Chemical fixation of carbon dioxide to cyclic carbonates under extremely mild conditions with highly active bifunctional catalysts

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Abstract

Chemical fixation of carbon dioxide to cyclic carbonates proceeds effectively under extremely mild temperature and pressure by using a bifunctional nucleophile–electrophile catalyst system of tetradentate Schiff-base aluminum complexes ((Salen)AlX) in conjunction with a quaternary ammonium salt (n-Bu$_4$NY) in the absence of any organic solvent. Electrophilicity of central Al^{3+} ion and the steric factor of substituent groups on the aromatic rings of (Salen)AlX (electrophile), and nucleophilicity and leaving ability of the anion Y$^-$ of n-Bu$_4$NY (nucleophile) have a great effect on the catalytic activity of the bifunctional catalyst.
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1. Introduction

Chemical fixation of CO$_2$ is of great interest in connection with the development of a truly environmentally benign process, since there are many possibilities for CO$_2$ to be used as a safe and cheap C$_1$ building block in organic synthesis [1,2]. One of the most promising methodologies in this area is the synthesis of five-membered cyclic carbonates via the coupling of CO$_2$ and epoxides (Scheme 1) [3]. These carbonates can be used as aprotic polar solvents and as precursors for polycarbonates and other polymeric materials [4]. In recent decades, numerous catalyst systems including amines [5], phosphines [6], quaternary ammonium salts [7,8], polyfluoroalkyl phosphonium iodides [9], ionic liquids [10–13], alkali metal salts alone [14], or in combination with crown ethers [15], halostannanes [16], organoantimony halide [17,18], MgO [19] or Mg–Al mixed oxides [20], solid base [21–23], porphyrin [24–26], phthalocyanine [27–29] and transition-metal complexes [30–33], have been developed for this transformation. Although the advances have been significant, these catalysts all currently suffer from low catalyst reactivity, the need for co-solvent, or the requirement for high pressure and/or high temperature. The

exploration of highly efficient catalysts for coupling CO$_2$ with epoxides under low temperature and low CO$_2$ pressure still remains a challenging problem, though organometallic Pd(0) complexes have been demonstrated to be effective in coupling CO$_2$ with the much higher reactivity of vinyl epoxides under mild conditions [34,35].
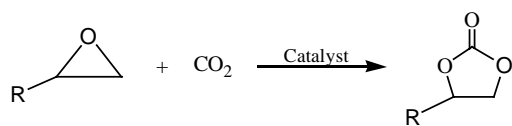
In previous work [36], we report a new highly active SalenAlCl–quaternary ammonium bromide (n-Bu$_4$NBr) catalyst system for the synthesis of ethylene carbonate from supercritical CO$_2$–ethylene oxide mixture. Further study indicates that the bifunctional catalyst also catalyze effectively the coupling reaction under extremely mild temperature and pressure. In this paper, we extend our research to reveal the structure–activity relationship of the bifunctional catalyst and further propose a reasonable design principle of the coupling catalysts. Our principal interests focus on two features: the effects of: (1) electrophilicity of central Al^{3+} ion and the steric factor of substituent groups on the aromatic rings of (Salen)AlX (electrophile), and (2) nucleophilicity and leaving ability of the anion Y$^-$ of n-Bu$_4$NY (nucleophile) on the catalytic activity of the bifunctional catalyst.

2. Experimental

Propylene oxide, ethylene oxide and 1,2-butene oxide were refluxed over a mixture of KOH and CaH$_2$,

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Scheme 1.

1a: $R_1 = R_2 = H$, X = Cl
1b: $R_1 = R_2 = H$, X = Et
1c: $R_1 = $ t-Bu, $R_2 = H$, X = Et
1d: $R_1 = R_2 = $ t-Bu, X = Et
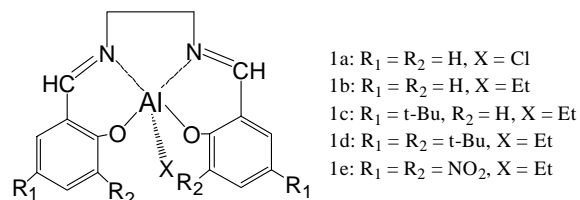1e: $R_1 = R_2 = NO_2$, X = Et

Scheme 2.

and fractionally distilled under a nitrogen atmosphere. Epichlorohydrin was refluxed over CaH_2 and fractionally distilled under a nitrogen atmosphere. Other epoxides were used as received from Acros Company. CO_2 was purified by passing through a column packed with 4 Å molecular sieve before use.

Triethylaluminum (Et_3Al) and chlorodiethylaluminum (Et_2AlCl) were fractionally distilled under reduced pressure in a nitrogen atmosphere.

The Schiff-base aluminum complexes (((Salen)AlX) were prepared by the reaction of the corresponding free bases with Et_3Al or Et_2AlCl according to the literature methods with slight modification [36–40]. These complexes are all sensitive to air or moisture and should be stored in a nitrogen atmosphere.

The coupling reaction of CO_2 and epoxides was carried out in a 50 ml stainless steel autoclave equipped with a magnetic stirrer. In a typical procedure, to a Schlenk-flask (50 ml) equipped with a three-way stop cock were successively added (Salen)AlX (0.24 mmol) and n-Bu$_4$NY (0.24 mmol) under dry nitrogen, and then epoxide (192 mmol) by means of a hypodermic syringe in a nitrogen atmosphere. When the catalysts were completely dissolved, the mixture solution was charged into the autoclave via a syringe in a CO_2 atmosphere. The autoclave was put into a bath and heated to the desired temperature. Then, CO_2 was charged into the autoclave and the pressure was kept constant during the reaction. After the expiration of the desired time, the excess gases were vented. The remainder mixture was degassed and fractionally distilled under reduced pressure for obtaining pure cyclic carbonates.

The conversions of propylene oxide, ethylene oxide and 1,2-butene oxide to corresponding cyclic carbonates were analyzed on a model 103 gas chromatograph made by Shanghai Analytic Instrument Factory, with butyl acetate as an internal standard. The conversions of other epoxides were determined by comparing the ratio of product to substrate in the [^{1}H] NMR spectrum of an aliquot of the reaction mixture (Varian INOVA-400 type spectrometer at 399.7 MHz). The [^{1}H] NMR (CDCl$_3$/TMS) data of these cyclic carbonates are listed as follows: ethylene carbonate: δ 4.51 (s, 4H); propylene carbonate: δ 1.49 (d, 3H), 4.02 (t, 1H), 4.55 (t, 1H), 4.85 (q, 1H); 1,2-butene carbonate: δ 1.03 (t, 3H), 1.80 (d, 1H), 4.17 (t, 1H), 4.55 (t, 1H), 4.70 (d, 1H); chloropropylene carbonate: δ 3.73–3.83 (m, 2H), 4.42 (q, 1H), 4.61 (t, 1H), 5.00 (m, 1H); phenyl ethylene carbonate: δ 4.28 (t, 1H), 4.74 (t, 1H), 5.62 (t, 1H), 7.3–7.4 (m, 5H); 4-(phenoxymethyl)-1,3-dioxolan-2-one: δ 4.12–4.16 (m, 2H), 4.52–4.63 (m, 2H), 5.02 (q, 1H), 6.90–7.33 (m, 5H, Ar).

3. Results and discussion

Since (Salen)AlX complexes and n-Bu$_4$NY shown in Scheme 2 and Table 1 are easily dissolved in neat epoxides surveyed, the catalyzed coupling of CO_2 and epoxides requires no organic co-solvent. Our initial studies showed that complex **1a** successfully catalyzed the coupling of CO_2 and propylene oxide (PO) in the presence of quaternary ammonium halides (Table 1 entries 3, 11, 12). No by-product such as polycarbonates or polyester was observed in the obtained products. However, in the absence of the quaternary ammonium salt, the polycarbonates (1733 cm^{-1} in FTIR spectrum) and propylene carbonate were formed with a very low rate at room temperature. For complex **1b** as catalyst alone, neither propylene carbonate nor polymer formed. It is important to note that these quaternary ammonium halides by themselves showed only very low catalytic

Table 1
Coupling of CO_2 and propylene oxide catalyzed by the (Salen)AlX–quaternary ammonium salt system under various conditions[a]

Entry	Catalyst (Salen)AlX	Co-catalyst n-Bu$_4$NY	Temperature (°C)	TOF[b] (h^{-1})
1	**1a**	-	25	<0.1[c]
2	**1b**	-	25	0
3	**1a**	n-Bu$_4$NI	25	61.5
4	**1b**	n-Bu$_4$NI	25	55.9
5	–	n-Bu$_4$NCl	25	<0.1
6	–	n-Bu$_4$NBr	25	0.3
7	–	n-Bu$_4$NI	25	0.7
8	**1a**	n-Bu$_4$NI	0	18.5
9	**1a**	n-Bu$_4$NI	15	33.4
10	**1a**	n-Bu$_4$NI	35	84.2
11	**1a**	n-Bu$_4$NCl	25	34.5
12	**1a**	n-Bu$_4$NBr	25	63.0
13	**1a**	n-Bu$_4$NNO$_3$	25	<0.1
14	**1a**	n-Bu$_4$NClO$_4$	25	0.2
15	**1a**	n-Bu$_4$NOTs	25	<0.1
16	**1a**	n-Bu$_4$NBF$_4$	25	0.3
17	**1a**	n-Bu$_4$NCH$_3$COO	25	2.9[c]
18	**1a**	18-crown-6–KI	25	57.9
19	**1c**	n-Bu$_4$NI	25	16.0
20	**1d**	n-Bu$_4$NI	25	8.9
21	**1e**	n-Bu$_4$NI	25	51.0

[a] Reaction conditions: (Salen)AlX = 2.40×10^{-4} mol, (Salen)AlX/n-Bu$_4$NY/epoxide = 1/1/800 (molar ratio), $p(CO_2) = 0.60$ MPa, $t = 8$ h.
[b] The rate is expressed in terms of the turnover frequency (TOF (mol of product (mol of catalyst h)$^{-1}$) = turnovers/h).
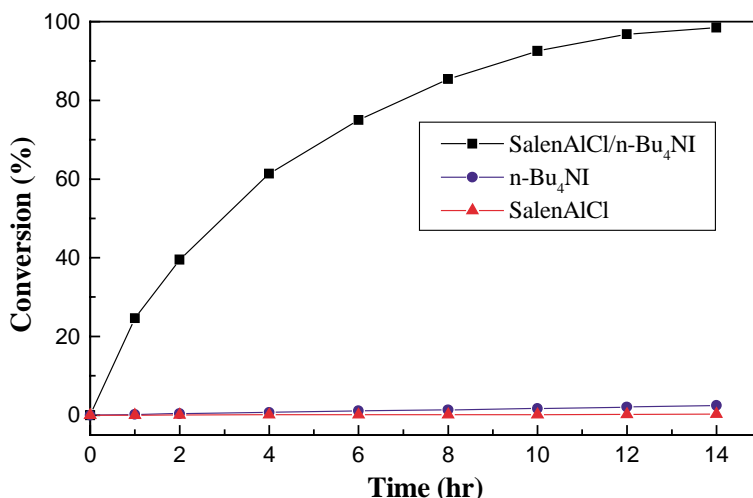[c] Polycarbonates was also produced with a very low formation rate.

Fig. 1. Conversion of propylene oxide to propylene carbonate at 0.6 MPa CO_2 pressure and 25 °C as a function of time (catalyst/propylene oxide = 1/400, molar ratio).

activity under the employed conditions. A rate conversion profile for the transformation of neat PO to the corresponding cyclic carbonate (Fig. 1) indicates that the complex **1a**–n-Bu$_4$NI system showed a 80–100-fold conversion rate over n-Bu$_4$NI and 500–1000-fold rate enhancement over complex **1a**. The results indicate a synergistic effect in the formation of propylene carbonate from CO_2 and propylene oxide by using the catalytic system of (Salen)AlX in conjunction with a quaternary ammonium halide. An investigation on the mechanism of the activation of CO_2 and epoxides in the presence of the bifunctional catalyst is now in progress by means of in situ FTIR and NMR methods.

The bifunctional catalyst system can operate very efficiently at low temperature of 0 °C and low CO_2 pressure of atmospheric. The enhancement of temperature had a pronounced positive effect on the rate (Table 1 entries 8–10). However, increasing the pressure beyond 0.6 MPa only resulted in a slight increase in activity (Fig. 2).

The anion of n-Bu$_4$NY significantly affected the catalytic activities of the bifunctional catalysts (Table 1 entries
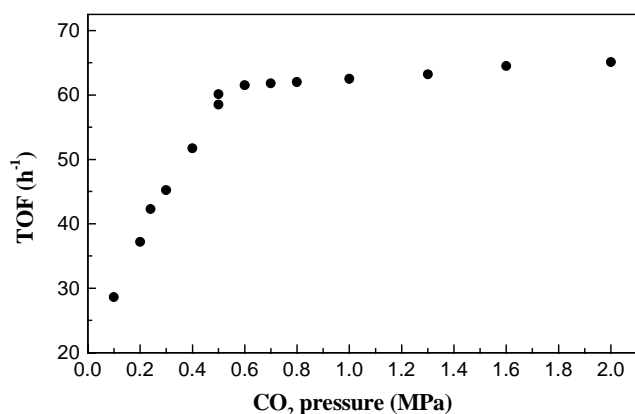
Table 2
Coupling of CO_2 and various epoxides catalyzed by complex **1a**–n-Bu$_4$NI system[a]

Substrate	Time (h)	Product	TON[b]	TOF (h^{-1})
2a	8		492	61.5
2b	5		434	86.8
2c	15		198	13.2
2d	8		410	51.2
2e	15		228	15.1
2f	2[c]		97	48.5

[a] Reaction conditions: **1a** (78.8 mg, 2.40 × 10^{-4} mol), **1a**/n-Bu$_4$NI/epoxide = 1/1/800 (molar ratio); $p(CO_2)$ = 0.60 MPa; temperature, 25 °C; conversion of epoxides (**2c**, **2d**, **2e** and **2f**) to corresponding cyclic carbonates was determined by comparing the ratio of product to substrate in the [^{1}H] NMR spectrum of an aliquot of the reaction mixture.
[b] Moles of cyclic carbonate produced per mole of catalyst.
[c] Ice-cream like semi-solid appeared in the system after the reaction proceeded for about 2 h.

Fig. 2. Effect of CO_2 pressure on the coupling of CO_2 and propylene oxide catalyzed by the complex **1a**–n-Bu$_4$NI system at 25 °C.

11–17). Essentially, only these catalyst systems comprising quaternary ammonium halide showed a considerably high activity, probably because halide anions have moderate nucleophilicity and high leaving ability. With 18-crown-6–KI complex as co-catalyst, a similar reactivity was observed under the same condition. Although acetate anion has higher nucleophilicity, complex **1a**–n-Bu$_4$NCH$_3$COO system showed very low activity probably resulting from low leaving ability of the anion. When the anion of n-Bu$_4$NY without any nucleophilicity, such as perchlorate and p-toluene-sulfonate, has high leaving ability, **1a**–n-Bu$_4$NY catalyst systems showed either no or very low activity.

Several (Salen)AlX complexes (**1a**–**e**) with varying substituent groups on the aromatic rings were investigated as catalysts for the coupling of CO_2 and PO (Table 1 entries 3, 4, and 19–21). Complex **1a** exhibited the highest catalytic activity of all the catalysts and is at least six times as active as complex **1d**. The order of the activity is **1a** > **1b** > **1e** > **1c** > **1d**, which is not consistent with the order of electrophilicity of these aluminum complexes: **1e** > **1a** > **1b** > **1c** > **1d**. The results indicate that the electrophilicity of central Al^{3+} ion and the steric factor of (Salen)AlX all significantly affect the catalytic properties.

The catalyst system was found to be applicable to a variety of terminal epoxides, providing the corresponding cyclic carbonates in high rates and 100% selectivity (Table 2). Ethylene oxide **2b** was found to be the most reactive epoxide, while styrene oxide **2e** and epichlorohydrin **2c** exhibited relatively low activity among the epoxides surveyed.

4. Conclusion

In summary, (Salen)AlX accompanied with a quaternary ammonium halide is highly efficient catalyst in the coupling of CO_2 with epoxides under extremely mild temperature and pressure. The structure–activity relationship of the bifunctional catalyst reveals an important design principle of catalyst for this coupling reaction, in which moderate electrophilicity and nucleophilicity as well as high leaving ability of nucleophile should be emphasized.

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