylation of



epoxide with carbon dioxide is as follows. Propylene oxide (0.4 mol) was added to 1-alkyl-3-methylimidazolium iodide (10 g) in a 125 mL Parr reactor at room temperature, and CO₂ (30 atm) was introduced into the reactor and then the mixture was heated up to the desired temperature. The reaction was started by stirring the mixture and continued for 1 h. After the reaction, the pressure was released and the product was quenched with ice-water and analyzed by NMR and GC-MS spectroscopy. The yields of carbonates were determined by GC using 1-methyl-2-pyrrolidinone as an internal standard. Under reaction conditions we studied, carbonate was the main product with trace amounts of a few byproducts.¹⁶

The results in Table I show that our concept of using ionic liquid both as a solvent as well as a catalyst works pretty well. Even though DMF was used in the same way in the production of styrene carbonate under supercritical condition, the reaction conditions were much harsher (150 °C for 15 h).¹⁷ Under our reaction conditions, only 3.5% of carbonate was obtained using DMF as a solvent even with added catalyst (run 10). Depending on the alkyl groups attached to the imidazole ring, the solubilities and melting points of the ionic liquid change significantly.¹⁸ When symmetrically substituted 1,3-dimethylimidazolium iodide ([C₁mim][I]),

Table I. Carboxylation of propylene oxide with carbon dioxide in different reaction system

Run	Catalyst	Solvent	Temp. / °C	Time / h	Yield of carbonate (%) ^a
1	None	[C ₁ mim][I]	50	1	7.9
2	None	[C ₁ mim][I]	60	1	11
3	None	[C ₁ mim][I]	70	1	85
4	None	[C ₁ mim][I]	80	1	78
5	None	[C ₁ mim][I]	30	1	5.8
6	None	[C ₁ mim][I]	40	1	26
7	None	[C ₁ mim][I]	50	1	87
8	None	[C ₁ mim][I]	60	1	86
9 ^b	ZnI ₂	[C ₁ mim][I]	40	1	100
10 ^c	ZnI ₂	DMF	40	1	3.5
11 ^d	Cr(III) Salen	DMA/CH ₂ Cl ₂	75	1.5	100
12 ^e	Mg-Al mixed oxide	DMF	120	24	88

^aThe yields are determined by GC analysis based on the area ratio of 1-methyl-2-pyrrolidinone as an internal reference. ^bZnI₂ (0.4 mmol) was added. ^cZnI₂ (0.4 mmol) and DMF (10 g) were added. ^dRef. 5. ^eRef. 4.

which is solid at room temperature, was used as a solvent, it does not become homogeneous until the reaction temperature goes above 70 °C (runs 1–4), but only acts as a solid catalyst dissolved in neat propylene oxide at low temperatures. In case of asymmetrically substituted 1-butyl-3-methylimidazolium iodide ([C₄mim][I]), which is liquid at room temperature, it can act as a solvent even at 40 °C. At higher temperatures, decrease in solubility of CO₂ in ionic liquid might play a role, since the reactant concentration is quite high (almost 40 M) under our reaction conditions. Whichever ionic liquid was used as a solvent, the yields are quite high and reaction conditions are extremely mild considering that no metallic catalysts have been used. Previous reports on synthesis of cyclic carbonates from CO₂ and epoxides suggest the parallel requirement of both Lewis-base-activation of the CO₂ and Lewis-acid-activation of the epoxide.^{4,6} Lewis basic activation of the CO₂ by iodide ion has been well understood. Therefore, adding simple Lewis acidic catalysts such as ZnI₂ can improve the reaction rate significantly (run 9). Without any sophisticated ligand, this catalyst system gives high turnover frequencies of almost 1000 h⁻¹.

Remaining reactants and products are both easily removed from the reaction mixture *via* distillation, completely eliminating the use of organic solvent.

In summary, this catalyst system is highly efficient toward the coupling of carbon dioxide with epoxides at mild temperatures. Also it represents an air stable, easily synthesized catalyst system for CO₂ fixation which requires no organic solvent.

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