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Effective synthesis of cyclic carbonates from CO_2 and epoxides catalyzed by KI/cucurbit[6]uril*

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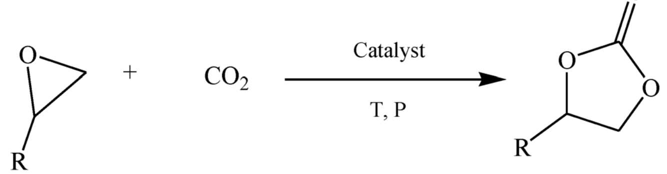
Abstract: The development of efficient, inexpensive, and nontoxic catalysts for cycloaddition of CO_2 with epoxides to produce five-membered cyclic carbonates is a very interesting topic. In this work, cycloaddition of CO_2 with propylene oxide (PO) to produce propylene carbonate (PC) catalyzed by potassium halides (KCl, KBr, and KI) in the presence of cucurbit[6]uril (CB[6]) was studied at various conditions. It was discovered that the potassium halides and CB[6] had excellent synergetic effect in promoting the reaction, and the KI/CB[6] catalytic system was the most efficient among them. The decrease of the activity and selectivity of KI/CB[6] was negligible after the catalytic system was reused five times. Further study indicated that the KI/CB[6] catalytic system was also very active and selective for the cycloaddition of CO_2 with other epoxides, such as glycidyl phenyl ether, epichlorohydrin, and styrene oxide. The mechanism for the synergetic effect of KI and CB[6] was also discussed.

Keywords: cucurbit[6]uril; cycloadditions; cyclic carbonates; potassium halides; synergetic effects.

INTRODUCTION

Conversion of carbon dioxide (CO_2) into valuable chemicals is of great importance because it is the main greenhouse gas and it is also nontoxic, inexpensive, and an abundant C1 building block [1]. One of the promising methods for the effective utilization of CO_2 is cycloaddition of CO_2 with epoxides to produce five-membered cyclic carbonates (Scheme 1) [2], which are widely used for various purposes,



Scheme 1 Cycloaddition of CO_2 to epoxide.

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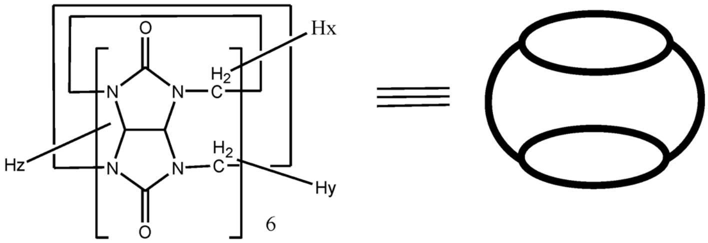
such as polar aprotic solvents, valuable raw materials, and intermediates in organic synthesis and precursors for producing polycarbonates [3].

In recent years, various catalysts and catalyst systems have been developed, including alkali-metal halides [4], organic bases [5], metal oxides [6], zeolites [7], titanosilicates [8], smectites [9], transition-metal complexes [10], Schiff base [11], ion-exchange resins [12], functional polymers [13], quaternary ammonium and phosphonium salts [14], ionic liquids [15], lanthanide oxychloride [16], gold nanoparticles supported on resins [17], and so on. Each kind of catalyst has advantages and drawbacks. It is well known that alkali-metal salts are inexpensive, abundant, and easily recyclable through simple separation. Unfortunately, the activity of alkali-metal salts alone is very low. However, it has been shown that addition of co-catalysts, such as PPh_3 and phenol [4f], crown ether [4h], and cellulose [4d], can enhance the activity of alkali-metal salt catalysts. Density functional theory study has indicated that the –OH group, potassium cation, and the iodine anion can form a ternary synergistic catalytic system, I^--(–OH)-K^+, which reduces the energy barrier of the rate-determining step of the reaction effectively [4c].

Cucurbit[6]uril (CB[6]) is a pumpkin-shaped macrocyclic compound formed by the cyclo-oligomerization of six glycoluril units, which form a rigid, annular, hollow cavity and with two highly polar carbonyl openings (Scheme 2) [18]. The inner surface of the CB[6] cavity is hydrophobic, and, in particular, both of its cavity openings are lined with carbonyl groups. The hydrophobic interior of CB[6] provides a potential site for inclusion of hydrocarbon molecules, and the carbonyl groups of CB[6] can interact with metallic cations such as alkali and alkali earth metals, transition metals, and lanthanides [19]. The catalytic performances of CB[6] for some reactions have also been studied [20].



Scheme 2 Structure of CB[6].

Although many efficient catalysts for the cycloaddition of CO_2 with epoxides have been developed, design of new catalyst systems for this kind of reactions is still an attractive topic. Especially, to the best of our knowledge, whether the compounds with carbonyl groups can act as co-catalysts for alkali-metal salts to promote the cycloaddition reactions has not been reported. In this work, we conducted the reactions using potassium halides as the catalysts in the presence of CB[6] at solvent-free condition. It was found that the salts and CB[6] had excellent synergetic effect to promote the reactions. We believe that the efficient and recyclable catalytic system has great potential of application. Furthermore, this work opens a new way for designing the effective catalytic systems for cycloaddition of CO_2 with epoxides to prepare cyclic carbonates.

RESULTS AND DISCUSSION

Effect of catalysts

The activity of various catalysts was tested using the reaction of propylene oxide (PO) and CO_2 to produce propylene carbonate (PC), and the results are summarized in Table 1. The yield of the product was very low when only CB[6] or a potassium halide was used as the catalyst (entries 1–4). The activity of

Table 1 Activities of various catalysts for the cycloadditon reaction of CO_2 and PO[a].

Entry	Catalyst	Yield of PC (%)[c]
1[b]	CB[6]	0.6
2	KCl	0.1
3	KBr	2.2
4	KI	36.2
5[b]	KCl + CB[6]	7.0
6[b]	KBr + CB[6]	30.6
7[b]	KI + CB[6]	98.0

[a]Reaction conditions: a stainless reactor of 22 ml, 20 mmol PO with 1.5 mol % catalyst, CO_2 pressure 4 MPa, reaction temperature 120 °C, reaction time 2 h.
[b]0.1 g CB[6] was added.
[c]Yields were determined by GC vs. an internal standard.

a potassium halide can be enhanced significantly by CB[6] (entries 5–7). The carbonyl groups in CB[6] have complexing effect with K^+, and this could be the reason that the yield of PC increased dramatically when CB[6] was added. The order of the activity of potassium halide was found to be KI > KBr > KCl (entries 2–7), which is consistent with the order of the nucleophilicity of the halide ions. Furthermore, the leaving ability of the halide anions is another important factor, which has great influence on the catalytic activity, and the activity increases with the leaving ability. The leaving ability of the halide anions is $I^- > Br^- > Cl^-$, which is consistent with the order of the nucleophilicity of these anions. The data in the table also showed that CB[6]/KI was very effective for the reaction. Therefore, CB[6]/KI was selected as the catalyst to study the effect of reaction conditions on the reaction.

Effect of CO_2 pressure on the yield of PC

Figure 1 demonstrates the dependence of CO_2 pressure on the yield of PC at 110 °C with a reaction time of 2 h. CO_2 pressure influenced the yield of PC strongly. The PC yield increased with increasing pressure in the low-pressure region but decreased in the high-pressure region. The maximum of the PC yield was reached at about 4 MPa. This phenomenon could be explained roughly by the phase behavior of the PO/CO_2 system at the reaction conditions determined using a view cell reported previously

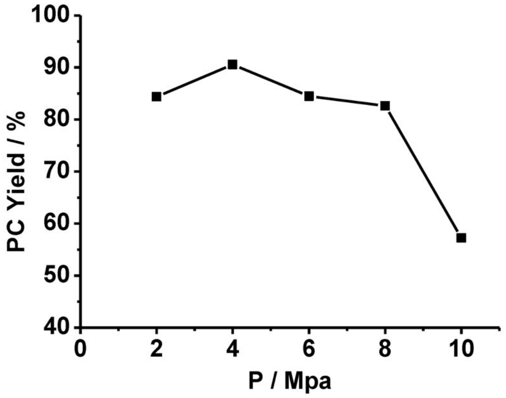


Fig. 1 Effect of CO_2 pressure on the yield of PC at 110 °C with a reaction time of 2 h. Reaction conditions: 20 mmol PO, 1.5 mol % KI, 0.1 g CB[6].

[21]. There were two phases in the reaction system. The top phase was the CO_2-rich phase, and the bottom phase was the PO-rich phase. The increase of pressure resulted in the increasing concentration of CO_2 in the bottom phase. As CO_2 was the reactant, this favored the reaction. On the other hand, the concentration of PO decreased with the increasing CO_2 pressure, which was unfavorable to the reaction. The competition of the two opposite factors led to the maximum yield at about 4 MPa.

Influence of reaction temperature on PC yield

The influence of reaction temperature on the yield of PC at 4 MPa with a reaction time of 2 h is given in Fig. 2. An increase in temperature resulted in an increase in the PC yield in the low-temperature region. A slight decrease of the PC yield in the high-temperature region was observed, which may be due to the formation of a small amount of by-products such as polymerized PC. Therefore, the optimized reaction temperature for the catalyst system was 120 °C.

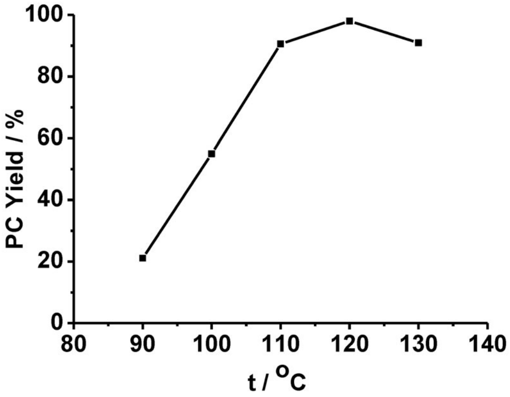


Fig. 2 Influence of reaction temperature on PC yield at 4 MPa with a reaction time of 2 h. Reaction conditions: 20 mmol PO, 1.5 mol % KI, 0.1 g CB[6].

Influence of reaction time

Figure 3 demonstrates the dependence of the PC yield on the reaction time at 120 °C under CO_2 pressure of 4 MPa. The results illustrate that the yield increased continuously at beginning and reached 98 %

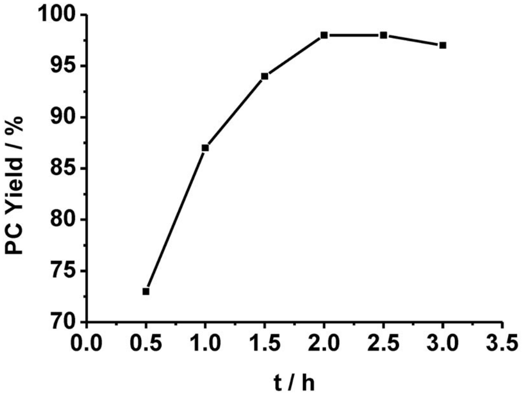


Fig. 3 Dependency of PC yield on reaction time at 120 °C and 4 MPa. Reaction conditions: 20 mmol PO, 1.5 mol % KI, 0.1 g CB[6].

within 2 h. Then the yield decreased slightly with prolonged reaction time. Therefore, the suitable reaction time for the system was 2 h.

Recyclability of the catalytic system

The reusability of the catalytic system was tested by the cycloaddition of CO_2 with PO to produce PC. In each cycle, CB[6]/KI was reused after extraction by ether and drying. The yields of PC for the five repeated runs are demonstrated in Fig. 4. It is shown that the yield of PC was almost constant in the five successive recycles, indicating that CB[6] was very stable under the reaction conditions.

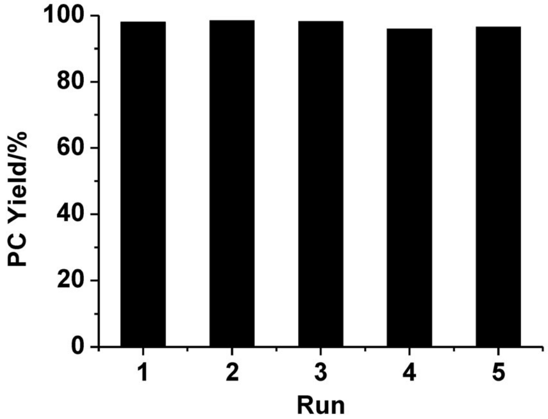
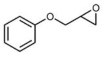
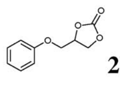
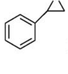
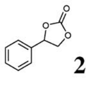
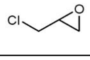
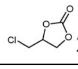


Fig. 4 Catalyst recycling. Reaction conditions: 20 mmol PO, 1.5 mol % KI, 0.1 g CB[6], 120 °C, 4 MPa, 2 h.

Different substrates

Under the optimized reaction conditions, cycloaddition of CO_2 with other epoxides was studied using the CB[6]/KI catalytic system, and the results are summarized in Table 2. It is obvious that the catalyst system was also very efficient for other epoxides, and the yields of the corresponding cyclic carbonates were in the range of 95–97 %. It can be seen that while the yield of the three carbonates (**2b–d**) were almost the same, their reaction time was different. Glycidyl phenyl ether (**1b**) gave the cyclic carbonate yield of 97 % within 3 h, but styrene oxide (**1c**) and epichlorohydrin (**1d**) needed 5 and 6 h, respectively,

Table 2 Synthesis of various carbonates catalyzed by KI in the presence of CB[6][a].

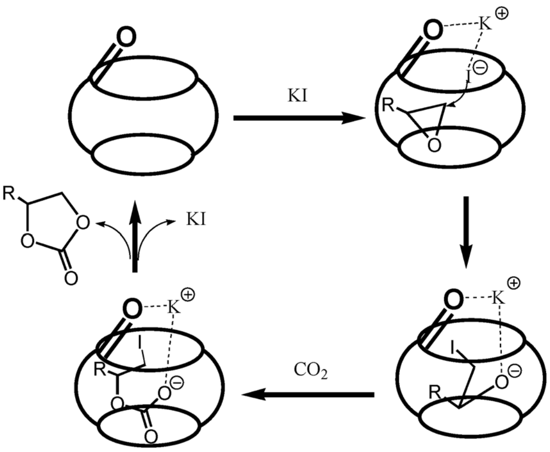
Entry	Epoxides	Products	Reaction time (h)	Yield (%)
1	 **1b**	 **2b**	3	97
2	 **1c**	 **2c**	5	95
3	 **1d**	 **2d**	6	96

[a]Reaction conditions: 20 mmol epoxide with 1.5 mol % KI, CO_2 pressure 4 MPa, reaction temperature 120 °C, 0.1 g CB[6].

to reach a high yield of the corresponding cyclic carbonates. This phenomenon can be easily understood. The electron-withdrawing CH_2Cl group of epichlorohydrin (**1d**) reduced the electron density of epoxide oxygen atom, while the activity of β-carbon center of styrene oxide (**1c**) was low.

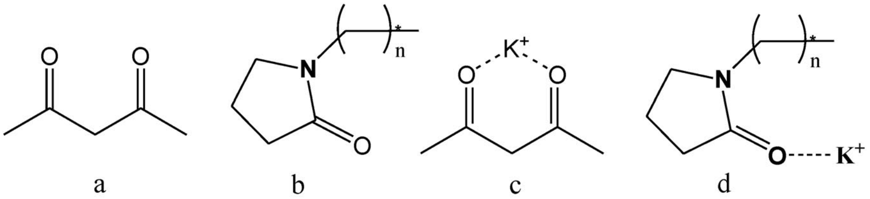
Mechanism

It was reported that the carbonyl group of CB[6] can interact with alkali cations [19]. Based on the results discussed above, a plausible mechanism for the coupling reaction of CO_2 with the epoxides is proposed, which is shown in Scheme 3. Firstly, the K^+ of the KI coordinates with the carbonyl groups of CB[6] through ion–dipole interactions, which reduces the interaction between K^+ and I^- and makes I^- more active. Secondly, the active I^- attacks the less hindered carbon atom of the epoxy ring, followed by a ring-opening step. Then, the oxygen anion of the opened epoxy ring interacts with CO_2 to form an alkylcarbonate anion, which is converted into the corresponding cyclic carbonate through the ring-closing step. Meanwhile, the catalyst is regenerated.



Scheme 3 Possible mechanism of the coupling of CO_2 with epoxide using KI/CB[6].

In order to provide more evidence for the effect of the carbonyl groups, we used acetylacetone (Scheme 4, a) and polyvinylpyrrolidone (Scheme 4, b) as the co-catalysts, which also contain carbonyl groups and interact with K^+ (Schemes 4c and 4d), to conduct the reaction. It was shown that acetylacetone and polyvinylpyrrolidone could also enhance the activity of KI. Under the same reaction conditions shown in Table 1, the yields of the reaction catalyzed by KI/acetylacetone and KI/polyvinylpyrrolidone were both 98 %. This supports the mechanism proposed.



Scheme 4 Structure of acetylacetone (a) and polyvinylpyrrolidone (b) and their interaction with K^+.

CONCLUSION

The catalytic performances of KCl, KBr, and KI for the cycloaddition of CO_2 with PO to produce PC have been studied in the presence of CB[6]. The potassium halides and CB[6] have excellent synergistic effect for catalyzing the reaction, and KI/CB[6] is most effective. Using KI/CB[6] as the catalyst, the optimal temperature, pressure, and reaction time for the reaction are 120 °C, 4 MPa, and 2 h, respectively. The KI/CB[6] catalytic system can be reused at least five times without notable reduction in activity and selectivity, indicating that the catalytic system is very stable at the reaction conditions. KI/CB[6] is also very active and selective for the cycloaddition of CO_2 with some other epoxides to produce the corresponding five-membered cyclic carbonates. The synergistic effect of potassium halides and CB[6] results mainly from the interaction of the carboyl groups of the CB[6] and the K^+ in the salts. The greener, inexpensive, active, selective, and stable catalytic system has potential application for synthesizing cyclic carbonates from CO_2 and epoxides.

EXPERIMENTAL

Materials

CO_2 was supplied by Beijing Analytical Instrument Factory with a purity of 99.99 %. PO, epichlorohydrin, sulfuric acid, potassium iodide, potassium chloride, and potassium bromide were analytical grade and were provided by Beijing Chemical Reagents Company. The glycoluril and other epoxides were purchased from ACROS ORGANICS. Formaldehyde was purchased from Xi Long Chemical Co., Ltd. All chemicals were used as received.

Preparation of CB[6]

The procedures to prepare CB[6] were similar to that reported previously [22]. In the experiment, glycoluril (10.0 g) and formaldehyde (84.6 g, 30 % in water) was added into a 500-mL flask, which was then heated to 100 °C in an oil bath. Then, 15 mL of water and 2 mL of sulfuric acid was added to the solution. The mixture was stirred for 3 h while the temperature was maintained at 100 °C. Then, the water and unreacted formaldehyde were evaporated under vacuum to obtain white solid mixture. The flask with the solid mixture was put into an oil bath of 140 °C until the mixture became transparent. After cooling to room temperature, the mixture was poured into a large amount of water. The precipitate obtained was washed twice with acetone and then dried under vacuum for 12 h at 60 °C before being used.

Cycloaddition reactions

The cycloaddition reactions were carried out in a 22-mL stainless steel reactor with magnetic stirrer. In a typical experiment, known amounts of catalyst, CB[6] and PO were added into the reactor. The reactor was maintained at the desired temperature, CO_2 was charged into the reactor until suitable pressure was reached, and pressure was kept constant during the reaction. After a suitable time, the reactor was cooled by ice water and CO_2 was released passing through a cold trap with ethyl acetate to absorb the trace amount of reactant and product entrained by CO_2. Then dodecane was added to the reactor as an internal standard. The product was analyzed by gas chromatography (GC) (Agilent 6820). The purity and structure of the product obtained at some typical experimental conditions were also checked by NMR spectroscopy and GC-MS methods. The procedures for other epoxides were similar, and the products were analyzed at room temperature on a Bruker 400 MHz NMR spectrometer using $CDCl_3$ as the solvent. In the experiments to test the reusability of the catalytic system, the KI/CB[6] was recovered by centrifugation, washed using ether to remove the product and dodecane, and then dried under vacuum for 12 h at 60 °C before reused. Spectral characterizations of the products (**2b–d**) are as follows:

*4-Phenyloxymethyl-1,3-dioxolan-2-one (**2b**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 6.8 Hz, 2H), 7.03 (t, *J* = 7.3 Hz, 1H), 6.92 (d, *J* = 8.2 Hz, 2H), 5.13 – 4.96 (m, 1H), 4.63 (t, *J* = 8.4 Hz, 1H), 4.56 (dd, *J* = 5.9, 2.6 Hz, 1H), 4.25 (dd, *J* = 10.5, 2.7 Hz, 1H), 4.16 (dd, *J* = 7.4, 3.1 Hz, 1H).

*4-Phenyl-1,3-dioxolan-2-one (**2c**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 6.92 (m, 5H), 5.68 (t, *J* = 11.2 Hz, 1H), 4.81 (t, *J* = 11.6 Hz, 1H), 4.34 (t, *J* = 11.5 Hz, 1H).

*4-Chloromethyl-1,3-dioxolan-2-one (**2d**)*

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.19 – 4.97 (m, 1H), 4.63 (t, *J* = 8.6 Hz, 1H), 4.42 (dd, *J* = 8.8, 5.7 Hz, 1H), 3.88 (dd, *J* = 12.4, 4.2 Hz, 1H), 3.76 (dd, *J* = 12.4, 3.4 Hz, 1H).

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