

Coupling Reaction of CO₂ with Epoxides by Binary Catalytic System of Lewis Acids and Onium Salts

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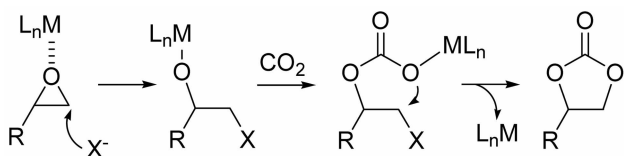
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Various off-the-shelf Lewis acids in conjunction with various onium salts are screened for coupling reaction of CO₂ with epoxides. Among the tested ones, VCl₃/*n*-Bu₄NOAc, VCl₃/(*n*-Bu₄NCl or PPnCl), FeCl₃/*n*-Bu₄NOAc, and AlCl₃/*n*-Bu₄NOAc are proved to be highly active. Propylene oxide, epichlorohydrin, styrene oxide, and cyclohexene oxide can be converted over 90% yields to the corresponding cyclic carbonates without the use of organic solvents under mild conditions by 0.1–1.0 mol% catalyst charge.

Key Words : Cyclic carbonate, Carbon dioxide, Epoxide, Coupling reaction

Introduction

CO₂ is abundant, inexpensive and nontoxic and development of chemistry utilizing CO₂ as a feedstock is currently hot research field.¹ The materials² or the compounds³ that are able to capture or bind CO₂ have drawn attention recently. The most promising methodology is transformation of CO₂ by coupling with epoxides into polycarbonates⁴ or cyclic carbonates which can be used as valuable chemicals.⁵ Various catalyst systems have been reported for transformation of CO₂ to the cyclic carbonates.⁶ Either organic compounds such as onium salts,⁷ bases,⁸ ionic liquids⁹ and DMF¹⁰ or metal complexes such as Re(CO)₅Br and lanthanide oxychloride¹¹ were reported to be able to act singly as a catalyst under some severe conditions. Binary systems composed of a metal complex such as ZnBr₂,¹² Al porphyrin,¹³ Co(III) porphyrin,¹⁴ or Cr(III) salen complexes¹⁵ and a organic base have been reported to show high activity under mild conditions. It has been proposed that the metal complex acts as a Lewis acid to which the epoxide coordinates for allowing the nucleophilic attack of the Lewis base. Binary system composed of *n*Bu₄Nl, instead of organic base, and ZnCl₂ was reported two decades ago.¹⁶ Recently, similar binary systems composed of onium halide and metal complex such as ZnBr₂,¹⁷ InCl₃¹⁸ or Ni(PPh₃)₂Cl₂/Ph₃Zn¹⁹ have been reported. The binary system of Co(III) salen complex in conjunction with quaternary ammonium salt was also reported to be very effective for the formation of polycarbonate by the coupling of CO₂ with propylene oxide.²⁰ It was proposed that the halide ion in the onium salt attacks the epoxide coordinated on the Lewis acidic metal (Scheme 1).



Scheme 1. Proposed Mechanism for Coupling Reaction of CO₂ with Epoxide.

These reports prompted us to screen various off-the-shelf Lewis acids in conjunction with various onium salts in the hope of finding a more efficient binary catalyst.

Results and Discussion

Various metal complexes which can potentially act as a Lewis acid are screened for the coupling reaction of CO₂ with propylene oxide under the conditions of 35 °C, 15 bar of CO₂ pressure, and 3 hour reaction time with 0.33 mol% charges of the metal complex and *n*-Bu₄NOAc without the use of any organic solvents. The conversions can be easily measured by the ¹H NMR spectroscopy. Among the tested Lewis acids, FeCl₃, AlCl₃, and VCl₃ give good result (Figure 1). Either the metal complex or the ammonium acetate alone shows negligible activity under the same conditions or at high temperature such as 90 °C. The combinations of HfCl₄(THF)₃/*n*-Bu₄NOAc, ZnCl₂/*n*-Bu₄NOAc, Al(OiPr)₃/*n*-Bu₄NOAc, Ti(OiPr)₃/*n*-Bu₄NOAc, La(OTf)₃/*n*-Bu₄NOAc, CeCl₃/*n*-Bu₄NOAc, CoCl₂/*n*-Bu₄NOAc, BF₃(OEt₂)/*n*-Bu₄NOAc, and B(C₆F₅)₃/*n*-Bu₄NOAc do not show any activity

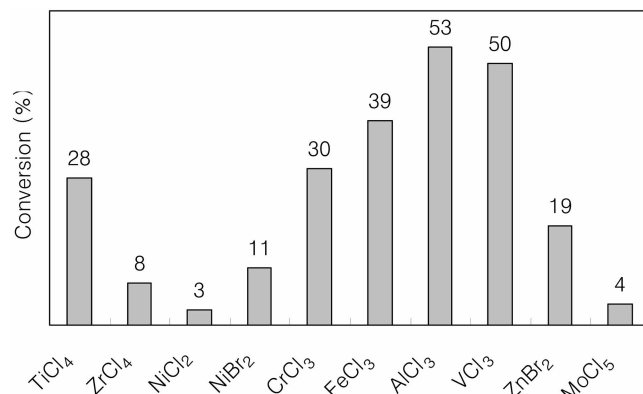


Figure 1. Conversion of propylene oxide to cyclic carbonate by (metal halide)/*n*-Bu₄NOAc systems (conditions: propylene oxide (7.0 mL, 100 mmol, neat), metal complex (0.33 mol%), *n*-Bu₄NOAc (0.33 mmol), *T* = 35 °C, *P*_(CO₂) = 15–10 bar, time = 3 hours).

under the same conditions. A binary catalyst system based on nickel ($\text{Ni}(\text{PPh}_3)_2\text{Cl}_2/\text{Ph}_3\text{Zn}/n\text{-Bu}_4\text{NBr}$) was reported to show high activity under rather severe conditions (2.5 MPa CO_2 pressure and 120 °C)¹⁹ but $\text{NiCl}_2/n\text{-Bu}_4\text{NOAc}$ and $\text{NiBr}_2/n\text{-Bu}_4\text{NOAc}$ show low activity in our reaction conditions (3 and 11%, respectively). Various Zn or Co-based catalyst systems were reported but the $\text{ZnCl}_2/n\text{-Bu}_4\text{NOAc}$ and $\text{CoCl}_2/n\text{-Bu}_4\text{NOAc}$ systems do not show any activity. The $\text{ZnBr}_2/n\text{-Bu}_4\text{NOAc}$ shows moderate activity (19% conversion). Aluminum-based catalysts are popular in the coupling reaction and the $\text{AlCl}_3/n\text{-Bu}_4\text{NOAc}$ system also shows good activity. Vanadium-based catalysts have not been reported yet but, in this study, it is first demonstrated that $\text{VCl}_3/n\text{-Bu}_4\text{NOAc}$ is able to act as a good catalyst for the coupling reaction.

Table 1 shows the effect of onium salts on the conversions. For AlCl_3 and FeCl_3 , the highest conversions are observed with $n\text{-Bu}_4\text{NOAc}$. Effect of the counter anion of the tetrabutylammonium salt is dramatic. For AlCl_3 , the activity increases from 1% to 14% and 20% as the counter anion of the tetrabutylammonium salt is changed from Cl to Br and I⁻, respectively. The trend is opposite for FeCl_3 and VCl_3 and the $n\text{-Bu}_4\text{NCl}$ gives better conversions than $n\text{-Bu}_4\text{NI}$. In case of VCl_3 , addition of $n\text{-Bu}_4\text{NCl}$ or PPNCl results in better activity than the addition of $n\text{-Bu}_4\text{NOAc}$. The $\text{VCl}_3/\text{PPNCl}$ gives the highest conversion among the binary systems screened in this work (73%). The binary systems based on bulky imidazolium chloride and NaOAc show low activity.

The newly discovered catalyst systems, $\text{FeCl}_3/n\text{-Bu}_4\text{NOAc}$, $\text{AlCl}_3/n\text{-Bu}_4\text{NOAc}$, $\text{VCl}_3/n\text{-Bu}_4\text{NOAc}$ and $\text{VCl}_3/(n\text{-Bu}_4\text{NCl}$ or $\text{PPNCl})$ are tested for the coupling reaction of various epoxides. The studies are focused on finding the reaction conditions that gives high conversion (>90%) without the use of organic solvents. The reactor containing epoxide and catalyst is pressurized with CO_2 gas to 15 bar and the reaction is monitored by the pressure drop. When the pressure drop ceases, the remained CO_2 gas is vented and an aliquot is taken for the ^1H NMR analysis. When the reaction temper-

ature is increased to 90 °C, high conversions of propylene oxide to cyclic carbonate are attained in 4 hours by the catalyst systems of $\text{FeCl}_3/n\text{-Bu}_4\text{NOAc}$, $\text{AlCl}_3/n\text{-Bu}_4\text{NOAc}$, and $\text{VCl}_3/n\text{-Bu}_4\text{NOAc}$ (90, 86, and 98%, respectively). Complete conversion is achieved in 5 hours at 120 °C by 0.33 mol% charge of the $\text{VCl}_3/n\text{-Bu}_4\text{NCl}$ (entry 4 in Table 2).

Styrene oxide was reported to be a sluggish substrate for the coupling reaction.^{9c,17} By the 0.33 mol% catalyst charge of the $\text{VCl}_3/n\text{-Bu}_4\text{NOAc}$, the CO_2 consumption ceases after 11 hours but the conversion is only 67%. By the addition of more catalyst (1.0 mol% of $\text{VCl}_3/n\text{-Bu}_4\text{NOAc}$), almost complete conversion (95%) is achieved in 3 hours (entry 6). Nearly quantitative conversions (98 and 96%) are also obtained by 1.0 mol% charge of $\text{FeCl}_3/n\text{-Bu}_4\text{NOAc}$ or $\text{AlCl}_3/n\text{-Bu}_4\text{NOAc}$ but the reaction rates are slower than that observed for the $\text{VCl}_3/n\text{-Bu}_4\text{NOAc}$ (entries 7 and 8). Five and seven hours instead of 3 hours are required to attain the same conversion. The $\text{VCl}_3/n\text{-Bu}_4\text{NCl}$ and $\text{VCl}_3/\text{PPNCl}$ systems are more robust and conversions of 90% and 85% are obtained at 120 °C by the addition of only 0.33 mol% catalyst (entries 9 and 10).

Epichlorohydrin shows higher rate for the coupling reaction than the propylene oxide when the $\text{VCl}_3/n\text{-Bu}_4\text{NOAc}$ is employed as a catalyst. The CO_2 consumption ceases in 2 hours at 90 °C when 0.33 mol% catalyst is charged but viscous solution is obtained indicating formation of some polymers. In the ^1H NMR spectrum of the solution, no epichlorohydrin signals are observed, but the signals of the desired cyclic carbonate are observed along with some unassignable signals. The cyclic carbonate is isolated by flash vacuum distillation and 78% selectivity for the cyclic carbonate is calculated by the weight of the distillate. It is not easy to assign unambiguously the signals in the ^1H NMR spectrum of the oily residue remained in the distillation pot. The $\text{FeCl}_3/n\text{-Bu}_4\text{NOAc}$ and $\text{AlCl}_3/n\text{-Bu}_4\text{NOAc}$ are sluggish for the transformation and 8 hours are required for moderate conversion (76 and 84%, respectively). At the more severe conditions (0.1 mol% catalyst charge and 120 °C), the $\text{VCl}_3/n\text{-Bu}_4\text{NOAc}$ gives high conversion (84%) in 8 hours. In this condition, only the cyclic carbonate is generated. The 90% conversion is attained at 120 °C in 16 hours with 0.1 mol% charge of the $\text{VCl}_3/\text{PPNCl}$ (entry 15).

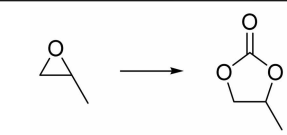
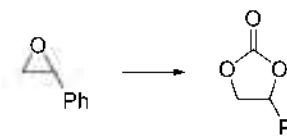
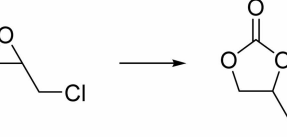
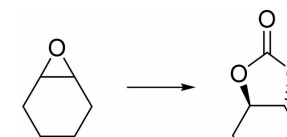
The disubstituted epoxide, cyclohexene oxide is as sluggish as styrene oxide and moderate conversions are attained at 90 °C when 0.33 mol% catalyst of $\text{VCl}_3/n\text{-Bu}_4\text{NOAc}$, $\text{AlCl}_3/n\text{-Bu}_4\text{NOAc}$ or $\text{FeCl}_3/n\text{-Bu}_4\text{NOAc}$ is added (entries 16-18). In case of $\text{VCl}_3/n\text{-Bu}_4\text{NOAc}$, very viscous solution is obtained, which indicates formation of some polymers (equation 1). In the ^1H NMR spectrum of the solution, a sharp cyclic carbonate OCH signal is observed at 4.54-4.80 ppm overlapped with a broad signal, which is assignable to the polycarbonate. The polymer is isolated by precipitation in methanol. The ^1H NMR analysis of the precipitated polymer indicates that it is nearly alternating copolymer of cyclohexene oxide and CO_2 (carbonate linkage, 89%). The selectivity for the cyclic carbonate over the polycarbonate

Table 1. Effect of Onium Salt on the Conversion of Propylene Oxide to the Cyclic Carbonate^a

	[Imidazolium]Cl = $\text{Ar}'\text{-N}^+\text{(C}_5\text{H}_4\text{N)}\text{-Ar}'$ ($\text{Ar}' = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$)		
	AlCl_3	FeCl_3	VCl_3
$n\text{-Bu}_4\text{NOAc}$	39% ^b	53%	50%
$n\text{-Bu}_4\text{NCl}$	1%	32%	68%
$n\text{-Bu}_4\text{NBr}$	14%	17%	30%
$n\text{-Bu}_4\text{NI}$	20%	10%	11%
[Imidazolium]Cl	7%	15%	23%
PPNCl	2%	14%	73%
NaOAc	0%	7%	10%

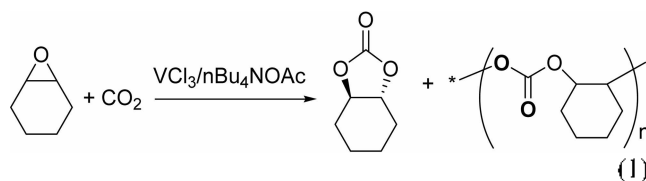
^aConditions: propylene oxide (7.0 mL, 100 mmol, neat), MCl_3 (0.33 mol%), onium salt (0.33 mmol), $T = 35$ °C, $P_{(\text{CO}_2)} = 15\text{-}10$ bar, time = 3 hours. Conversion measured by the ^1H NMR spectrum.

Table 2. Coupling Reaction of CO₂ with Various Epoxides^a

Entry	Catalyst	Temperature (°C)	Time (h)	Conversion (%)
				
1	VCl ₃ / <i>n</i> -Bu ₄ NOAc	90	4	98
2	FeCl ₃ / <i>n</i> -Bu ₄ NOAc	90	4	90
3	AlCl ₃ / <i>n</i> -Bu ₄ NOAc	90	4	86
4	VCl ₃ / <i>n</i> -Bu ₄ NCl	120	5	100
				
5	VCl ₃ / <i>n</i> -Bu ₄ NOAc	90	11	67
6	VCl ₃ / <i>n</i> -Bu ₄ NOAc ^b	90	3	95
7	FeCl ₃ / <i>n</i> -Bu ₄ NOAc ^b	90	5	98
8	AlCl ₃ / <i>n</i> -Bu ₄ NOAc ^b	90	7	96
9	VCl ₃ / <i>n</i> -Bu ₄ NCl	120	11	90
10	VCl ₃ /PPNCl	120	17	85
				
10	VCl ₃ / <i>n</i> -Bu ₄ NOAc	90	2	100 (78) ^d
11	FeCl ₃ / <i>n</i> -Bu ₄ NOAc	90	8	76
12	AlCl ₃ / <i>n</i> -Bu ₄ NOAc	90	8	84
13	VCl ₃ / <i>n</i> -Bu ₄ NOAc ^c	120	8	84
14	VCl ₃ / <i>n</i> -Bu ₄ NCl ^c	120	10	68
15	VCl ₃ /PPNCl ^c	120	16	90
				
16	VCl ₃ / <i>n</i> -Bu ₄ NOAc	90	15	56 (79) ^d
17	FeCl ₃ / <i>n</i> -Bu ₄ NOAc	90	19	77
18	AlCl ₃ / <i>n</i> -Bu ₄ NOAc	90	17	42
19	VCl ₃ / <i>n</i> -Bu ₄ NCl	120	19	100
20	VCl ₃ /PPNCl	120	19	95

^aConditions: substrate (7.0 mL), catalyst (0.33 mol%), $P_{(\text{CO}_2)}$ 15–10 psig. ^b1.0 mol% catalyst. ^c0.1 mol% catalyst. ^dThe value in the parenthesis is selectivity for the cyclic carbonate over the polymer.

calculated by the weight of the precipitated polymer and the integration value in the ¹H NMR spectrum is 79%. The molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the precipitated polymer determined on GPC are 3900 and 1.1, respectively. When the reaction is carried out at 120 °C with VCl₃/*n*-Bu₄NCl or VCl₃/PPNCl, almost complete conversion is achieved (entries 19–20). No polymers are generated in these conditions.



Conclusion

Various Lewis acids in conjunction with *n*-Bu₄NOAc are screened to select new efficient binary catalytic systems for coupling reaction of CO₂ with epoxide. The AlCl₃, VCl₃ and FeCl₃ are selected by the screening and the effect of onium salts on the conversion is studied with the three metal complexes by changing *n*-Bu₄NOAc with various onium salts. In cases of AlCl₃ and FeCl₃, the *n*-Bu₄NOAc is proved to be the best choice among the tested onium salts while VCl₃ gives more efficient binary catalyst when combined with *n*-Bu₄NCl or PPNCl. The propylene oxide, epichlorohydrin, styrene oxide, and cyclohexene oxide can be converted to the corresponding cyclic carbonates over 90% yields by 0.1–1.0 mol% charge of the selected binary catalysts without the use of organic solvents.

Experimentals

Typical procedure for the coupling reaction. The CO₂ gas (99.99%) was purified by passing through a column containing molecular sieves. All epoxides were dried by stirring over CaH₂ and it was transferred under the vacuum to a reservoir. Metal complex (0.33 mol%), onium salt (0.33 mol%) and epoxide (7.0 mL) were added in a reactor (50 mL) inside glovebox. After the reactor was assembled, it was brought out from the glovebox. The reactor was pressurized to 15 bar and heated to the desired temperature. When the pressure was dropped below 10 bar, additional CO₂ gas was charged to 15 bar. When the pressure drop ceased, the CO₂ gas was vented and the conversion was measured by the ¹H NMR analysis of the solution.

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