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Research Note

Highly active electrophile–nucleophile catalyst system for the cycloaddition of CO_2 to epoxides at ambient temperature

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Abstract

The cycloaddition of CO_2 to epoxides proceeds effectively under extremely mild temperatures and pressures by using a bifunctional catalyst system of tetradentate Schiff-base aluminum complexes (SalenAlX) as electrophile in conjunction with polyether–KY complexes as nucleophile. The steric factor of the substituent groups on the aromatic rings of SalenAlX and the nucleophilicity and leaving ability of the anion Y^{-1} of polyether–KY complexes all have great effects on the activity of the bifunctional catalyst system. The reaction of CO_2 with (*S*)-propylene oxide in the presence of the SalenAlEt/18-crown-6–KI catalyst system gives (*S*)-propylene carbonate in $> 99\%$ ee with retention of stereochemistry.

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Keywords: Carbon dioxide; Epoxide; Cyclic carbonate; Cycloaddition; Salen–aluminum complexes; 18-crown-6; KI; Synergistic effect

1. Introduction

Conversion of carbon dioxide to industrially useful compounds has received much attention because of its potential use as an abundant carbon source and its indirect role as an environmental pollutant [1]. One of the most promising reactions in this area is the synthesis of five-membered cyclic carbonates via the cycloaddition of CO_2 to epoxides [2]. These carbonates can be used as aprotic polar solvents and as precursors for polycarbonates and other polymeric materials [3]. In recent decades, numerous catalyst systems, including amines [4], quaternary ammonium or phosphonium salts [5,6], ionic liquids [7], alkali metal salts alone [8] or in combination with crown ethers [9], halostannanes [10], organoantimony halide [11], MgO [12] or Mg–Al mixed oxides [13], solid base [14,15], porphyrin [16,17], phthalocyanine [18], and transition-metal complexes [19], have been developed for this transformation. While the advances have been significant, all suffer from low catalyst reactivity, the need for cosolvent, or the requirement for high pressure and/or high temperature. Very recently, some highly efficient catalyst systems have been reported to give excellent activity, but they usually exhibit no or very low catalytic activity at ambient temperature [20–22]. For example, for a recently reported catalyst system, Cr(III)Salen/DMAP, which operated at 100 psig CO_2 pressure, the decrease of reaction temperature from 75 to 25 °C resulted in TOF from 254 h^{-1} rapidly decreasing to 3 h^{-1} [20]. Therefore, the exploration of highly efficient catalysts for coupling CO_2 with epoxides under low temperatures 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 [23,24]. The key to accomplishing this goal is the rational design of improved catalysts based on a mechanistic understanding. A general pattern in the reaction of CO_2 with epoxides has emerged wherein catalysis involves activation of both epoxides and CO_2 [13]. Our recent research found that the synergistic actions of an electrophile (SalenMX complexes) in conjunction with a nucle-

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ophile (quaternary ammonium salts) were more effective in catalyzing this reaction [25].

In the present paper, we report a new bifunctional catalyst system based on polyether–KY complexes as nucleophile and tetradentate Schiff-base aluminum complexes (SalenAlX) with varying diamine backbones, or/and the axial X group or/and substitute groups on the aromatic rings, as electrophile for cooperatively catalyzing the cycloaddition of CO_2 to epoxides, and further elucidating the structure–activity relationship and synergistic mechanism of the bifunctional catalyst system.

2. Experimental

2.1. Chemicals

Propylene oxide, ethylene oxide, and 1,2-butene oxide were refluxed over a mixture of KOH and CaH_2, and fractionally distilled under a nitrogen atmosphere. Epichlorohydrin was refluxed over CaH_2 and fractionally distilled under a nitrogen atmosphere. (*S*)-Propylene oxide and 1,2-hexene oxide were used as received from Acros Company. *trans*-Deuterio-1,2-hexene oxide was synthesized according to the literature [26,27]. 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. $(1R,2R)$-N,N'-bis(3,5-di-*t*-butylsalicydene)-1,2-cyclohexanediaminoaluminum chloride was used as received from Strem Company.

2.2. Catalysts preparation and characterization

The Schiff-base aluminum complexes (SalenAlX) were prepared according to the literature methods [28,29]. These complexes are all sensitive to air or moisture and should be stored in a nitrogen atmosphere. ($t-$Bu)SalenAlEt **1b**, ^1H NMR (Varian INOVA-400-type spectrometer, 400 MHz, $CDCl_3$/TMS): δ −0.37 (q, 2H, $AlCH_2CH_3$), 0.73 (t, 3H, $AlCH_2CH_3$), 1.29 (s, 18H, $C(CH_3)_3$), 3.65 (m, 2H, NCH_2), 3.95 (m, 2H, NCH_2), 6.85–7.48 (m, 6H, PhH), 8.33 (s, 2H, PhCH). (t-Bu)$_2$SalenAlEt **1c**, ^1H NMR $CDCl_3$/TMS: δ −0.38 (q, 2H, $AlCH_2CH_3$), 0.73 (t, 3H, $AlCH_2CH_3$), 1.30 (s, 18H, $C(CH_3)_3$), 1.54 (s, 18H, $C(CH_3)_3$), 3.67 (m, 2H, NCH_2), 3.93 (m, 2H, NCH_2), 6.97 (d, 2H, PhH), 7.50 (d, 2H, PhH), 8.30 (s, 2H, PhCH). SalophenAlEt **1h**, ^1H NMR $CDCl_3$/TMS: δ −0.40 (q, 2H, $AlCH_2CH_3$), 0.61 (t, 3H, $AlCH_2CH_3$), 6.77–7.71 (m, 12H, PhH), 8.79 (s, 2H, PhCH).

2.3. Cycloaddition reactions

The 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 stopcock were successively added KI (0.24 mmol), 18-crown-6 (0.24 mmol), and then propylene oxide (192 mmol) by means of a hypodermic syringe in a nitrogen atmosphere. The 18-crown-6–KI complex was formed and easily dissolved in propylene oxide, and then SalenAlEt **1a** was added under dry nitrogen. 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.

2.4. Characterization of cyclic carbonates

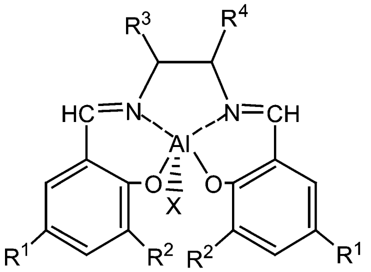
The ^1H NMR (Varian INOVA-400-type spectrometer, 400 MHz, $CDCl_3$/TMS) data of these cyclic carbonates are listed as follows: ethylene carbonate {δ 4.51 (s, 4H)}; propylene carbonate {δ 1.50 (3H, d, $J = 6.4$ Hz, CH_3), 4.05 (1H, t, $J = 8.0$ Hz, CH), 4.55 (1H, t, $J = 8.0$ Hz, CH), 4.85 (1H, m, CH)}; 1,2-butene carbonate {δ 1.03 (3H, t, $J = 7.6$ Hz, CH_3), 1.75–1.86 (2H, m, CH_2), 4.11 (1H, dd, $J = 8.4$, $J = 6.8$ Hz, CH), 4.55 (1H, t, $J = 8.2$ Hz, CH), 4.66–4.73 (1H, m, CH)}; chloropropylene carbonate {δ 3.73–3.89 (2H, m, CH_2), 4.42 (1H, dd, $J = 5.6$, $J = 5.6$ Hz, CH), 4.62 (1H, t, $J = 8.6$ Hz, CH), 5.03–5.09 (1H, m, CH)}; 1,2-hexene carbonate {δ 0.93 (3H, t, $J = 6.6$ Hz, CH_3), 1.37–1.49 (4H, m, $-CH_2CH_2-$), 1.67–1.85 (2H, m, CH_2), 4.08 (1H, t, $J = 7.6$ Hz, CH), 4.54 (1H, t, $J = 8.2$ Hz, CH), 4.68–4.75 (1H, m, CH)}.

trans-Deuterio-1,2-hexene carbonate: ^1H NMR (400 MHz, $CDCl_3$/TMS): {δ 0.93 (3H, t, $J = 6.6$ Hz, CH_3), 1.36–1.41 (4H, m, $-CH_2CH_2-$), 1.67–1.83 (2H, m, CH_2), 4.05 (1H,d, $J = 6.8$ Hz, CHD), 4.70 (1H, dd, $J = 6.4$, $J = 6.4$ Hz, CH)}; ^{13}C NMR (100 MHz, $CDCl_3$): {δ 13.95, 22.42, 26.59, 33.73, 69.24 (t, $J_{C-D} = 23.5$ Hz), 77.13, 155.26}.

The enantiomeric excesses (ee's) of the resulting propylene carbonate was determined by chiral GC analysis (GC column, 2,6-dibutyl-3-butyryl-β-Cyclodex, 30 m × 0.25 mm id × 0.25 µm film; injecton temperature = 250 °C; detection temperature = 250 °C; 160 °C, isothermal, $t_{R[(R)-PC]} = 9.37$ min, $t_{R[(S)-PC]} = 9.63$ min)) using a Hewlett Packard 5890 gas chromatograph with N_2 as a carry gas.

3. Results and discussion

Since all SalenAl(III) complexes shown in Scheme 1 and 18-crown-6–KI complexes are easily dissolved in neat epoxides surveyed, the cycloaddition of CO_2 to epoxides does not require any organic cosolvent. During our investigation, we found that the five-membered propylene carbonate could be obtained in TOF of 57.9 h^{-1} from complex **1a** (0.125 mol%) and 18-crown-6–KI (0.125 mol%) cocatalyzed reactions of



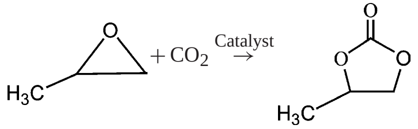
1a: $R^1 = R^2 = H, X = Et$
1b: $R^1 = t\text{-}Bu, R^2 = H, X = Et$
1c: $R^1 = R^2 = t\text{-}Bu, X = Et$
1d: $R^1 = R^2 = H, X = Cl$
1e: $R^1 = R^2 = H, X = Br$
1f: $R^1 = R^2 = H, X = OMe$
1g: $R^1 = R^2 = H, X = \mathrm{O\underset{CH_3}{C}HCH_2\text{-}(O\underset{H_3C}{C}HCH_2)_2\text{-}Cl}$
1a-1g: $R^3 = R^4 = H$
1h: $R^1 = R^2 = H, R^3 = R^4 = \text{-}(CH)_4\text{-}, X = Et$
1i: $R^1 = R^2 = t\text{-}Bu, R^3 = R^4 = \text{trans-}(CH_2)_4\text{-}, X = Cl$

Scheme 1.

CO_2 with propylene oxide under extremely mild conditions (25 °C, 0.6 MPa CO_2) (Table 1, entry 1). No by-product such as polycarbonates or polyether was observed in the resulting products. It is important to note that neither **1a** nor the 18-crown-6–KI complex by itself showed any or only very low catalytic activity under the employed conditions (Table 1, entries 2 and 3). The coexistence of **1a** and 18-crown-6–KI complexes is essential to effectively catalyze this reaction.

Several SalenAl(III)X complexes (Scheme 1) with varying substitute groups on the aromatic rings (**1a**–**c**), or the axial X group (**1d**–**g**), or/and diamine backbones (**1h, 1i**) were investigated as catalysts for the cycloaddition of CO_2 to propylene oxide (Table 1, entries 4–11). In the presence of 18-crown-6–KI, complexes **1a** and **1d**–**g** were proved to be more effective in catalyzing this reaction, and their activities are at least five times as active as complex **1c**. We believe this may be due to the high electrophilicity and the more accessible coordination site available for the epoxide of these complexes. The results also indicate that the epoxide was predominately activated by its coordination to central Al^{3+} ions at the opposite of axial X group of SalenAl(III)X complexes. The facts that the addition of n-Bu_3N to the **1a**/18-crown-6–KI catalyst system resulted in its catalytic activity (TOF) from 57.9 h^{-1} rapidly decreasing to 9.6 h^{-1} (Table 1, entry 19), and that the bifunctional catalyst system based on a chiral aluminum complex **1i** and 18-crown-6–KI preferentially consumed (*S*)-propylene oxide over (*R*)-propylene oxide with K_{rel} of 1.8 (Table 1, entry 11), all support this conclusion.

Table 1
Reaction of CO_2 with propylene oxide in the presence of a SalenAl(III) complex in conjunction with a polyether–KY complex[a]



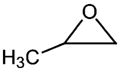
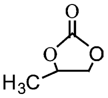
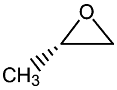
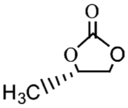
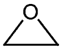
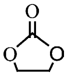
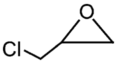
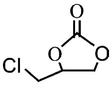
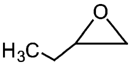
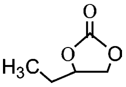
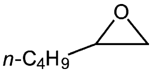
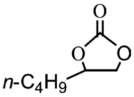
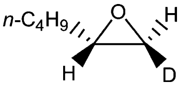
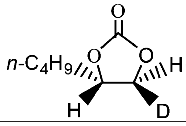
Entry	Catalyst SalenAlX	Cocatalyst polyether–KY	TOF (h^{-1})
1	**1a**	18-crown-6–KI	57.9
2	**1a**	None	0
3	None	18-crown-6–KI	0.8
4	**1b**	18-crown-6–KI	18.4
5	**1c**	18-crown-6–KI	10.1
6	**1d**	18-crown-6–KI	60.8
7	**1e**	18-crown-6–KI	62.3
8	**1f**	18-crown-6–KI	59.6
9	**1g**	18-crown-6–KI	63.9
10	**1h**	18-crown-6–KI	19.3
11[b]	**1i**	18-crown-6–KI	29.7
12	**1a**	18-crown-6–KBr	56.7
13[c]	**1a**	18-crown-6–KCl	3.0
14	**1a**	18-crown-6–KOTs	0.2
15	**1a**	18-crown-6–KOAc	2.0
16[c]	**1a**	18-crown-6–KSCN	2.4
17[c]	**1a**	18-crown-6–KOPh	4.1
18	**1d**	PEG400–KI	13.2
19[d]	**1a**	18-crown-6–KI/n-Bu_3N	9.6

[a] Reaction conditions: SalenAlX (2.4×10^{-4} mol), SalenAlX/polyether–KY/epoxide = 1/1/800 (molar ratio), temperature = 25 °C, $t = 8$ h.
[b] The ee of the resulted propylene carbonate is 24.9%.
[c] CH_3CN (5 ml) was added as cosolvent.
[d] 18-crown-6–KI/n-Bu_3N = 1/10 (molar ratio).

On the other hand, the anion Y^- of inorganic salts in the complexes 18-crown-6–KY also significantly affected the catalytic activity of the bifunctional catalyst system (Table 1, entries 12–17). Essentially, only these catalyst systems comprising I^- or Br^- anions show a considerably high activity, probably because these anions have a high nucleophility and leaving ability. Although acetate and phenolic anions have high nucleophilicity, complex **1a**/18-crown-6–KOAc or KOPh system shows very low activity, probably resulting from the low leaving ability of these anions. It is generally known that p-toluene sulfonate is a better leaving group, but due to its low nucleophilicity, the **1a**/18-crown-6–KOTs system also could not effectively catalyze this reaction. Unfortunately, the PEG 400–KI complex in conjunction with **1d** could also catalyze this reaction, but its activation is less than one-quarter of that of 18-crown-6–KI/**1d** catalyst system (Table 1, entry 18).

The catalyst system was found to be applicable to a variety of terminal epoxides, quantitatively providing the corresponding cyclic carbonates in 100% selectivity (Table 2). Ethylene oxide **2c** was found to be the most reactive epoxide, while epichlorohydrin **2d** exhibits relatively low activity among the epoxides surveyed. Notably, the reaction of CO_2 with (*S*)-propylene oxide **2b** in the presence of

Table 2
The cycloaddition of CO_2 to various epoxides catalyzed by **1a**/18-crown-6–KI system[a]

Substrate	Time (h)	Product	Yield[b] (%)
 **2a**	12	 **3a**	98
 **2b**	12	 **3b**	98
 **2c**	8	 **3c**	96
 **2d**	48	 **3d**	95
 **2e**	14	 **3e**	99
 **2f**	24	 **3f**	97
 **2g**	24	 **3g**	95

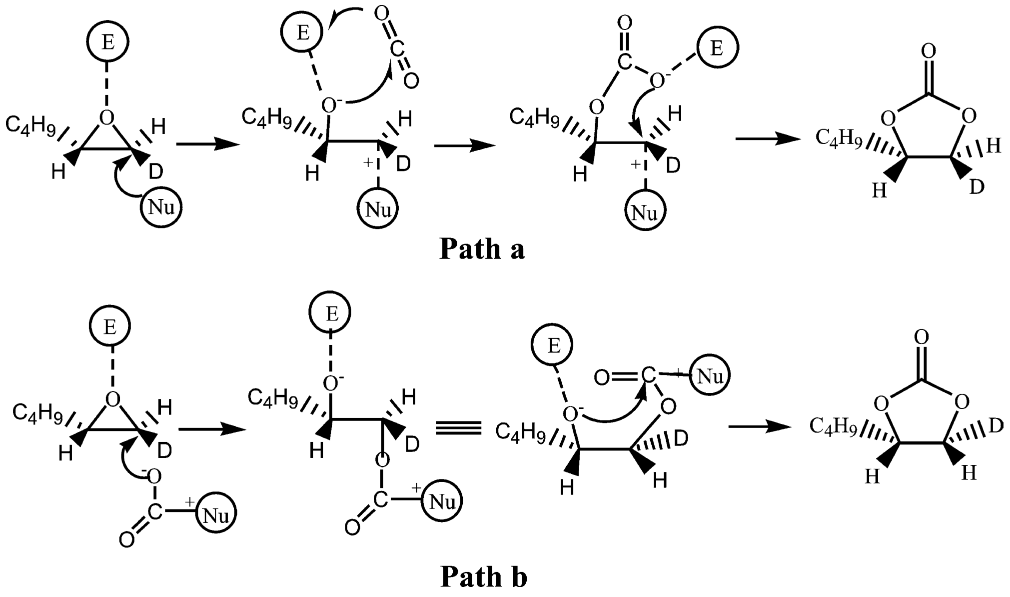
[a] Reaction conditions: **1a** (16.1 mg, 5×10^{-5} mol), **1a**/18-crown-6–KI/epoxide = 1/1/400 (molar ratio); $p(CO_2) = 0.60$ MPa; temperature, 25 °C; the reaction was carried out in 10 ml autoclave.

[b] Isolated yield.

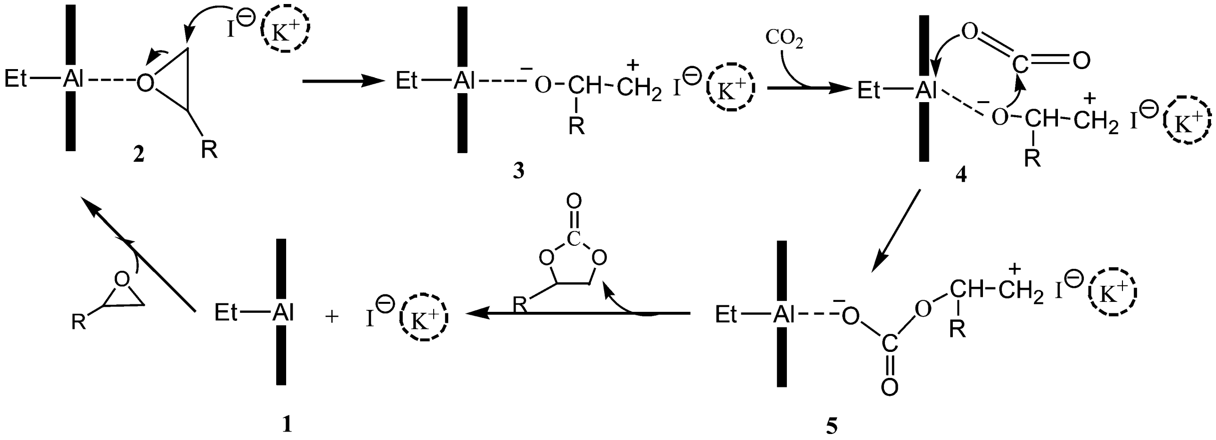
the **1a**/18-crown-6–KI catalyst system gave (*S*)-propylene carbonate **3b** in > 99% ee with retention of stereochemistry.

Very recently, Shen and co-workers reported that binaphthyldiamino Salen-type Zn, Cu, and Co complexes could effectively catalyze the cycloaddition of CO_2 to terminal epoxides in the presence of various catalytic amounts of organic bases [30]. A Lewis acid- and Lewis base-cocatalyzed mechanism is proposed, on the basis of the reaction of *trans*-deuterioethene oxide with CO_2. For the **1a**/18-crown-6–KI catalyst system, it is clear that the electrophilicity of Al^{3+} in complex **1a** and the nucleophilicity of I^- in the 18-crown-6–KI complex cooperatively catalyze the cycloaddition of CO_2 to epoxides. In order to clearify the reaction mechanism, we also synthesized *trans*-deuterio-1,2-hexene oxide **2g** and utilized it as the substrate in the reaction with CO_2 catalyzed by the **1a**/18-crown-6–KI system (Table 2). We found that *trans*-deuterio-1,2-hexene carbonate **3g** was formed exclusively. The result suggests that the formation of cyclic carbonate in our reaction system proceeds via **path a** as shown in Scheme 2, in which the epoxide is first activated by its coordination to the central $Al^{3+}$of complex **1a** and then opened by nucleophilic attack of free I^- of the 18-crown-6–KI complex at the less substituted C–O bond, and further reacts with CO_2 to give the corresponding deuterated cyclic carbonate. On the contrary, if the reaction proceeds via **path b**, *cis*-deuterio-1,2-hexene carbonate should be the dominant product.

Based on the facts described above, a plausible mechanism for this cycloaddition is proposed as shown in Scheme 3. We believe epoxides are ring-opened at the less substituted C–O bond to form **3** in view of the synergistic effect of the bifunctional catalyst, which probably results from nucleophilicity of free I^- of the 18-crown-6–KI complex and the electrophilic interaction of SalenAl(III) with epoxides. The activation of CO_2 is generally initiated by nucleophilic attack of the alcoholate $[OCH(R)CH_2I^-K^+\text{–18-crown-6}]$ at the Lewis acid carbon atom of CO_2, and weak interaction



Scheme 2.



Scheme 3.

between the central metal ion and the lone pairs of one oxygen of CO_2. The synergistic effect is sufficient to lead to the formation of linear carbonate **5**, which is transformed into five-membered cyclic carbonates via intramolecular cyclic elimination.

Acknowledgments

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