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Succinimide-KI: An efficient binary catalyst system for mild, solvent-free cycloaddition of CO_2 to epoxides



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ABSTRACT

In this study, we have for the first time demonstrated that succinimide (SI)-KI is an efficient catalyst system to synthesize propylene carbonate (PC) from carbon dioxide (CO_2) and propylene oxide (PO) at a solvent-free condition. A synergistic effect was observed between SI and KI that largely increased the reaction yield. It enabled the cycloaddition reaction to take place at 70 °C under a low pressure (0.4 MPa) for only 4 h, with a PC yield as high as 97.5%. The overall condition is milder than the reaction catalyzed by most of the other KI involved co-catalyst systems reported in literatures. The excellent catalytic ability was explained by the increased KI solubility in PO due to the presence of SI and the weak acidity of NH in SI which can be enhanced by KI. A reaction mechanism was proposed based on a reaction kinetics study. SI-KI was applicable to cycloaddition of CO_2 with other epoxides. It may offer an inexpensive, environmentally-friendly route to synthesis of propylene carbonate from CO_2 .

1. Introduction

Turning greenhouse gas (CO₂) into usable materials has been a hot topic in the fields of environment, chemistry and materials science [1–5]. A promising method is to produce five-membered cyclic carbonates through cycloaddition of CO₂ to epoxides [3–5]. Five-membered cyclic carbonates have been widely used as aprotic polar solvents for chemical engineering, electrolytes for lithium-ion batteries, and starting materials for pharmacy, preparation of polycarbonates and polyurethane and other new material synthesis [6–8].

 CO_2 -epoxide cycloaddition is an energy-intense reaction due to the high oxidation state and inherent thermodynamic stability of CO_2 . Metal oxides [9], alkali metal halides [5,10], ionic liquids (ILs) [11–14], transition metal complexes [15,16], metal-organic frameworks (MOFs) [17,18] and *N*-succinimides [19,20] have been reported as catalysts to lower the energy barrier and promote the CO_2 -epoxide cycloaddition reaction. Among them, alkali metal salts have received particular attention owing to their abundance, non-toxicity and low price [21–31]. However, alkali-metal salts alone usually have a low cycloaddition catalytic activity. To improve catalysis activity, the alkali metal catalysts are either loaded on a porous carrier or combined with a co-catalysis. Co-catalysis was extensively studied because the process is simple, convenient and effective.

Four co-catalyst systems have been reported. The first co-catalyst system, which is also the most studied one, is hydrogen-bond donor (HBD), such as β -cyclodextrin [21], cellulose [22], lignin [23], C60 fullerene [24], pentaerythritol [25], sugarcane bagasse [26], tannic acid [27], formic acid [28], boron phosphate [29] and polyvinyl alcohol [30]. HBD can form hydrogen bonds with the oxygen atom of epoxide, activating the epoxide molecule and therefore accelerating the reaction. When HBD contains a basic moiety such as triethanolamine [31], amino alcohols [32], polydopamine [33], amino acid [34,35] and wool powder [36], the co-catalyst activate the CO₂ molecule in the meanwhile, showing higher activity. The second co-catalyst system is ligand compounds [37–40], including crown-ethers [37] cucurbit[6] uril [38], polydibenzo-18-crown-6 [39] and lecithin [40] which can coordinate with alkali metal cations to enhance their solubility. The ligand compounds can also reduce the interaction between metal cation and halide ion facilitating nucleophilic attack of halide ions to the epoxide. The third co-catalyst system is Lewis acids (e.g., metalorganic framework-5 [41], titanocene dichloride [42], titanate nanotube [43]). Lewis acids are able to enhance the cycloaddition of CO₂ to epoxide through activation of epoxy rings. The last co-catalyst system is modified polyethylene glycol such as α , ω -hydroxyl telechelic polyethylene

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glycol (PEG400) [44] and tetraethylene glycol [45] which can chelate the potassium cation of KBr or KI, respectively, and meanwhile activate epoxide oxygen atom through a hydrogen bond interaction. With these catalysts, the reaction was reported to undertaken at a mild condition (e.g. 40–60 °C and atmospheric pressure). However, most of the CO₂epoxide cycloaddition catalyzed by the **co**-catalyst systems containing alkali metal salts have to be carried out at a harsh reaction condition (e.g. > 100 °C, > 1 MPa) in the presence of organic solvents. CO₂-epoxide catalysis cycloaddition under a mild, solvent-free condition has much less reported.

Recently, N-succinimides was reported to show catalytic activity for epoxide- CO_2 cycloaddition and the catalysis mechanism was highly dependent on the molecular structure of N-succinimide and catalytic condition. Jamison et al [19] used N-Bromosuccinimide (NBS) and benzoyl peroxide as co-catalyst for cycloaddition of CO_2 to epoxide. The reaction was carried out in N, N-dimethylformamide which functioned as both solvent and CO_2 nucleophilic activation agent. He et al [20] combined N-iodosuccinimide (NIS) with DBU as a co-catalyst for cycloaddition of CO_2 to epoxide. This reaction was carried out under a mild, free-solvent condition. However, when NIS was replaced with SI, the SI-DBU showed lower catalysis activity than NIS-DBU. As far as we knew, using SI and alkali metal as co-catalyst for CO_2 -epoxide cycloaddition has not been reported in research literature.

In this study, we have for the first time demonstrated that SI-potassium iodide (KI) is a very efficient catalyst system for cycloaddition of CO_2 to epoxide without using any solvent. A synergistic effect was observed between the two catalyst components. SI-KI enables the reaction to take place at a mild condition (e.g. 70 °C and 0.4 MPa pressure) with a reaction yield as high as 97.5%. A reaction mechanism was proposed based on a reaction kinetics study. Our SI-KI system differs to the previous co-catalysts for CO_2 -epoxide cycloaddition in not only the initial material but also the intermediate originated from them. By replacing SI with 5 cyclic imides to perform the same reaction, we further showed that cyclic imide-KI also showed catalytic activity. SI and KI are both low cost chemicals with low toxicity. SI-KI may form a new catalyst system for effective synthesis of cyclic carbonates from CO_2 and epoxides.

2. Experimental section

2.1. Chemicals

 CO_2 with a purity of 99.99% was obtained commercially from a local plant. All the epoxides, potassium halides, amides and imides are of analytical grade, which were purchased from the Aladdin and used as received. Deuterochloroform (CDCl₃) was purchased from Sigma-Aldrich and used as received.

2.2. Cycloaddition of CO_2 to epoxides

Epoxide- CO_2 cycloaddition reactions were carried out in a 100 ml stainless steel reactor equipped with a magnetic stirrer. In the typical procedure, the desired amount of potassium halide and cyclic imide was placed into the reactor and purged with CO_2 for three times. Then 20 mmol PO was added into the reactor and the reactor was sealed. CO_2 was introduced into the reactor until the pressure reached the desired value. Subsequently, the reactor was heated to the reaction temperature. After a certain reaction time, the autoclave was cooled in an ice water bath, and the excess CO_2 was vented slowly. Isolated yields were obtained by distillation or silica gel column chromatography using a mixture consisting of petroleum ether and ethyl acetate as an eluent. The chemical structures of the products were confirmed by ¹H NMR, ¹³C NMR and LC–MS. For comparison, two amides (i.e., butyrolactam (BL) and N-ethylacetamide (NEA)) were used separately as a co-catalyst with KI to conduct the reaction at the same condition.

2.3. Solubility of the catalysts in PO

The solubility of KI in PO was measured by weight method at room temperature. In brief, 830 mg KI (5 mmol) was added into PO (7 ml, 100 mmol). The mixture was then ultra-sonicated for 5 min and sealed in desiccator for three days to allow sufficient dissolving of KI in PO. The mixture was centrifuged and 5 ml supernatant liquor was removed. PO in the supernatant and the rest of the mixture were volatilized and dried in vacuum at room temperature until the total mass of the two parts of KI was equal to the initial mass of KI (830 mg). The similar experiments were carried out to measure the solubility of SI and KI + SI in PO. The experiments were repeated for three times to ensure accuracy and repeatability.

2.4. Kinetic experiments

The experimental procedure was similar to the above process in the above-mentioned steel reactor. The difference is that KI, SI and PO were firstly dissolved in PC (90 mmol) and the cycloaddition was carried out under the designated temperature and 0.4 MPa (CO_2 was continuously supplied to the reactor during the reaction process.). After the reaction was completed, the autoclave was cooled in an ice water bath and the excess CO_2 was vented slowly. The conversion was determined by means of ¹H NMR spectroscopy using CDCl₃ as the solvent

2.5. Reusability test

20 mmol PO, 1 mmol SI, and 1 mmol KI were added into the reactor. The reaction was carried out at 70 °C and 0.4 MPa CO_2 initial pressure for 4 h. Then, the reactor was cooled in ice water bath, and the excess CO_2 was vented slowly. A small amount of the product was taken out for ¹H-NMR analysis. The residual PO was removed out under reduced pressure and another 20 mmol PO was subsequently added each time for the next cycle of reaction without separation of PC and catalyst from the reaction system. For comparison, another series of the simulated experiments were carried out in the similar condition. In this case, a desired amount of PC equivalent to that was produced in the actual reaction during the reusability test was added.

2.6. Characterizations

¹H and ¹³C NMR spectra were measured on a Bruker DPX-400 spectrometer and LC–MS spectra were measured on an AmaZon SL spectrometer. The SEM-EDS analyses were conducted using a Gemini 500 Scanning Electron Microscope (Carl Zeiss, Germany) combined with Energy-Dispersive X-ray spectrometer (Oxford Instruments, Abingdon, Oxfordshire, United Kingdom).

3. Results and discussion

3.1. SI-KI catalytic cycloaddition of CO₂ to PO

Scheme 1 shows the cycloaddition reaction between CO_2 and PO. No solvent was involved in the cycloaddition reaction. The PC yield was obtained by experiment methods such as distillation. Table 1 shows the effect of SI-KI content on PC yield. When SI:KI was kept at 1:1 (mol/mol) meanwhile the contents of SI and KI (based on PO) were

$$\begin{array}{c} O \\ + CO_2 \\ \hline 70^{\circ}C, p(CO_2)=0.4MPa \\ \hline 4h, solvent free \end{array}$$



Table 1

Influence of catalyst content on the formation of PC^a.

Entry	SI (mol %)	KI (mol %)	Yield (%) ^b	TON ^c
1	2.5	2.5	47.2	18.9
2	4	4	87.4	21.9
3	5	5	97.5	19.5
4	6	6	97.9	16.3
5	4	6	88.0	14.7
6	6	4	90.7	22.7
7	5	4	88.3	22.1
8	4	5	87.9	17.6

a) Reaction conditions: PO (20 mmol), CO₂ (initial pressure 0.4 MPa), 70 $^{\circ}$ C, and 4 h. b) PC yield. c) TON: mole of synthesized PC per mole of KI.

simultaneously increased from 2.5 mol % to 5.0 mol% (entries 1–3), the PC yield increased. At the SI: KI: PO molar ratio of 5: 5: 100, the PC yield reached a plateau value, being 97.5%. Higher SI and KI contents, e.g. SI: KI: PO ratio at 6: 6: 100 (mol: mol: mol) (entry 4), led to very little increase in PC yield. In addition, decreasing one of the components (either SI or KI) meanwhile keeping the other component at 5 mol % (relative to PO) also led to decrease in PC yield (entries 7 and 8). Therefore, SI: KI: PO = 5: 5: 100 (mol: mol: mol) was found to be the optimal reaction condition, which was used in the further experiments unless specification.

The effects of reaction temperature, CO_2 pressure and reaction time on PC yield were examined. Fig. 1a shows the effect of reaction pressure on PC yield. With increasing the pressure from 0.1 MPa to 0.4 MPa, the PC yield increased from 24.0%–97.5%. Further increasing the CO_2 pressure conversely lead to a slight decrease in PC yield. A similar trend was also reported in other catalytic systems [21,22,26,31,38,42], and it was attributed to that increasing CO_2 pressure led to increase of initial CO_2 concentration in the reaction system.

Fig. 1b shows the influence of reaction temperature on PC yield. Temperature was found to play an important role in the reaction process. When the temperature was increased from 40 °C to 70 °C, the PC yield increased from 8.1%–97.5%. With further increasing the temperature to 80 °C, the PC yield was almost unchanged.

The dependence of the PC yield on reaction time was also investigated as shown in Fig. 1c. The PC yield increased from 16.3%–97.5% when reaction time changed from 1 h to 4 h. The yield showed almost no change when further prolonging the reaction time. Based on the reaction results, the reaction condition of 70 °C, 0.4 MPa and 4 h was chosen as an optimal condition for further experiments.

We also summarized the literature reports about PO-CO₂ cycloaddition catalysed by KI and co-catalyst (see Table S1). Our SI-KI catalysed cycloaddition is undertaken at 70 °C under a low initial CO₂ pressure (0.4 MPa) for 4 h. It is relatively milder than the reaction catalyzed by other KI involved co-catalyst systems reported in literatures, except KI-tetraethylene glycol. However, the KI-tetraethylene glycol involved reaction consumed much larger amount of the catalyst than KI-SI, and it took longer reaction time as well.

To probe the role of SI and KI in the reaction, control experiments



Scheme 2. The interaction between KI and SI.

were performed with and without the presence of the catalyst component. For the reaction just catalysed by KI, it had a very low PC yield, around 2.8%. When SI alone was used to catalyse the reaction, only trace amount of PC was prepared. These results indicate that SI and KI form an efficient catalytic system for the cycloaddition of CO_2 to PO and a catalytic synergistic effect exists between the two catalyst components.

In structure, the carbonyl group and oxygen ion in SI possess three resonance structures (Scheme 2). It was reported that when the carbonyl group has an interaction with the potassium cation of KI, activity of iodine ion can be enhanced [38,40].

To examine the possible interaction between KI and SI, we measured the ¹H-NMR spectra of SI in the presence of KI. As shown in Fig. 2, the NH proton of SI moved up-field to 8.29 ppm in the SI- KI system when compared with the pure SI (NH proton chemical shift at 8.67 ppm), which may stem from the shield effect of iodine ion.

It was also reported that hydrogen bonding can promote the cycloaddition of epoxides with CO_2 [21–30,46–48] and the formation of hydrogen bonding led to shift of H atom signal to the downfield in ¹H NMR spectra [21,44–46]. Indeed, the ¹H-NMR spectra shows that SI-KI in the presence of PO led to the NH proton of SI moving downfield to 9.09 ppm (Fig. 2), indicating the formation of hydrogen bonds in the system.

To probe to role of catalysts, we measured the solubility of KI and SI in the reaction system (Table S2). KI alone had a very small solubility in PO, being 2.38 mg in 1.4 ml PO (20 mmol). However, the presence of 99.1 mg SI (1 mmol) led to 376.5% increase in KI solubility, i.e. 8.96 mg in 1.4 ml PO (Supporting information). Considering the low PC yield for the reaction catalyzed only by KI and much improved PC yield for the reaction in the presence of SI, both KI and SI play critical roles in catalysis of the reaction.

3.2. Effect of halide and cyclic imide types on catalytic activity

The effect of halide type on catalysis activity was examined. In the same condition, KBr and KCl showed almost no catalytic activity for the



Fig. 1. Effect of the reaction conditions on the PC yield (20 mmol PO, 5 mol% SI and 5 mol% KI relative to PO, respectively, were used.). (a) Effect of CO₂ pressure on the yield of PC (70 °C, 4 h); (b) Effect of reaction temperature on the yield of PC (0.4 MPa, 4 h); (c) Effect of reaction time on the yield of PC (70 °C, 0.4 Mpa).



Fig. 2. The ¹H-NMR spectra of SI, SI + KI and SI + KI + PO.

PO-CO2 cycloaddition. When separately combined with SI, they also showed very low PC yield, 3.0% for SI-KBr catalysed reaction and 2.9% for the SI-KCl system. This could be attributable to the difference in nucleophilicity and leaving ability of the halide. I- has stronger nucleophilicity and leaving ability than Cl- and Br-[21,23,26,27,31,33,35].

To examine the role of SI on the CO₂-PO cycloaddition, we separately combined 5 other cyclic imides, i.e., maleimide (MI), phthalimide (PI), 1, 2-cyclohexanedicarboximide (CHDC), N-hydroxysuccinimide (NHS) and N-methylsuccinimide (NMS) with KI for catalytic cycloaddition (Table 2, entries 3–7). The reasons for choosing these chemicals are because MI and PI have a similar NH group as SI, while they differ from SI in that MI has a carbon-carbon double bond π -conjugated system whereas PI has a large π -conjugated system than MI because of the benzene ring in the molecule. CHDC had a similar molecular structure to PI except for that the molecule contain a hexane ring rather than a benzene ring. NHS and NMS belonged to N-substituted SI derivatives. For NHS, the NH proton is substituted by a hydroxyl group. However, NMS has no active proton in the molecule because of the substitution of the NH proton by methyl group.

Table 2 lists the PC yield of the cyclic imide-KI catalytic cycloaddition. In comparison with SI-KI, the other cyclic imides with KI led to a much lower PC yield (Table 2, entries 3–7). The one without NH proton, i.e. NMS, had the lowest PC yield among the reaction systems. For comparison, butyrolactam (BL) and N-ethylacetamide (NEA) were also used with KI to catalyse CO₂-PO cycloaddition (entries 8 and 9), as listed in Table 2. The catalytic activity for BL-KI was slightly lower than that of CHDC–KI, whereas NEA-KI had a lower catalytic activity than BL-KI.

To understand the about structure effect, pKa of the "NH"-type proton was examined. As listed in Table 2, pKa shows a certain effect on PC yield. A large or small pKa value resulted in low PC yield. This can be explained by the ability to form hydrogen bond with the oxygen atom of epoxide. When acidity of an imide was too strong (low pKa value), strong hydrogen bond was formed, which baffled the insertion of carbon dioxide to hydrogen bond [50]. However, when the acidity was too weak (high pKa value), the weak hydrogen bond failed to activate the ring opening of epoxide [51,52].

It should be pointed out that the amides had higher pKa value than the cyclic imides. The weak acidity could hinder them to effectively form hydrogen bond with epoxide. NHS has lower pKa value therefore stronger acidity than PI. However, NHS-KI has much higher PC yield (10.8%) than PI-KI. This might be due to the high steric hindrance from the PI benzene ring and low solubility of PI in PO and PC.

Table 2	
The PC yield of the catalytic cycloaddition reactions ^a	

Entry	Co-catalyst	pK _a ^b	Yield (%)	TON ^c
1 2	None $O = \begin{pmatrix} H \\ N \end{pmatrix} = O (SI)$ (SI)	 9.66[[49]49a] (14.6[[49]49b])	2.8 97.5	0.56 19.5
3		9.46[[49]49c]	11.4	2.28
4	NH (PI) (PI)	8.3[[49]49a] (13.4[[49]49d])	4.2	0.84
5	NH (CHDC)	11.97 ± 0.02 [[49]49e]	54.9	10.98
6	OH OH O(NHS) O(NHS)	6.0[[49]49f]	10.8	2.16
7			4.0	0.8
8	(BL)	11.26[49 g] (24.2[[49]49b])	46.9	9.38
9	O H (NEA)	$14.6 \pm 0.2[49 h]$	28.6	5.72

a) Reaction conditions: PO (20 mmol), co-cat. (5 mol %), KI (5 mol %), CO_2 (initial pressure 0.4 MPa), 70 °C, and 4 h. b) pKa value of the cyclic imides or amides in water or dimethyl sulfoxide (brackets)[49]. c) TON: mole of synthesized PC per mole of KI.

3.3. SI-KI catalytic cycloaddition of CO_2 to other epoxides

Using SI-KI as catalyst, we also tested the cycloaddition of CO_2 to other epoxides. All the reactions were carried out at 70 °C and initial CO_2 pressure of 0.4 MPa. The results are listed in Table 3. It was interesting to note that SI-KI catalyst was applicable for all mono-substituted terminal epoxides. For some reactions, a reaction time slightly longer than 4 h could be beneficial to get a high reaction yield. Styrene oxide needs 19 h to attain a high yield (entry 6), which was attributed to its low reactivity of its β -carbon centre. For cyclohexene oxide (entry 7), only 9.6% cyclic carbonate was obtained even if the reaction time was prolonged to 96 h, presumably due to the high steric hindrance caused by its ring structure. In the literature [53], the cyclic carbonate was reported to have *cis*- and *trans*- isomers. We also examined the cyclic carbonate isomers using ¹H NMR and ¹³C NMR (Supporting Information) and found the produced cyclic carbonate exclusively had a cis isomer.

3.4. Reusability test

The reusability of SI-KI catalyst was examined using the PO- CO_2 reaction system. To avoid possible catalyst loss during the separation, SI-KI wasn't separated after each cycle. After each reaction cycle, the residue PO was removed simply by distillation in vacuum, and fresh PO and CO_2 were subsequently introduced into the reactor to perform another cycle of reaction. As shown in Fig. 3, PC yield decreases gradually with increasing the reaction cycles. To find out the possible reactions, we conducted a simulated experiment by using fresh SI-KI with the amount of PC that was equivalent to the actually produced during the reusability test added. It was found that PC yield was declined with increasing PC content in reaction system. Moreover, PC yield in

Table 3Cycloaddition of CO2 to other epoxides a.

Entry	Epoxides	Products	Time (h)	Yield (%) ^b	TON ^c
1	ola ^{1a}	$\sqrt{\frac{0}{0}}$ $\sqrt{\frac{2a}{2a}}$	4	97.5	19.5
2	° ° ° ° ° ° ° ° ° ° ° ° ° °		4	98.1	19.6
3		$\sim \circ \sim \circ \circ$	4	95.5	19.1
4		$0 \rightarrow 0^{\text{Cl}} 2^{\text{cl}}$	4	96.1	19.2
5	le 0, 1e		6	94.3	18.9
6	le le lf lf	2e	19	97.0	19.4
7	o lg ^{1g}	$ \begin{array}{c} 2f \\ H \\ H \\ H \\ 2g \end{array} $	96	9.6	1.9

a)Reaction conditions: PO (20 mmol), SI (5 mol%), KI (5 mol%), CO₂ (initial pressure 0.4 MPa), 70 °C. b) Isolated PC Yield. c) TON: mole of synthesized PC per mole of KI.



Fig. 3. Recyclability test results and the reaction in the presence of equivalent amount of PC (simulated run). Reaction conditions: PO (20 mmol), SI (5 mol% PO), KI (5 mol% PO), CO₂ (initial pressure 0.4 MPa), 70 °C, and 4 h.

repeated cycles was almost the same to that of the reusability test, indicating that the decrease in PC yield in repeated runs was derived from the dilute effect of PC to PO. In addition, SI-KI system had a good stability for multiple cycles of reaction.

3.5. Reaction kinetics of catalytic CO₂-PO cycloaddition

To explore the reaction mechanism of cyclic carbonate synthesis, a kinetic study was carried out using PC as solvent. Based on the previous reports [54], there was a first-order rate dependence of both epoxides and CO_2 . Thus, the rate equation for the PO-CO₂ coupling reaction catalysed by SI-KI can be described as Eq. (1),

$$Rate = k [PO] [CO2] [KI]^a [SI]^b$$
(1)

where [PO], $[CO_2]$, [KI] and [SI] are the PO, CO_2 , KI and SI concentrations, respectively. *a* and *b* are the orders of reaction with respect to KI and SI, respectively. *t* is reaction time. Here, we assumed that the concentrations of KI and SI were constant during the reaction and CO_2 was in large excess due to the semi-batch operation. Therefore, Eq. (1) can be re-written as Eq. (2),

$$Rate = kobs1[PO], kobs1 = k[CO2][KI]^a[SI]^b$$
(2)

where and k_{obs1} was the observed pseudo-first order rate constant for PO conversion. k_{obs1} can be obtained from the slope of a linear plot of the natural logarithm of the changing sample concentration with time (Eqs. (3) and (4))

$$Rate = \frac{-d[PO]}{dt} \tag{3}$$

$$-\ln[PO] = k_{obs1}t\tag{4}$$

Furthermore, using the Arrhenius equation, the activation energy for the cycloaddition reaction can be determined from the relationship between k_{obs1} and temperature, (Eq. (5))

$$kobs1 = A \exp(-Ea/RT)$$
⁽⁵⁾

$$\ln kobs1 = \ln A - Ea/RT \tag{6}$$

where *R* is the universal gas constant (8.314 J mol⁻¹ K⁻¹), and *T* is the absolute temperature (K), *A* and *E*_a are the pre-exponential factor (min⁻¹) and the activation energy (kJ/mol), respectively. The natural logarithm of PO concentration change with time at different temperatures is shown in Fig. S2. Nearly linear relationships were obtained. Based on the ln [PO] result, k_{obs1} was calculated using Eq. (5). Fig. 4a shows the activation energy at different temperatures. By fitting the data, pseudo-first order rate constant (ln k_{obs}) against the reciprocal absolute temperature (K/T). Based on the data and Eq. (6), the activation energy was calculated to be 22.7 kJ/mol.

For comparison, we also measured the activation energy for using KI alone for catalysis of the reaction (see the data in Fig. S3 & 4a), which



Fig. 4. (a) Arrhenius plot for the determination of activation energy using SI-KI co-catalyst system (\blacksquare) and KI alone (\bullet), (b) fitting curve of the natural logarithm of the observed pseudo-first order rate constant (lnkobs) against the natural logarithm of the catalyst concentration (ln [KI] and ln [SI]).



Scheme 3. Proposed mechanism for SI-KI catalysed cycloaddition of CO₂ to epoxide.

was 43.0 kJ/mol. Han et al [55] calculated the energy barrier of the cycloaddition catalysed by KI alone using a density functional theory (DFT) method. In gas phase, activation energy calculated was 36–41 kcal/mol, which is comparable to our experimental results.

These results that activation energy for the SI-KI involved reaction was 20.3 kJ/mol lower than that of the KI involved one suggest that the presence of SI largely reduces the energy barrier to carry out the reaction.

Apart from the energy barrier, reaction order was estimated. We assumed that the steady state conditions at the beginning of the reaction, CO_2 and PO concentrations, were more or less constant. Eq. (1) can be rewritten as Eq. (7) or Eq. (8) as needed,

$$Rate = kobs2[KI]^a, kobs2 = k[CO2][PO][SI]^b$$
(7)

$$Rate = kobs3[SI]^b, kobs3 = k[CO2][PO][KI]^a$$
(8)

in which k_{obs2} and k_{obs3} represents the rate constant, respectively. By taking the natural logarithm of Eq. (7), Eq. (9) was obtained.

. . .

$$\ln Rate = \ln kobs2 + a \ln[KI] \tag{9}$$

To obtain the reaction order of KI, four reactions were performed at

four different concentrations (n) of KI, respectively. KI and SI were completely dissolved in the mixture of PC and PO before reacting. The kinetic data were fitted by the natural logarithm of the observed pseudo-first order rate constant (ln k_{obs2}) against the natural logarithm of the KI concentrations (ln [KI]) (Eq. (9)) (Fig. S4 & 4b). The logarithmic plot revealed that *a* is close to 1.0, indicating a first-order dependence on KI.

The same method was used to estimate the reaction order of SI (see details in Fig. S5 & 4b). The kinetic data were fitted by the natural logarithm of the observed pseudo first-order rate constant (ln k_{obs3}) against the natural logarithm of the SI concentrations (ln [SI]) (Eq. (10)).

$$\ln Rate = \ln kobs3 + b \ln[SI] \tag{10}$$

The kinetic data from the double logarithmic plot revealed that b is close to 1.0 indicating a first order dependence on SI. This means that one molecular SI and one molecular KI were actively involved in the mechanistic cycle.

3.6. Possible mechanism

It has been reported that a synergistic effect between various HBDs (or Lewis acids) and nucleophile group in the catalyst system can promote the cycloaddition of carbon dioxide and epoxides [21–30,56–59]. In our case, hydrogen proton in cyclic imide exhibits weak acidity and acts as HBD to activate epoxide through forming hydrogen bond with the oxygen atom of epoxide, while the halide anion serves as a nucleophilic group.

The reaction mechanism was proposed, as illustrated in Scheme 3. Firstly, the interaction between SI and KI adduct takes increases the activity of iodine ion. Secondly, Imide NH activates the epoxide molecule by forming a hydrogen-bond. KI Subsequently attacks the less-hindered β -carbon atom of the activated epoxide, resulting to ring-opening of epoxide. The addition of *II* to a carbon dioxide molecule generates an alkyl carbonate anion (*III*). Finally, intramolecular ring closure of *III* happen to generate the corresponding cyclic carbonate and the catalyst for the completion of the catalytic cycle.

The synergistic effect occurs when both iodide anion and SI are involved in the reaction. The presence of SI not only enhances activation of epoxide, but also increase the activity of iodine ion due to the interaction between KI and SI.

4. Conclusion

We have shown that SI and KI can form an efficient binary catalyst system for cycloaddition of CO_2 to epoxides. A synergistic effect was observed between SI and KI that largely increased the reaction yield. It enabled the addition reaction to take place at 70 °C and 0.4 MPa pressure and a short reaction time to achieve a high reaction yield (as high as 97.5%). The SI-KI catalyzed reaction can be conducted in a condition milder than the same reaction catalyzed by most of the other KI involved co-catalyst systems reported in literature. The binary catalytic system was applicable to different epoxides. It may offer an inexpensive, environmentally-friendly route to synthesis of propylene carbonate from CO_2 .

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2019.03.012.

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