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Rational study of DBU salts for the CO₂ insertion into epoxides for the synthesis of cyclic carbonates

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ABSTRACT. A series of alkylated or protonated bicyclic amidine or DBU organocatalysts were investigated for the synthesis of cyclic carbonates from CO₂ and epoxides. The impact of the counter anion was examined in protonated samples where salts featuring halides displayed superior activity as a consequence of the nucleophilicity of the halide. The simple iodide salt of DBU

([HDBU]I) displayed the highest activity for the carboxylation of styrene oxide at 70 °C and 1 atmosphere of CO₂ pressure, obtaining 96% conversion after just 4 h. Alkylated salts showed lower catalytic activity than the analogous protonated salts. [HDBU]I also demonstrated broad substrate scope with a number of epoxides successfully converted to corresponding carbonates, including cyclohexene oxide which is a challenging substrate. Furthermore, the catalyst could be recycled up to 6 times without losing catalytic activity. Molecular modelling was conducted to provide mechanistic insight and supported the importance of the nucleophilicity of the counter anion in the insertion of CO₂ into epoxides and corroborated the experimental observations.

Introduction

The discharge of greenhouse gases, in particular CO₂ into the atmosphere is implicated in the worsening environmental problems associated with climate change.¹ As such, current developments are focussed on reducing these emissions by implementing cleaner energy and transport technologies as well as capturing emissions. It is envisioned that captured CO₂ can succeed petroleum derivatives as a cheap, sustainable chemical feedstock.²⁻⁸ One of the most promising applications for CO₂ lie in its transformation into high added-value cyclic carbonates⁹⁻¹³ that serve as a monomer set for a diverse assortment of sustainable polymers such as non-isocyanate poly(hydroxyurethanes) (NIPU)¹⁴⁻¹⁶ and polycarbonates.¹⁷⁻¹⁸ Additionally cyclic carbonates can be directly used as benign polar solvents for application in organic synthesis,¹⁹ or as liquid electrolytes in battery technology.²⁰ Since CO₂ is thermodynamically stable, a catalytic system that activates CO₂ and/or epoxide is needed for this ring expansion transformation. A large number of catalytic methods have been developed for this purpose, including the use of organometallic catalysts,²¹⁻²² guanidines,²³⁻²⁴ amidines,²⁵ phosphonium salts,²⁶⁻²⁷ imidazolium salts,²⁸⁻²⁹ quaternary amines.³⁰⁻³¹ Although metal-based catalysts typically outperform organic

counterparts, there is great interest to develop novel metal-free processes when metal residues are undesirable in the final product. Additionally, high pressures and/or high temperatures are often necessary for satisfactory conversion and the development of techniques featuring mild (ambient) experimental conditions for potential industrialization of these processes remains challenging.

Some of the most efficient organocatalysts reported in the literature for the synthesis of cyclic carbonates are based on DBU,³²⁻⁴³ since it is able to activate CO_2 to afford a catalytically active zwitterionic carbamate species⁴⁴ and favours the ring expansion of epoxides.⁴⁵ There are two different approaches to developing catalytic DBU derivatives. In the first case DBU is combined with a separate epoxide activator (e.g., via hydrogen bond or acid-base Lewis interaction) in a binary system. Alternatively, DBU can be protonated or alkylated to create a salt where the counter-ion can open the epoxide via nucleophilic attack (Scheme 1).¹²

Scheme 1. Proposed organocatalytic mechanisms for the synthesis of five-membered cyclic carbonates using DBU as catalyst (left pathway) and DBU salts (right pathway).

For example, Zhang et al. developed a sustainable methodology using DBU with different saccharides as catalysts for the synthesis of functional five-membered cyclic carbonates from epoxides. Despite of the benefit of the presence of hydroxyl groups, which are able to activate the epoxide through hydrogen bond interactions, these methodologies operate at very high pressure (20 atm) and the catalyst loading are relatively high (15 mol% DBU/1 mol% 2-deoxy-D-ribose). Similarly, Wang et al. developed a cooperative binary system formed by different halo-succinimides and DBU, where the halide anion was demonstrated to be important to obtain high conversions. Beside binary systems, some other more complex methodologies such as an inclusion complex system composed by a pentafluorophenolate DBU salt [HDBU]PFPhO (guest) and β -cyclodextrin (host) developed by Li et al. have also been described. In this work, it was shown that this kind of inclusion complex is able to immobilise the DBU derivative more efficiently and thus improved the catalytic activity as well as catalyst recyclability. Even though the system operates under quite low catalyst loading (0.15/0.15 mol%) (0.15/0.15), high pressures and temperatures (30 atm and 130 °C) are required to obtain high conversions.

Herein, we present a systematic evaluation of the performance of 14 DBU-derived catalysts in the cycloaddition reaction of CO₂ and various epoxides under mild, solvent free conditions. After optimizing the counter-ion choice by screening various protonated derivatives, we synthesised and screened a broad range of alkyl and benzyl substituted compounds featuring halide anions. An optimal methodology that operates under mild conditions and the recyclability of the catalyst is reported. Finally, the reaction mechanism and catalyst reactivity was investigated using density functional theory calculations.

Experimental Section

Material and methods. All commercially available starting materials were purchased from Sigma-Aldrich, Alfa Aesar or Acros Organics and used as received unless otherwise indicated. CO₂ was purchased from Air Liquide (99.995%). NMR spectra were recorded on a Bruker Avance 300 MHz spectrometer or Bruker Avance III HD 300 or 400 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) and referenced to the residual solvent signal (CDCl₃: ¹H, δ = 7.26 ppm, ¹³C, δ = 77.2 ppm, TMS: ¹H, δ = 0.00 ppm). Multiplicities are reported as s = singlet, brs = broad singlet, d = doublet, dd = doublet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, ddt = doublet of doublet of triplets, t = triplet, tt = triplet of triplets q = quartet, quint = quintet, m = multiplet. Multiplicity is followed by coupling constant (*J*) in Hz and integration. Mass spectra were recorded on a Bruker HCT+ ESI spectrometer. Elemental analysis was performed in duplicate by Warwick Analytical Services.

Synthesis of [HDBU]X X = halide salts. Ammonium halide (6.69 mmol) was dissolved in MeOH (6.7 mL, 1M), then DBU (6.69 mmol) was added. A reflux condenser was attached to the flask and the mixture was heated up to reflux overnight. Solvent was evaporated and the crude was recrystallized from CH₂Cl₂/Hexane. A solid was obtained.

Synthesis of [HDBU]X (X = BF₄, PhCO₂, MsO, TfO, TsO) salts. In a round bottom flask DBU (6.69 mmol) was dissolved in MeCN (6.7 mL, 1 M). Stoichiometric amount of H-X (6.69 mmol) was added dropwise to the DBU solution at 0 °C. Once addition was finished the mixture was stirred overnight at room temperature. Liquors were evaporated under vacuum to afford a solid which was recrystallized from CH₂Cl₂/Hexane. In some examples a colourless oil was obtained and used without further purification.

Synthesis of [R-DBU]X salts. Under inert atmosphere, a solution of alkyl or aryl halide (6.69 mmol) dissolved in dry MeCN (6.7 mL, 1M) was added by cannula transfer to DBU (6.69 mmol)

dissolved in dry MeCN (6.7 mL, 1M) at 0 °C. Once addition was finished the mixture was stirred overnight at room temperature. Progression of the reaction was tracked by TLC. Upon completion, the solvent was removed under vacuum to afford a solid which was recrystallized from CH₂Cl₂/Hexane. In some examples, further purification was obtained by flash column chromatography.

General method of the synthesis of cyclic carbonates. In a round bottom flask, [R-DBU]X (0.88 mmol) salt was dissolved in epoxide (8.77 mmol), reaction mixture was heated up to 70 °C for four hours under a CO₂ atmosphere (balloon). After four hours reaction mixture was cooled down to room temperature and an oily residue was obtained. An aliquot of the reaction crude was taken and conversion of epoxide was calculated by ¹H NMR spectroscopy. The carbonate was isolated by flash column chromatography using a mixture of ethyl acetate/hexane. Detailed procedures are available in the Supporting Information (SI).

Results and Discussion

Several protic, alkyl and aryl DBU-salt catalysts were prepared and tested around for the cycloaddition of CO₂ to various epoxides. Protic DBU derivatives (**1-8**) were synthesised either by neutralization of DBU with the corresponding acid. or by stoichiometric addition of an ammonium halide to DBU (Scheme 1).

Scheme 1. Synthesis of DBU based catalysts.

Each of the 8 protic DBU-salts were tested as catalysts for the cycloaddition reaction between CO_2 and styrene oxide, chosen as a substrate as a consequence of its commercial availability and the simplicity to calculate the reaction conversion by integration of the ^1H NMR spectra signals that correspond to styrene oxide ($\delta = 3.87, 3.15$ and 2.81 ppm) and styrene carbonate ($\delta = 5.68, 4.80$ and 4.35 ppm) (Scheme 2, Table 1). While most counterions displayed no or low activity (Table 1 entries 4 – 8), the halide anions displayed high yields of cyclic carbonate product (Table 1, entries 1, 2 and 3). Most notably, the activity followed the series $\text{I}^- > \text{Br}^- > \text{Cl}^-$ with [HDBU]I achieving 96% epoxide conversion under the conditions applied. These results demonstrate that while DBU is very effective at activating CO_2 ,⁴⁴ the so afforded DBU- CO_2 carbamate specie it is insufficiently nucleophilic to efficiently ring open the epoxide substrate under our optimized conditions, since our optimal conditions are quite mild, both epoxide activation using a DBU salt and ring-opening of the epoxide with an anion are required to promote an efficient CO_2 insertion.

The high activity of the iodide salts in comparison to other anions can be explained by either poor solubility of the catalyst in the neat reaction mixture or the low nucleophilicity of the anion.

Given the superior activity of the halide counterions for the protic DBU salts, derivatives featuring halide anions were targeted. These salts were prepared by simple nucleophilic substitution between the appropriate alkyl or benzyl halide and DBU and subsequently tested in the carboxylation of styrene oxide. In all cases the incorporation of alkyl group substituent was detrimental for the CO₂ insertion. Methyl, ethyl and benzyl substituents showed moderate activity (40, 36 and 41% epoxide conversion respectively) although significantly increasing the length of the alkyl chain rendered an improvement in the activity of the catalyst (76% epoxide conversion, Table 1, entry 13). Hydrogen bond donor moieties are known to enhance the activity of the catalyst as they activate the oxygen of the epoxide and therefore they make the carbons in positions 1,2 more electrophilic and easier to be opened by a nucleophile leading to mild conditions to conduct this transformation.⁴⁶ As such, [HO(CH₂)₆DBU]⁺Br⁻ was tested for activity. This catalyst resulted in a good conversion (71%) of epoxide to carbonate (Table 1, entry 12) although remained lower than the protic DBU bromide salt (77% epoxide conversion, Table 2, entry 2). The influence of the hydroxyl group was demonstrated to render a positive effect in the conversion when compared with the hexyl derivative (Table 2, entry 14). The effect of the catalyst loading was also studied using [HDBU]I (Table 2). Unsurprisingly, the reaction conversion was positively correlated to the amount of catalyst present with 10 mol% loading resulting in near complete consumption of the epoxide (Table 2, entry 4).

Scheme 2. Synthesis of styrene carbonate using different DBU salts.

Table 1. Reaction studies for styrene oxide and CO₂ cycloaddition catalyzed by DBU salts.^a

Entry	R	X	Conv. ^b (%)	TOF ^c (h ⁻¹)
1	H	Cl	60	1.5
2	H	Br	77	1.93
3	H	I	96	2.40
4	H	BF ₄	0	0
5	H	PhCO ₂	13	0.33
6	H	MsO	0	0
7	H	TfO	5	0.13
8	H	TsO	0	0
9	Me	I	40	1.00
10	Et	I	36	0.90
11	Bn	I	41	1.03
12	HO-(CH ₂) ₆	Br	71	1.78
13	CH ₃ -(CH ₂) ₉	I	75	1.88
14	Hx	Br	50	1.25
15 ^d	N.A	N.A	3	0.08
16 ^e	N.A	N.A	0	0

^a Reactions carried out at 70 °C and 1 bar of pressure for 4 h using 10 mol% of catalyst. ^b Conversion determined by ¹H NMR spectroscopy on the crude reaction mixture. ^c TOF = moles of product/(moles of catalyst × time). ^d DBU used as catalyst. ^e NH₄I used as catalyst.

In order to expand the scope of cyclic carbonates that can be prepared using the [HDBU]I salt, a wider range of epoxide substrates were explored. Under the optimised experimental conditions (10 mol% catalyst, 70 °C and 4 h) high conversions were observed for allyl glycidyl ether, benzyl glycidyl ether, epichlorohydrin and glycidol (Table 3, entries 6, 7, 8 and 9 respectively). Nevertheless, in some cases due to the negligible solubility of [HDBU]I in the epoxide much lower conversions were observed (Table 3, entries 2 and 4). In these two cases, in order to further explore

if these substrates could be converted, dimethylformamide (DMF) was added to the reaction mixtures as a co-solvent to produced homogeneous solutions in which to conduct the reactions. The complete consumption of epoxide was obtained in both cases (Table 3, entries 3 and 5). However, should be noted that some reports have shown that DMF is also capable of activating CO₂ and enhanced reaction rates in similar cycloaddition reactions.⁴⁷⁻⁴⁸ In order to investigate the scope of the catalyst, we investigated the cycloaddition of cyclohexene oxide, one of the most challenging substrates due to the large steric hindrance.

Table 2. Catalyst loading screening for the synthesis of styrene carbonate catalyzed by [HDBU]I^a

Entry	Catalyst Loading (%)	Conversion ^b (%)
1	1	54
2	2.5	66
3	5	80
4	10	96

^a Reactions carried out at 70 °C and 1 bar of pressure for 4 hours. ^b Conversion determined by ¹H NMR spectroscopy on the crude reaction mixture.

While under our optimised reaction conditions, no conversion of the epoxide was observed (Table 3, entry 10), increasing the CO₂ pressure to 4 MPa and temperature to 140 °C, we have been able to obtain 100% conversion of the epoxide to cyclohexene carbonate (Table 3, entry 11). Finally, the recyclability of the catalyst was also studied. We used allyl glycidyl ether as a model substrate for the catalyst recycling study. Recycling reaction study was performed under our optimized conditions *i.e.* 10 mol% [HDBU]I at 70 °C under 1 bar CO₂ pressure for 4 h. After the reaction was complete, the catalyst was recovered by reduced pressure distillation of the allyl glycidyl carbonate before being reused in the next reaction under the same conditions. A total of six experiments were performed.

Table 3. Cycloaddition of CO₂ to various epoxides catalyzed by [HDBU]I.

Entry	Cyclic carbonate	Conv. ^a (%)	Yield ^d (%)
1		96	85
2		59	
3		100 ^b	83
4		14	
5		100 ^b	87
6		99	87
7		91	82
8		96	73
9		90	65
10		0	0
11		100 ^c	79

^a Conversion determined by ¹H NMR spectroscopy on the crude reaction mixture. ^b DMF used as solvent. ^c 3MPa, 140 °C, 48 hours in DMF. ^d Product was isolated by flash column chromatography in silica gel.

In the first 5 runs no significant decrease of the catalytic activity of the [HDBU]I was observed with the conversion remaining between 97-99 % (Figure 1). While the catalyst remained highly efficient, the sixth run led to a slight reduction in epoxide conversion to 93%, most likely a result of mechanical losses through the catalyst recovery process.

Figure 1. Conversion of allyl glycidyl ether from recycled catalyst.

The range of reaction variables that have been studied with comparable organocatalysts to date make direct comparison between systems challenging. Nevertheless, it is clear that the most active metallo-organo catalysts are more active, for example, as Maeda et al. reported, use of a Zn-based porphyrin yielded 82% of 1,2-hexylene carbonate when only 0.05 mol% of catalyst was used under atmospheric pressure at 20 °C for 48 h.⁴⁹ For the organocatalytic synthesis of five-membered cyclic carbonates, ammonium salts such tetrabutylammonium iodide (TBAI) and tetrabutylammonium bromide (TBABr) have been used as cornerstones in a plethora of binary methodologies as co-catalyst, in both organometallic and organocatalytic studies.^{30, 50-53} Certainly, when TBAI is used along with hydrogen bond donor moieties such 2-pyridinemethanol, in a 1:1 ratio and 8 mol% of catalyst loading, styrene carbonate is obtained with 85% yield at room pressure, at 45 °C and 20 h.⁵⁴ This binary system was demonstrated to be recycled up to 6 runs without significant losses of catalytic performance. This example is quite representative in terms of how complex is to evaluate the virtues of the catalysts reported for this reaction, since compared to the system presented in this manuscript, although similar isolated yields are reported, our protocol works in shorter periods of time while Wang et al. used a lower temperature.

In order to gain a deeper insight into the ring expansion of epoxides with CO₂ in the presence of protic ionic salts based on DBU, a comprehensive computational mechanistic study was performed. Density functional theory (DFT) calculations were performed on the conversion of propylene oxide to a cyclic carbonate catalyzed by the protonated halide salts – [HDBU]Cl, [HDBU]Br and [HDBU]I as catalyst with the Gaussian 16 suite of programs.⁵⁵ Previous mechanistic calculations have been reported for the cycloaddition of CO₂ and epoxides with two suggested pathways (Scheme 3).⁵⁶⁻⁵⁸

In the first case the epoxide activation occurs simultaneously with CO₂, (Scheme 3, path a), while second path involves stepwise activation of the epoxide before subsequent addition of CO₂, (Scheme 3, path b). Even though the nucleophilic ring opening of the epoxide is possible from either side, attack on the more substituted carbon is energetically disfavoured due to steric hindrance.

Scheme 3. Proposed mechanisms for the incorporation of CO₂ into epoxide.

Figure 2. Potential energy surfaces of the cycloaddition of CO₂ to propylene oxide catalyzed by [HDBU]I, path (a) and (b), first transition state.

As a consequence, only the mechanisms involving addition to the secondary carbon are considered. Among the three catalysts, [HDBU]I displays the most favourable energetic profile in accordance with experimental results (Figures S45-S48 ESI). As such, detailed analysis of the reaction paths will be discussed for only [HDBU]I, (Figure 2). Complete structural and energetic data for transitions states and intermediates for all reactions can be found in the Supporting Information. The first transition state (TS1) of path (a) is destabilised by 8.6 kcal·mol⁻¹ compared to the reactants, with an energetic barrier of 20.9 kcal·mol⁻¹ relative to the reactant's complex (Figure 2 – path a). Alternatively, TS1 for path (b) (stepwise reaction profile) is energetically disfavoured by 21.2 kcal·mol⁻¹ relative to the initial conditions and with an energetic barrier of 30.9 kcal (Figure 2 – path b). The large difference of the reaction barriers between either path (~10 kcal·mol⁻¹) is remarkably consistent regardless of catalyst choice (that can also be observed for the other catalysts). This suggests that the reaction will mainly proceed *via* the simultaneous activation of the ring and addition to CO₂ (Scheme 3 – path a). TS 1 corresponds to the formation of an oxy-anion through the breaking of the carbon-oxygen bond of the epoxide.

The nucleophilic attack of the [HDBU] salt on the non-substituted carbon of the epoxide, concurrently with the activation of CO₂, results in the ring opening of the epoxide (Figure 2, Int. 1a). For this transition state the energy barrier is 20.9 kcal·mol⁻¹ for I⁻, 26.2 kcal·mol⁻¹ for Br⁻ and 26.8 kcal·mol⁻¹ for Cl⁻, leading to the following relative reactivity: [HDBU]I > [HDBU]Br ≈ [HDBU]Cl, (Figure 3). TS2 involves the formation of the carbonate ring *via* intramolecular ring-closure of the intermediate (Int. 1b), the corresponding anion being released, regenerating the [HDBU] salt catalyst (Int. 2). Lower energies are required to overcome this transition state, 15.6 kcal·mol⁻¹ for I⁻, 16.7 kcal·mol⁻¹ for Br⁻ and 19.9 kcal·mol⁻¹ for Cl⁻. Therefore, TS1 is the rate-limiting step of the reaction, (Figure 3). The comparative study of [HDBU] salts led to the following relative catalytic activity: [HDBU]I > [HDBU]Br > [HDBU]Cl, each energetic barrier is lower when [HDBU]I is employed as catalyst. Consequently, DFT calculations wholly support the experimental findings that demonstrate the superior catalytic ability of [HDBU]I.

Figure 3. Energy profile for the formation of 4-methyl-1,3-dioxolan-2-one from propylene oxide and CO₂ catalysed by [HDBU]I.

Conclusions

A systematic evaluation of DBU-based salts in the catalytic conversion of cyclic carbonates from the ring expansion of epoxides has been developed. The cyclocarbonation of terminal epoxides proceeded with moderate to high yields using very mild conditions when protonated salts were employed while alkylation of the DBU decreased its catalytic performance. The experimental findings were corroborated with DFT calculations on various reaction systems. Development of novel organocatalysts able to perform the reaction presented in this manuscript, as well as, the incorporation of CO₂ in such a challenging substrate as oxetane is, is currently under investigation.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website at DOI: XXX. Complementary procedures, ¹H and ¹³C NMR spectra and energy reaction profiles (PDF).

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Notes

The authors declare no competing financial interest.

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FOR TABLE OF CONTENTS USE ONLY

- ✓ Mild conditions (Room pressure)
- ✓ Metal free methodology
- ✓ 6 recycling runs
- ✓ Broad substrate scope (8 examples)