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Fixation of CO₂ into cyclic carbonates by halogen bonding catalysis

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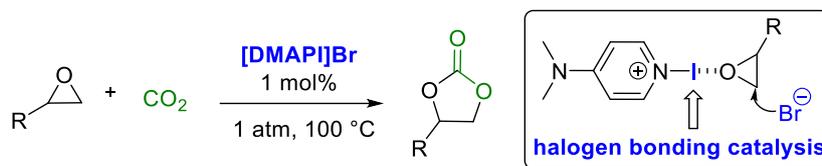
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Abstract

Halogen bonding, parallel to hydrogen bonding, was introduced into the catalytic cycloaddition of carbon dioxide into epoxide (CCE) reactions. A series of halogen bond donor (XBD) catalysts of *N*-iodopyridinium halide featured with N–I bond were synthesized and evaluated in CCE reactions. The optimal XBD catalyst, 4-(dimethylamino)-*N*-iodopyridinium bromide ([DMAPI]Br), under screened conditions at 100 °C, ambient pressure, and 1 mol % catalyst loading, realized 93% conversion of styrene oxide into cyclic carbonate in 6 h. The substrate scope was successfully extended with excellent yields (mostly 93% up) and quantitative selectivity (more than 99%). ¹H NMR titrations of the catalyst [DMAPI]Br on substrate epoxide certified that N–I bond directly coordinated with the epoxide oxygen. Plausible mechanism of halogen bonding catalysis was proposed, in which DMAPI cation functioned as halogen bond donor activated the epoxide and the counter anion bromide attacked the methylene carbon to initiate the ring-opening of the epoxide. CCE reactions promoted by *N*-iodopyridinium halide exemplified a first case of halogen-bonding catalysis in epoxide activation and CO₂ transformation.

KEYWORDS: carbon dioxide, cyclic carbonate, epoxide, halogen bonding, organocatalysis

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CO₂ fixation by halogen bonding catalysis: Halogen bond is introduced into the catalytic cycloaddition of CO₂ into epoxide (CCE) reactions. *N*-iodopyridinium halide salts are used as cationic halogen bond donor catalyst to activate the epoxides under ambient pressure to produce quantitative yields. We aim to exploit a supplementary approach to classical hydrogen bond to promote CCE reactions.

Introduction

The rapid increase of the level of carbon dioxide (CO₂) in the atmosphere caused by industrialization, particularly the intensive exploitation of fossil fuels, has led to environmental problems such as global warming, rising of sea levels, and extreme weather events.^[1] Chemical conversions of carbon dioxide into valuable products is one of the most promising strategy to this issue.^[2] Albeit photosynthesis is the predominant pathway of carbon circulation, it is prospective that incorporation of carbon dioxide as a renewable carbon source^[3] into value-added chemicals with the assistance of efficient catalysis^[4] can be a supplementary approach to recycle CO₂ from oil and gas consumptions. Energy intensive process is required in chemical fixation of carbon dioxide mainly because the carbon in CO₂ is in its most oxidized state.^[5] One feasible approach to overcome the high energy barrier was to choose high-energy reactants to compensate the thermodynamic barrier and utilize efficient catalyst to reduce the activation energy.^[6] In this regard, the cycloaddition of CO₂ with epoxide (CCE) reaction to afford cyclic organic carbonates was a viable and atom-efficient strategy. These cyclic carbonates can be used as aprotic polar solvents,^[7] electrolyte for lithium batteries,^[8] monomers for polycarbonates^[9] and synthon of polyurethanes.^[10] So far, a series of metal complex catalysts^[11] and organocatalysts^[12] have been explored and successfully applied in CCE reactions. Noncovalent interaction, predominately hydrogen bonding, is popular in organocatalysis in the last decade.^[13]

The halogen bond (XB), a hydrophobic and soft analogue to hydrogen bond,^[14] is defined by IUPAC in 2013 as a kind of noncovalent interaction between an electrophilic region of polarized halogen substituent X and a Lewis basic moiety.^[15] The molecule providing halogen atom is usually the acceptor of electrons, which is called “halogen bond donor” (XBD). Another molecule is “halogen bond acceptor”^[16] acting as the donor of electrons. Disclosed by previously theoretical and experimental studies, the distribution of the electrostatic energy on surface of halogen substituents is anisotropic,^[17] resulting in high electron density perpendicular to R–X bond and an electropositive region in elongation of R–X bond which is called “σ-hole” afterwards.^[18] Unique features deriving from “σ-hole” has been gradually observed for halogen bonding, that is, high directionality (approximately 180°),^[19] strength

tunability (in an order of $I > Br > Cl > F$),^[20] hydrophobicity, and donor atom dimensions^[21] (Figure 1). Although XB was known as electrophilic centers for 150 years,^[22] systematic investigations were performed in the last two decades,^[23] most of which were focus on supramolecular chemistry^[24] and crystal engineering.^[25] Since the first attempt to introduce XB into Hantzsch ester reduction was taken by Bolm in 2008,^[26] researchers turned attention to the application of halogen bonding catalysis in organic synthesis as a complement to hydrogen bonding,^[27] and fortunately achieved success in Diels-Alder reaction,^[28] Nazarov cyclisation reaction,^[29] Friedel-Crafts reaction^[30] and so on. Distinctive hypotheses were proposed to explain the activation of carbon-bromine bonds^[31] and carbonyl group by halogen bonding. Typically, DFT calculation studies by Huber et al. in 2017 verified the transition state of Michael reaction catalyzed by C–I moiety of halogen bond donor catalyst, indicating that halogen bonding activated oxygen of the carbonyl.^[32] To our best knowledge, halogen bonding has not been exploited in CO₂ fixation.^[33]

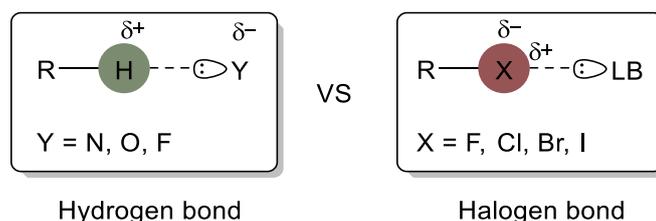
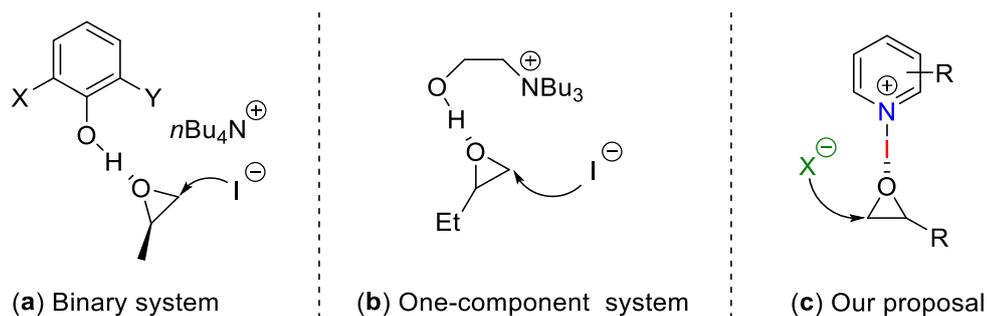


Figure 1. Hydrogen bond VS Halogen bond. LB = Lewis base, X = halogen.

CCE reactions were well promoted by hydrogen bonding catalysis. Both binary^[34] (Scheme 1a) and one-component^[35] (Scheme 1b) H-bonding organocatalysts were designed, in which H-bond donor activated the epoxide and the nucleophilic anion, usually halide anion accompanied by an onium counterion, attacked the methylene carbon to trigger the ring-opening of the epoxide. The parallelism of halogen bonding to the well appreciated hydrogen bonding inspired us to exploit the possibility of X-bonding in catalytic transformation of CO₂ in CCE reactions.



Scheme 1. (a) Binary component system of phenolic compounds combined with $n\text{Bu}_4\text{NI}$ by Kleij.^[34] (b) Bifunctional ammonium salts featured with an alcohol moiety and halide anion by Werner.^[35b] (c) Our proposal.

Herein, we propose a kind of halogen bond donor (XBD) consisted of *N*-iodopyridinium cation and halide anion (X^-) as one-component organocatalyst (Scheme 1c), and disclose halogen bonding catalysis in CCE reactions for the first time.

Results and Discussion

Design of the *N*-iodopyridinium X-bond donor catalysts and evaluation of the catalytic performances in CCE reactions.

Reconciling with the polarizability of halogen atoms, halogen bond donor (XBD) R–X exhibits more Lewis acidity, i.e., stronger halogen bond, in an order $X = \text{Cl} < \text{Br} < \text{I}$.^[36] For most situations where strong halogen bonding was needed, iodine atom was employed as XBD atom. R group was structurally diversified, however, classical XBDs were featured with C–I bond. Initially neutral XBD emerged as an example of haloperfluoroalkanes^[26] and polyfluorinated aryl iodides.^[37] Cationic XBDs were subsequently designed to form stronger halogen bonding, the most representative of which were a series of imidazolium-based XBDs.^[38] Nevertheless, there are few researches so far on N–I type XBDs in organocatalysis. Symmetric $[\text{N–I–N}]^+$ halonium complexes were synthesized, in which iodine accepted electrons in both lobes of empty p-orbital forming a structure of three-center halogen bond of halonium ions. This kind of halonium complexes were usually employed as a mild iodine transfer reagent as an example of $[\text{bis}(\text{pyridine})\text{iodine}(\text{I})]^+$ tetrafluoroborate.^[39] To our best knowledge, cationic XBD characterized with N–I bond has not been exploited in organocatalysis although N–I X-bonding was well documented in crystal engineering.^[40] The polarity of N–I bond is larger than that of C–I bond and the electro negativity of nitrogen will enhance the electron deficiency in the elongation of N–I bond and thus form stronger halogen bond.

N-iodopyridinium halide was therefore identified and chosen as XBD to catalyze CCE reactions. Prototype *N*-iodopyridinium chloride and *N*-iodopyridinium bromide were prepared for their easy syntheses and stabilities at high temperatures. Under conditions of 120 °C and ambient pressure, the experiments were conducted using styrene oxide (SO) as reference substrate in the presence of 1 mol % of the catalysts, the conversion of which were 42% and 60% respectively (Table 1, entries 5 and 15). In view of electron effect, steric hindrance effect, and halide anion, an array of *N*-iodopyridinium halide catalysts (Figure 2, **1–14**) were synthesized by reactions of substituted pyridines and iodine chloride or iodine bromide,^[41] and their catalytic activities as halogen bond donors were evaluated. The obtained results are shown in Table 1. Control experiment without loading of any catalysts was carried out under

the same conditions with the result of none production of carbonate as expected (Table 1, entry 1).

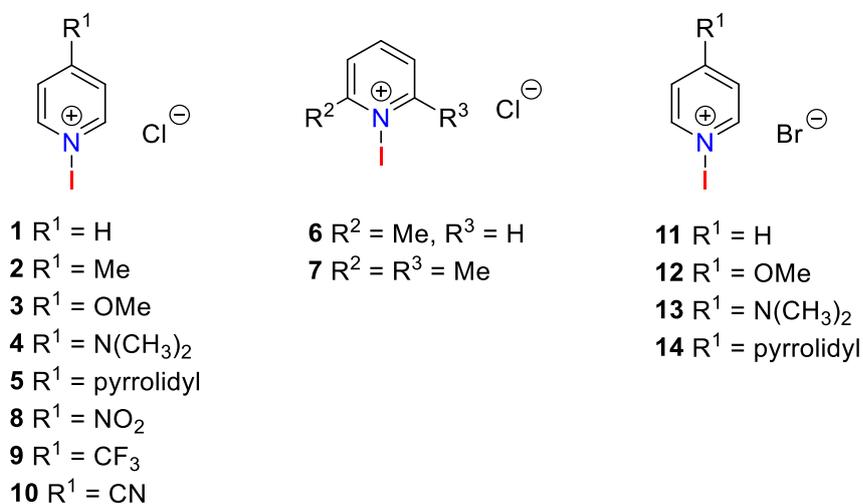


Figure 2. *N*-iodopyridinium halide catalysts with different groups were synthesized as candidate catalysts used in CCE reactions.

The conversions of SO using catalysts substituted by electron-donating groups (EDGs) in para-position of nitrogen atom (catalysts **2–5**) are apparently higher than that of catalyst **1** except for catalyst **3**, the conversion of which was 31% (Table 1, entries 6–9). Conversely, electron-withdrawing substituents (catalysts **8–10**) resulted in sharp decrease of conversions, best of which was only 26% (Table 1, entries 12–14). These phenomena were quite different from those observed in ionic hydrogen bonding. The electron effect of substituents on *N*-iodopyridinium aromatic ring in influencing the N–I halogen bonding abilities was not simply judged by the dipoles of N–I, which was straightforwardly predicted by the electron-donating or electron-withdrawing effect of the substitutional groups. Halogen bonding by its nature was event of multipole moment that exhibited anisotropy electron density distributions, where the electrophilic region, the σ -hole, was 180° to the N–I bond. EDGs on the 4-position of *N*-iodopyridinium made the N–I stronger XBD^[42] and showed shorter N–I⋯E distances,^[43] which suggested EDGs permitted better XBD catalyst.

Catalysts **11–14** were also synthesized for the purpose of making a comparison of two kinds of halide anions. Results showed that 4-(dimethylamino)-*N*-iodopyridinium bromide ([DMAPI]Br) exhibited the highest conversion, up to 94%, (Table 1, entry 17) higher than

classical bromide salt tetrabutylammonium bromide (TBAB) (Table 1, entry 19). The difference in conversions between chloride anion and bromide anion was marginal, albeit the bromine salts of catalyst **2** was not synthesized successfully (Table 1, entries 15–18). Attempts to synthesize *N*-iodopyridinium iodide catalysts failed for its lability under room temperature, which was consistent with previous literature.^[44]

Catalysts **6** and **7** with one and two *ortho*-methyl substitutions were designed to differentiate the influence of the steric hindrance. When a methyl group was attached to the *ortho*-position of nitrogen atom (catalyst **6**), the conversion decreased sharply down to 19% (Table 1, entry 10); no conversion was detected when catalyst **7** with two methyl groups was used (Table 1, entry 11). It is unfortunate that catalysts with longer and bulky alkyl groups on the two *ortho*-positions of nitrogen atom were not prepared successfully probably because the iodine cation was too huge to be accommodated. However, we can still conclude that steric hindrance has a negative impact on the catalytic efficiency of halogen bond donor.

Table 1. CCE reactions of styrene oxide (SO) with carbon dioxide to obtain styrene carbonate (SC) catalyzed by catalysts **1-14**.^[a]

SO + CO₂ (1 atm) $\xrightarrow[120^{\circ}\text{C}; 4\text{h}]{\text{XBD catalyst}}$ SC

Entry	Catalyst	t [h]	Yield [%] ^[b]	Selectivity [%] ^[b]
1	-	4	-	-
2	DMAP	4	26	99
3	I ₂	4	0	0
4	I ₂	4	0	0
5	1	4	42	99
6	2	4	68	99
7	3	4	31	99
8	4	4	66	99
9	5	4	77	99
10	6	4	19	99
11	7	4	0	0
12	8	4	26	99
13	9	4	0	0
14	10	4	4	99

15	11	4	60	99
16	12	4	30	99
17	13	4	94	99
18	14	4	67	99
19	TBAB	4	69	99
20	NaBr	4	0	0
21	EPB	4	45	99

[a] Reaction conditions: SO (10 mmol), CO₂ (1 atm), catalyst (1 mol %), 120 °C; [b] determined by ¹H NMR with CDCl₃ as solvent.

Screening of reaction conditions.

[DMAPI]Br (catalyst **13**) was finally chosen as the optimal catalyst utilized in the screening of reaction conditions. Efforts to lower the reaction temperature and catalyst loading under ambient pressure were taken to test the reactivity of the catalyst and determine the optimal reaction conditions (Table 2). Lowering the temperatures from 120 °C to 60 °C, catalytic reactivity reached a maximum at the temperature of 100 °C (Table 2, entry 2). When the temperature was higher or lower than 100 °C, the conversion decreased slightly to 88% or sharply to 5% respectively (Table 2, entries 1, 3 and 4). It is visibly suggested that 100 °C is the preferred temperature for the catalyst and that higher or lower ones received decreasing yields.

At 100 °C, a monotonous decrease of conversion from 94% to 22% was observed by lowering the catalyst loading from 2% to 0.1% (Table 2, entries 1 and 5–7). It is worth noting that conversion of SO increased just slightly from 93% to 94% in 6 h when catalyst loading was increased from 1% to 2% (Table 2, entries 1 and 7). In overall consideration of cost and practical conversions, 1 mol % catalyst loading and 100 °C (Figure 3) were finally decided as optimal conditions which subsequent researches were based on.

Table 2. Screening of reaction conditions of CCE reactions of styrene oxide (SO) and carbon dioxide to obtain styrene carbonate (SC) catalyzed by [DMAPI]Br.^[a]

Entry	Catalyst loading [mol %]	T [°C]	t [h]	Yield [%] ^[b]	Selectivity [%] ^[b]
1	1.0	120	6	88	99
2	1.0	100	6	93	99
3	1.0	80	6	47	99
4	1.0	60	6	5	99

5	0.1	100	6	22	99
6	0.5	100	6	73	99
7	2	100	6	94	99

^aReaction conditions: SO (10 mmol), CO₂ (1 atm), [DMAPI]Br; [b] determined by ¹H NMR with CDCl₃ as solvent.

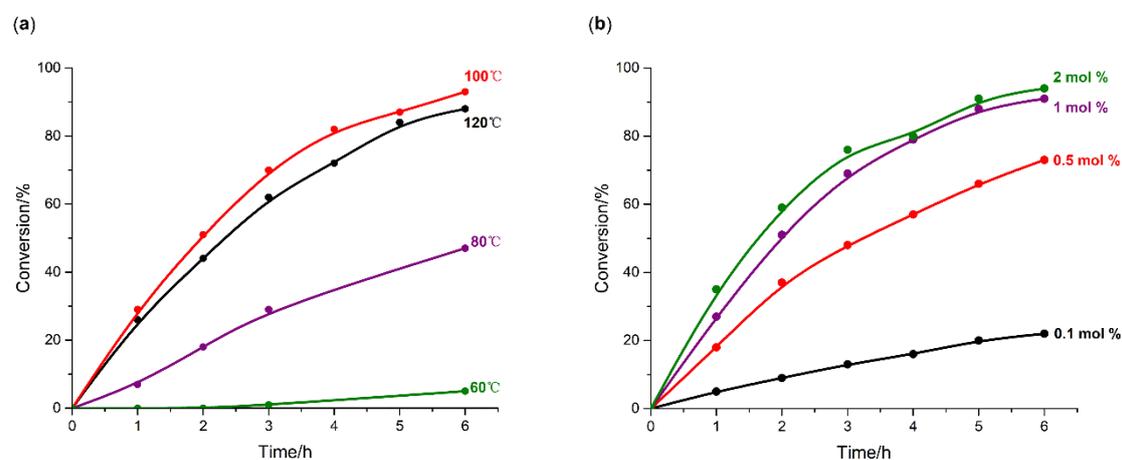
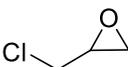
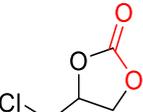


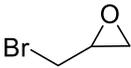
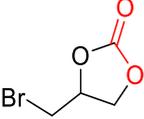
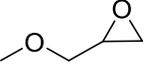
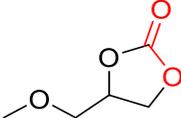
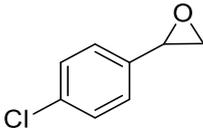
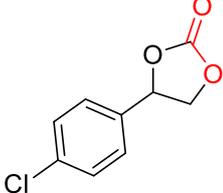
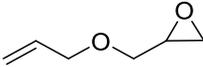
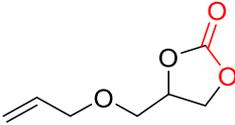
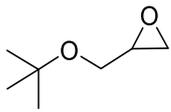
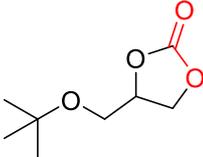
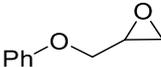
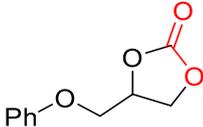
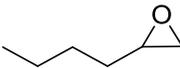
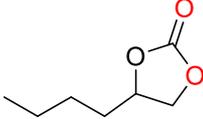
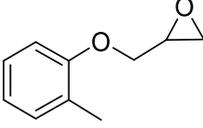
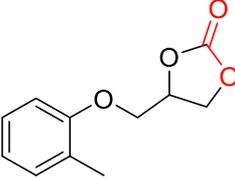
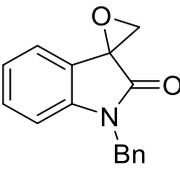
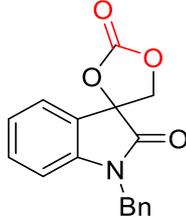
Figure 3. Screening of reaction temperature (a) and catalyst loading (b).

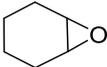
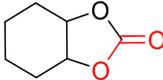
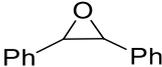
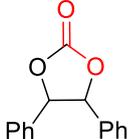
Substrate scope studies

Under the optimum conditions, efforts to extend the substrate scope of the protocol were taken, the results of which are presented in Table 3. Obviously, most of the epoxides were transformed into their corresponding cyclic carbonates with nearly full conversion ranging from 93% to 99% with 99% selectivity. A steric demanding epoxide 2-[(2-methylphenoxy)methyl]oxirane (Table 3, entry 9) and a spiro-epoxy oxindole (Table 3, entry 10) exhibited moderate conversions (50% up) due to their steric hindrance. Internal epoxides cyclohexene oxide and cis-stilbene oxide were tested that resulted no conversion (Table 3, entries 11 and 12). Pure cyclic carbonates were obtained simply by column chromatography and the structures were verified by ¹H NMR and ¹³C NMR.

Table 3. Extension of the scope of epoxide substrates with carbon dioxide catalyzed by [DMAPI]Br under optimum conditions.^[a]

Entry	Substrate	Product	Yield [%] ^[b]	Selectivity [%] ^[b]
1			96	99

2			99	99
3			94	99
4			75	99
5			96	99
6			96	99
7			93	99
8			93	99
9			58	99
10			50	99

11			0	0
12			0	0

[a] Reaction conditions: epoxide substrates (10 mmol), CO₂ (1 atm), 1 mol % of [DMAPI]Br, 100 °C, 5h;
 [b] determined by ¹H NMR and ¹³C NMR with CDCl₃ as solvent.

Proposed mechanism for CCE reactions catalyzed by halogen bond donors.

Halogen anion played a crucial role of nucleophilic attack during the process of ring-opening of the epoxide, which is generally known. However, inorganic bromide salt NaBr as catalyst cannot promote CCE reaction (Table 1, entry 20) demonstrating that cationic moiety is equally important to catalytic procedure. ¹H NMR titration experiments were performed to figure out the role that cationic moiety of halogen bond donor catalyst played in CCE reactions (as shown in Figure 4). The ratios of catalyst and SO were changed from 0/1 to 2/1. Small changes in the chemical shifts of the NMR were observed. Gradually increasing the amount of the substrate SO, chemical shift of the hydrogen on the carbon adjacent to the nitrogen atom of pyridine ring ranged from 8.173 to 8.201 ppm. Meanwhile, the methine proton on SO exhibited the same trend from 3.908 to 3.911 ppm. These phenomena were ascribed to the delocalization of electron densities by halogen bonding between iodine atom in catalyst [DMAPI]Br and oxygen atom on SO. When the ratio of catalyst and SO came up to 2/1, the substrate was saturated with catalyst and the chemical shift of hydrogen atom in two positions did not change anymore. Alpha proton of the pyridinium, nevertheless, may coordinate with the epoxide by hydrogen bond. Comparison experiment where *N*-ethyl pyridinium bromide (EPB) was employed to catalyze CCE reactions for its easy accessibility and ignorable hydrogen bond of ethyl group was performed to obtain 45% conversion of SO (Table 1, entry 21) while the iodopyridinium bromide promoted the 60% conversion (Table 1, entry 15). These results indicated that the existence of halogen atom, further, the halogen bonding, promoted CCE reactions.

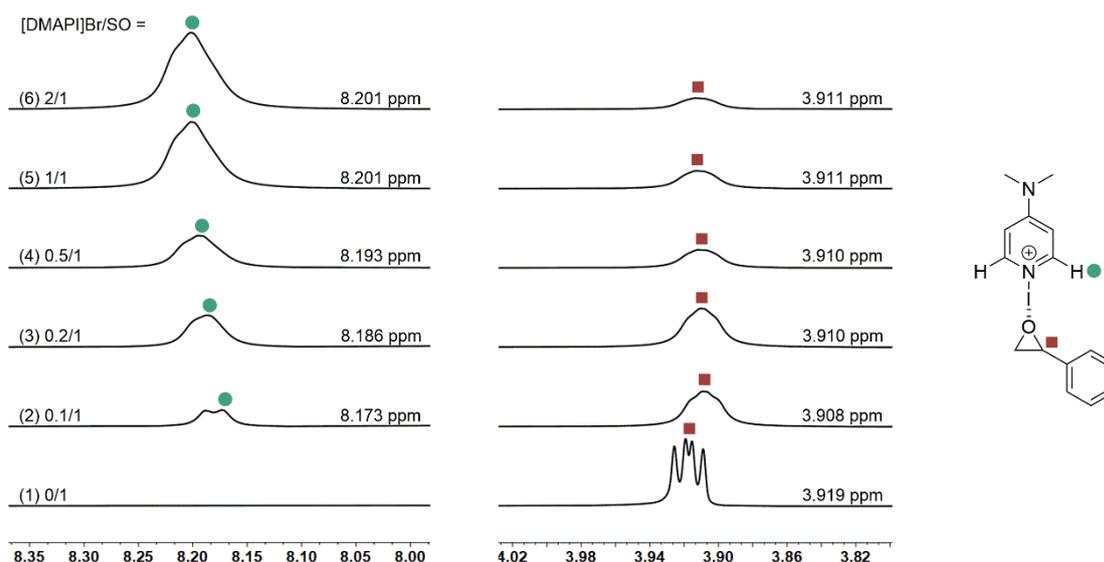
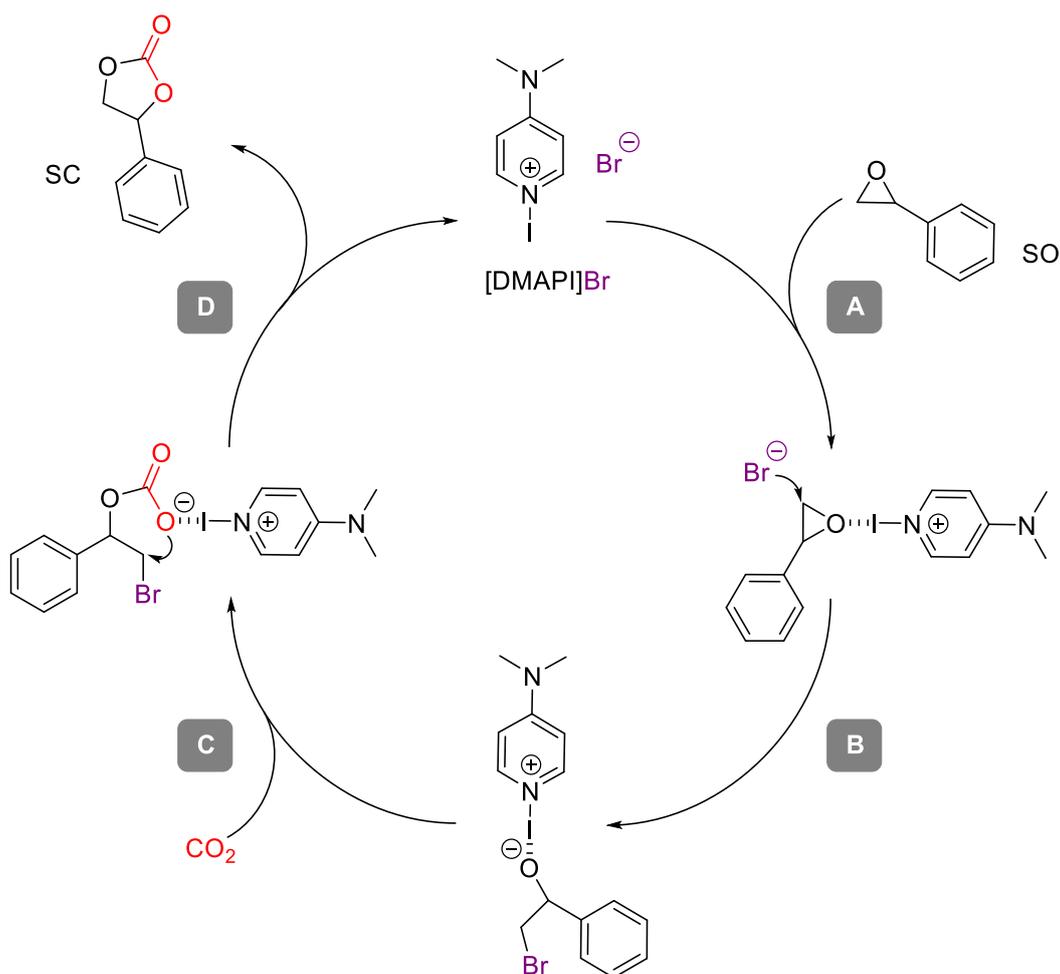


Figure 4. The chemical shift of hydrogen atom next to nitrogen atom in [DMAPI]Br in the ^1H NMR spectra ($\text{DMSO}-d_6$) (left) and the methine proton of SO (right) observed by titrations of [DMAPI]Br with SO; [DMAPI]Br/SO ratios: (1) 0/1, (2) 0.1/1, (3) 0.2/1, (4) 0.5/1, (5) 1/1, (6) 2/1.

A series of experiments were carried out to exclude the possibility of the decomposition of the catalyst, where [DMAPI]Br was possibly collapsed into DMAP and IBr or elemental iodine. However, experiments employed IBr or I_2 as catalyst demonstrated no conversion of SO (Table 1, entries 3 and 4) and merely 26% conversion was obtained when using DMAP as catalyst under the same conditions by 4 hours (Table 1, entry 2). As a matter of fact, the salt [DMAPI]Br resulted in a sharp increase of conversion, up to 94% (Table 1, entry 17). Therefore, DMAP, IBr or I_2 , individually, were not able to promote the reactions. It was the salt composed of DMAP and IBr in [DMAPI]Br structure that worked in the transformation of SO into cyclic carbonate. Additionally, thermogravimetric analysis was conducted to find only 2.905% loss of mass when the temperature was heated to 100.01 °C (See Supporting Information, S21). The weight loss was attributed to the residual water absorbed; however, no appreciable weight loss was observed at temperatures higher than 120 °C, which was the up limit of the CCE reactions. These data exclude the possibility of the decomposition of the [DMAPI]Br catalyst in the reactions. Evidence of X-ray structural analysis of single crystal of catalyst 4-(trifluoromethyl)-*N*-iodopyridinium chloride (catalyst **9**) also validated the existence of N-I covalent bond (See Supporting Information, S21).

With a view to previous reports and above-mentioned experimental data, a probable

mechanism that contributed to the formation of carbonates from SO was proposed. The positive charge enhanced N–I halogen bond of the iodopyridinium^[45] was a strong X-bond donor that will coordinated with the electron rich oxygen of the epoxide by strong X-bonding. Subsequently, the epoxide was activated, in which the polarity of C–O bond of the epoxide increased and the electron density of carbon atom decreased (Scheme 2, step A). Nucleophilic bromide anion attacked the electron deficient methylene carbon of SO, the ensued ring-opening of the epoxide formed alkoxide which was stabilized by the halogen bond donor (Scheme 2, step B). Further insertion of a carbon dioxide between the alkoxide and the XBD produced carbonate anion (Scheme 2, step C). Finally, ring-closure by intramolecular attack of carbonate anion on the proximity C–Br carbon expelled bromide anion and released the product cyclic carbonate. Concurrently, catalyst [DMAPI]Br was regenerated and took part in the following catalytic cycles (Scheme 2, step D).



Scheme 2. Possible mechanism for the formation of cyclic carbonates from epoxides and carbon dioxide by halogen bonding catalysis.

Conclusion

Halogen bonding catalysis was introduced into the cycloaddition of CO₂ into epoxides to produce cyclic carbonates. *N*-Iodopyridinium halide, a kind of cationic halogen bond donor based upon N–I bond, was chosen as catalyst for its electron deficiency enhanced by positively charged pyridinium nitrogen. A series of halogen bond donor catalysts were synthesized to assess the influences of electron and steric effects of the pyridiniums, and the nucleophilicity of the halide counter anions. 4-Dimethylamino-*N*-iodopyridinium bromide ([DMAPI]Br) was evaluated as the optimal catalyst in CCE reactions. Epoxides with variety of substituents were transformed into the corresponding cyclic carbonates successfully with excellent conversions and quantitative selectivities under the optimal conditions of 100 °C, ambient pressure, and 1 mol % catalyst loading. The catalytic process was proposed where the N–I moiety of the pyridinium formed halogen bonding with the epoxide to activate the substrate and the halide anion attacked the carbon of methylene to initiate ring-opening. ¹H NMR titration experiments of [DMAPI]Br on styrene oxide verified the activation of the substrate by halogen bond donor catalyst. Further investigations of N–X and C–X type halogen bond donor catalyst will be carried out to gain more knowledge about halogen bonding catalysis.

Experimental section

Materials. Epoxides were purchased from Alfa Aesar. Carbon dioxide with a purity of 99.999% was commercially available from Nanjing Shangyuan Co. Pyridines with different substituents, ICl and IBr were purchased from Energy Chemical. All reagents were utilized without any further purification.

Characterizations. ¹H NMR and ¹³C NMR spectra were obtained on a Bruker ARX-250 spectrometer operating at 400 MHz in deuterated solvent at ambient temperature. The structures of pure catalysts and obtained cyclic carbonates were verified by ¹H NMR and ¹³C NMR spectra with CDCl₃ as solvent. Conversions and selectivities of epoxides were determined by ¹H NMR.

General Procedure for the Synthesis of Catalysts 1-14. Catalysts were synthesized by the reaction of substituted pyridines with interhalides ICl or IBr. For instance, during the formation

of 4-dimethylamino-*N*-iodopyridinium bromide ([DMAPI]Br), the solution of IBr (0.47 mL, 10 mmol, 1.0 eq) in 20 mL of dry CH₂Cl₂ was slowly added in a solution of dimethylamionpyridine (1.22 g, 10 mmol, 1.0 eq) in 5 mL of dry CH₂Cl₂ in two hours. The obtained reddish-brown solution was stirred under room temperature for another hour. Crude product was concentrated by rotary evaporation and then was washed using anhydrous ethanol for three times. Pure catalyst was obtained after drying for few hours. The procedures of other catalysts were similar to that of [DMAPI]Br.

Representative Experimental Procedure for the Cycloaddition of Epoxide and CO₂ to Cyclic Carbonate. The cycloaddition reaction of carbon dioxide into epoxides (CCE) reactions were operated in a Schlenk flask. The inert gas used was argon. After Schlenk operations, catalyst and epoxide were added into the flask in order in the case of argon. After the argon in the flask was replaced by carbon dioxide, the Schlenk flask was put into the oil bath pan with a carbon dioxide balloon. In a typical reaction procedure, the reactor was charged with [DMAPI]Br (33 mg, 0.1 mmol, 0.01 eq) and styrene oxide (1.2 mL, 10 mmol, 1 eq) at 100 °C with a carbon dioxide balloon. The conversions of cyclic carbonate obtained were determined by ¹H NMR spectra with CDCl₃ as solvent. Pure carbonates were obtained by column chromatography with eluent of petroleum ether (PE) and ethyl acetate (EA) (5/1). The structures of carbonates were verified by ¹H NMR and ¹³C NMR with CDCl₃ as solvent.

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Notes

The authors declare no competing financial interest.

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