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Halogen-free fixation of carbon dioxide into cyclic carbonates *via* bifunctional organocatalysts[†]

Bifunctional organocatalysts bearing diamine and carboxylic acid groups were used for the preparation of cyclic carbonates by cycloaddition reactions of CO_2 and epoxides. Hydrogen-bonding interactions originating from carboxylic acids are of enormous importance due to their contribution in enabling the opening of the epoxide ring. In addition, the diamine can activate the CO_2 via carbamate formation and accelerate its transformation to cyclic carbonates. As a result of this synergy, this metal-free system shows excellent catalytic activities with high yields (92–99%) and selectivities (99%), and thus, provides a promising halogen-free and green pathway for the synthesis of cyclic carbonates from CO_2 and epoxides.

Since pre-industrial times, the carbon dioxide (CO_2) concentration in the atmosphere has been steadily increasing due to the combustion of fossil fuels for energy production. With historically slow energy transitions, the use of fossil fuels for energy production seems to continue, and so increased attention is directed towards the development of new ideas that can help reduce CO_2 emissions.¹ In this context, the conversion of CO_2 is a very interesting direction to explore. Considering that CO_2 is not only a component of greenhouse gases, but also a useful carbon source in organic synthesis due to its abundance, nontoxicity and recyclability, it offers a promising strategy to address global warming and create a renewable carbon economy.^{2–6} However, for many reactions, utilization of CO_2 is challenging and requires the development and implementation of advanced catalytic materials.

With regard to the use of CO_2 in chemical synthesis, there are numerous reactions leading to a wide range of useful compounds under study.^{7,8} Among them, organic carbonates are industrially valuable materials that are often employed as electrolytes in lithium ion batteries and as solvents due to their low toxicity, high boiling points, and biodegradability.⁹ Moreover, they are utilized as starting materials for the synthesis of polycarbonates^{10,11} and polyurethanes,¹² where the production of polycarbonates amounts to two million tonnes annually, a number that increases every year. Currently, some carbonates are synthesized with phosgene, a highly toxic material that is banned in many countries and is further controlled by an international treaty concerning chemical weapons. Also, the process leads to hazardous chlorinated waste. As such, significant benefits would come from green reaction pathways. In this regard, the synthesis of cyclic carbonates by cycloaddition of CO₂ and epoxides has great potential for green and clean big scale productions, if environmentally friendly catalytic materials are available. Due to the industrial relevance of cyclic carbonates, a large number of catalysts and reaction conditions were tested for their preparation from CO2 and various epoxides. The systems reported include both homogeneous and heterogeneous catalysts with or without transition metals, e.g. organometallic compounds,¹³⁻¹⁵ metal-salen complexes,^{16,17} metal-organic frameworks,18-22 zeolitic imidazolate frameworks,23,24 ionic liquids²⁵⁻²⁷ and organocatalysts.²⁸⁻³⁰ As the opening of epoxide rings is the critical step in the cycloaddition of CO_2 , these catalytic systems often contain halogen atoms (mostly Ior Br⁻, rarely Cl⁻) that are conducive to ring-openings by nucleophilic attacks. In particular, metal-based multifunctional catalytic systems with halides show relatively high catalytic activity even under mild conditions. Ema et al. reported porphyrin-based catalysts which are modified with different alkylammonium bromide groups on the sides of the ligand and centered with Mg(II) metals.^{31,32} The synergy between Lewis acidic Mg centers and bromides results in a high catalytic activity for the synthesis of cyclic carbonates from epox-

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ides and CO2. The studies of North et al. show a similar cooperation with an Al(III)/Br⁻ system for the same reaction by using Al-salen complexes in the presence of alkylammonium bromide salts.^{14,15} Moreover, a series of porous ionic polymers and poly(ionic liquid)s were reported by Wang et al. for the conversion of CO₂ into cyclic carbonates.^{33,34} These heterogeneous materials contain halogens as counter ions and show high catalytic activities under mild reaction conditions such as atmospheric CO₂ pressure and low reaction temperatures. However, due to the toxic and non-green nature of halogens, an undesired and problematic situation is created in terms of developing green solutions to use and convert CO₂. Hence, recent efforts have been directed towards finding metal and halogen-free catalytic systems, such as the case with hydrogen-bond catalysis. Hydrogen-bond catalysts are a special class of organocatalysts that bear functional groups such as hydroxyl or carboxylic acid in their structures, and owing to certain acidity of hydrogen atoms in these groups, they have the ability to catalyse different reactions, including the cycloaddition reaction of CO₂ to epoxides.^{35,36} While halogens in conventional catalysts could open the epoxide rings via attacking the carbon atoms neighbouring the oxygen atom, hydrogen-bond catalysts could activate the epoxides with hydrogenbonding interactions.

Herein, we report the use of carboxylic acid and diaminebased bifunctional organocatalysts for cycloaddition reactions of CO₂ to epoxides. While carboxylic acid groups have the ability to push hydrogen-bonding interactions with the epoxide and arrange the ring-opening, diamines can accelerate the cycloaddition reaction due to the activation of CO₂ *via* carbamate formation.^{37,38} As ring-opening is the rate-determining step in this reaction,^{39,40} changes in the structure and acidity of the hydrogens in carboxylic acids have a direct influence on the reaction process. Due to the synergy between a Brønsted acid and a Lewis base in the compounds used, the reaction proceeds effectively without using any halogens and additives. Therefore, this method provides a promising halogen-free and green pathway for the synthesis of cyclic carbonates from CO₂ and epoxides.

Bifunctional organocatalysts used in this work were prepared using a modified procedure from our previous works,^{41,42} which is an easy catalyst-free methodology for constructing aromatic C–N bonds and building blocks in high yields. The catalytic compounds 1–7 were obtained as pure solids confirmed by ¹H and ¹³C NMR analyses and could be directly used for catalytic reactions (discussed in the ESI†).

For the cycloaddition reaction of CO_2 to epoxides, 1,2-epoxybutane was selected as a model substrate to check the applicability of catalytic materials and to find out ideal reaction conditions such as reaction time, temperature, CO_2 pressure, catalyst loading and solvent (Table 1 and Fig. 1). As shown in Table 1, the cycloaddition reaction of CO_2 to 1,2-epoxybutane carried out in the absence of any solvent shows no noteworthy conversion (entry 4), even if potassium iodate was used as an additive at different temperatures (entries 1–3). Since the catalyst 1 with diamine and carboxylic acid groups is highly polar,

Table 1 Cycloaddition of CO_2 into 1,2-epoxybutane under various conditions $^{\text{a}}$



1		-	00	· T
$2^{b,c}$	_	1	100	<1
3 ^b	—	1	100	1
4	—	1	140	4
5	DMSO	1	140	47
6	DMA	1	140	82
7	DMF	1	140	83
8	DMF	—	30	0
9 ^c	DMF	—	100	<1
10	DMF	—	100	<1
11	DMF	—	120	13
12	DMF	—	140	34
13 ^d	DMF	—	120	15
$14^{d,e}$	DMF	1	120	96

^{*a*} Reaction conditions (unless otherwise mentioned): 1,2-Epoxybutane (10 mmol), catalyst (5 mol%), solvent (2 mL), CO₂ (2 MPa), reaction time (24 h). ^{*b*} KI (5 mol%) used as an additive. ^{*c*} Reaction time (10 h). ^{*d*} CO₂ (3 MPa). ^{*e*} Catalyst (7 mol%). DMSO, dimethyl sulfoxide; DMA, dimethylacetamide; and DMF, dimethylformamide. The yields were determined by GC using dodecane as an internal standard.



Fig. 1 Activity of the bifunctional diamine catalyst **1** in the cycloaddition reaction of CO₂ and 1,2-epoxybutane (10 mmol) into 1,2-butylene carbonate (*cf.* equation in Table 1) using DMF (2 mL) as the solvent: (a) effect of temperature by using 2 MPa CO₂, 24 h reaction time and 5 mol% of **1**; (b) effect of CO₂ pressure by using 150 °C as the reaction temperature, 24 h reaction time and 5 mol% of **1**; (c) effect of catalyst loading by using 150 °C as the reaction temperature, 2 MPa CO₂ and 24 h reaction time; (d) effect of reaction time by using 150 °C as the reaction temperature, 2 MPa CO₂ and 5 mol% of **1**.

it requires polar solvents or milieus in order to get dissolved and to be catalytically active (even in polar solvents such as alcohols or acetonitrile, the solubility of catalytic materials (1-7) is extremely low). Indeed, by using highly polar solvents such as dimethyl sulfoxide (DMSO), dimethylacetamide (DMA) or dimethylformamide (DMF), the reaction takes place and a remarkable increase in the yield of cyclic carbonate is observed (entries 5-7). By replacing DMSO with less viscous DMA, the yield of the product increases from 47 to 82%, while between two amides DMA and DMF with a yield of 83%, no significant change in the yield was observed, indicating no direct influence of the aldehyde hydrogen in DMF on the reaction process. The catalytic activity of DMF was also studied through catalyst-free reactions at various temperatures and CO₂ pressure (entries 8-13), and DMF showed no significant activity at temperatures up to 100 °C with yields below 1%, while at higher temperatures (120 and 140 °C) it was able to convert CO2 and 1,2-epoxybutane to the corresponding cyclic carbonate to some extent (with yields of 13 and 34%, respectively). This is in agreement with previous works, which reported on the ability of amides for the activation of CO₂, e.g. via nucleophilic activation by DMF.⁴³⁻⁴⁵ In the absence of a catalyst, an increase of CO2 pressure from 2 to 3 MPa did not lead to a noteworthy rise in the yield (entries 11 and 13). In contrast, by reactions with catalyst 1, increasing the catalyst loading to 7 mol% and the CO2 pressure to 3 MPa led to a higher product yield (96%) at milder reaction temperatures (cf. entries 7 and 14).

Fig. 1 shows the effect of changes in reaction parameters on product formation. The yield increases with increasing temperature and reaches the maximum at 150 °C (Fig. 1a). Similarly, the yield increases with increasing CO₂ pressure and has its maximum value at 2 MPa (Fig. 1b). Interestingly, at a pressure of 0.5 MPa, no 1,2-butylene carbonate (BC) was detected; however, quite high yields over 98% for 1,2-butanediol were obtained. By increasing the CO₂ pressure to 3 MPa, any further change in the yield was noted. By increasing the catalyst loading from 3 to 4 mol%, a very steep increase in the yield was observed and from 4 to 7 mol% the changes in the product yield were rather moderate (Fig. 1c). Finally, the yield also increased with longer reaction times and in particular, it increased steeply up to 20 h and reached the maximum after 24 h (Fig. 1d). As a result, the appropriate reaction conditions for the given reaction were found to be 150 °C reaction temperature, 2 MPa CO₂ pressure, 5 mol% catalyst loading and 24 h reaction time.

As carboxylic acid and amine functions are keys for the catalytic activity of **1**, we envisioned that its performance can be affected through manipulations in the electronic properties of both functional groups. To investigate this systematically, diamine/carboxylic acid based catalytic compounds with altering alkyl chains between the amines (C2 to C4) and differently positioned carboxylic acid groups (*para* and *meta*) were prepared and applied to the same reaction (*cf.* Scheme 1 and Table 2). So with an increasing number of CH₂ groups in the alkyl chain between the amines, the yield of the product drops



Scheme 1 Bifunctional diamine catalysts with altering chain lengths between the amines and carboxylic acid groups at *para* (1-3, 7) or *meta* positions (4-6).

Table 2Overview of the catalytic activity of a series of bifunctionaldiamine-carboxylic acid catalysts 1-6 (cf. Scheme 1)^a



^{*a*} Reaction conditions: 1,2-Epoxybutane (10 mmol), catalyst (7 mol%), DMF (2 mL), temperature (120 °C), CO_2 (2 MPa), reaction time (24 h). The yields and selectivities were determined by GC using dodecane as an internal standard.

slowly (Table 2, entries 1-3 and 4-6). This is reasonable because the longer the alkyl chain between the amines, the more inductive it is towards carboxylic acids and thus reduces their acidity. Less acidic carboxylic acid groups promote weaker hydrogen-bonding interactions and cause an inferior activation of the epoxide which ultimately leads to lower yields of cyclic carbonates. By switching from para to meta carboxylic acid substituted analogues, the yields increase slightly (Table 2, entries 1 and 4; 2 and 5; and 3 and 6). The lower activity of para-substituted catalysts is due to the electron donation of amines to para-COOH groups via the resonance effect leading to a decrease in their acidity, which is not the case with meta-substituted COOH groups (see Fig. S8[†]). Structural modifications of the catalysts influence both the acidity of carboxylic acids and the basicity of amines. However, since ring-opening is the rate-determining step in the cycloaddition of CO₂ to epoxides,^{39,40} the changes in the acidity of the COOH groups are crucial. According to this study, catalysts 1 and 4 with two-membered alkyl chains between the amines show the highest catalytic activities after a 24 h reaction time with 86 and 93% yields, respectively.

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The performance of diamine/carboxylic acid-based catalyst **1** was tested for a series of different terminal epoxides using optimized reaction conditions (Table 3). The catalyst showed excellent activity for the cycloaddition reaction of CO_2 to the majority of epoxides with very high yields (92–99%). Only by the reaction with cyclohexene oxide, due to its less reactivity a relatively lower yield of 30% was observed. Cyclohexene oxide is an internal epoxide with high steric hindrance around the epoxide ring and hence it is considered as a very challenging substrate for reaction with CO_2 .^{46–48}

In order to gather intimate knowledge of the reaction mechanism, potential interactions between the diamine/carboxylic acid-based catalyst (1) and substrates were monitored by ¹H, ¹³C NMR and FT-IR experiments (Fig. 2 and Fig. S9†). As shown in the ¹H NMR spectra of 1 in Fig. 2a, chemical shifts for acidic hydrogens from carboxylic acid groups and

Table 3 Synthesis of cyclic carbonates from epoxides and CO₂ using bifunctional diamine catalyst 1^a



^{*a*} Reaction conditions: Epoxide (10 mmol), catalyst **1** (5 mol%), DMF (2 mL), temperature (150 °C), CO_2 (2 MPa), reaction time (24 h). The yields and selectivities (99% for all six products in entries 1–6) were determined by GC using dodecane as an internal standard.



Fig. 2 ¹H and ¹³C NMR investigations on the possible interactions between bifunctional organocatalyst **1** and substrates of the cyclo-addition reaction (*cf.* equation in Table 1): (a) changes in the ¹H NMR spectrum of the catalyst **1** after mixing with 1,2-epoxybutane as the epoxide at various temperatures between 25 and 100 °C using DMF-*d*₇ as the solvent and an epoxide/catalyst ratio of 20:1; (b) changes in the ¹³C NMR spectrum of the catalyst **1** after adsorbing CO₂ at 60 °C under 1 MPa pressure (NMR analyses were performed using DMSO-*d*₆ as the solvent at 25 °C).

less acidic ones from amines move upfield with increasing temperatures.

After the addition of 1,2-epoxybutane to the solution of catalyst 1 in DMF- d_7 at 25 °C, the ¹H peak for the COOH proton at 12.25 ppm weakened and widened strongly. At temperatures over 50 °C of the catalyst 1/epoxide mixture, the COOH peak disappeared completely, while ¹H peaks from amines (6.05-6.52 ppm) remained unchanged at all temperatures. The disappearance of the COOH peak in the ¹H NMR spectra results from interactions of the acidic hydrogen and this shows clearly that diamine/carboxylic acid catalyst 1 undergoes strong hydrogen-bonding interactions with the epoxide already at room temperature. In contrast, the amine groups in 1 show no visible interactions with the epoxide according to unvarying ¹H peaks. Potential interactions between the catalyst 1 and CO₂ were examined via ¹³C NMR, where after absorbing CO_2 in the catalyst solution in DMSO- d_6 , a new peak at 112.5 ppm appeared (Fig. 2b), indicating the activation of CO₂ by a diamine/carboxylic acid based catalyst. Furthermore, in FT-IR analyses of catalyst 1, a new absorption

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peak at 1810 cm^{-1} was observed after interaction with CO₂, which potentially belongs to the C=O vibration of the carbamate salt formed between 1 and CO₂ (Fig. S9[†]). These observations are consistent with the previous reports related to CO₂ activation by amines embedded or grafted in materials such as liquids.49-52 metal-organic frameworks and ionic Furthermore, additional catalytic tests were conducted to understand the origin of CO₂ in the cyclic carbonates formed and to reveal the effect of the functional groups of the catalysts as well as the synergy between them (Table S1[†]). By using catalyst 1 with pre-adsorbed CO_2 (cf. ESI^{\dagger} for details), the reaction was carried out under an argon atmosphere and a product yield of 18% was obtained. The same reaction using catalyst 1 without pre-adsorbed CO2 under an argon atmosphere showed no yield, which makes sense due to the lack of CO₂ in the reaction system. In contrast, the third reaction with catalyst 1 without pre-adsorbed CO₂ under a CO₂ atmosphere resulted in 86% yield (entries 1-3, Table S1[†]). These experiments show that the conversion takes place with pre-adsorbed CO₂ (readily activated CO₂ by diamines) giving a low yield (18%) due to the limited amount of CO₂. On the other hand, in the reaction without pre-adsorbed CO2 we observe a much higher yield (86%), because the reaction takes place under a CO_2 atmosphere with enough CO2 availability. Therefore, CO2 in the product might have originated from both pre-adsorbed CO₂ and CO₂ gas in the reactor via gradually being taken and activated by the catalyst. To control the effect of functional groups in the catalyst, besides the original catalyst with COOH and amino groups (1), we used two other materials as catalysts, in which either COOH groups are replaced with COOEt (7) or amino groups with ethers (8). The reactions catalyzed by these three compounds under the same conditions resulted in 86, 23 and 61% yields, respectively. In addition, the reaction with a mixed catalyst of 7 and 8 (50:50) gave 74% yield (entries 3-6, Table S1[†]). Since COOH groups are responsible for the activation of epoxides (rate-determining step), the catalyst with COOEt groups (7) shows the lowest activity (23%). The catalyst with ether groups (8) shows a 25% lower yield compared to our original catalyst (1), indicating the importance of amines for the catalytic activity of these materials. In addition, a mixed catalyst of 7 and 8 (50:50) was found to be more active with a yield of 74%, unlike when they are used alone, because it provides both COOH and amino groups for catalysis. If both functional groups are available in the same compound as in 1 (higher concentration of both functional groups), the yield increases to its maximum under given conditions (86%) and hence demonstrates that the cycloaddition reaction of CO₂ into epoxides is promoted by the synergy between COOH and amino groups.

In the light of the insights gained from NMR, FT-IR and DFT studies (Fig. S10[†]), we proposed a bimolecular reaction mechanism for the cycloaddition of CO_2 into epoxides using diamine/carboxylic acid bifunctional organocatalysts (Scheme 2). According to this, both DMF as the solvent and the diamine embedded in the structure of the catalyst activate CO_2 via the formation of a DMF/CO₂ adduct and carbamate,



Scheme 2 Proposed mechanism for the cycloaddition of CO₂ into epoxides with bifunctional diamine catalysts.

respectively, while carboxylic acid groups activate the epoxide by hydrogen-bonding interactions and lead to polarization of epoxide-O–C bonds. Subsequently, activated CO_2 bound with the amine in the form of carbamate (and/or in the DMF/CO₂ adduct) attacks the less-hindered carbon atom of the epoxide and causes the opening of the ring. Comparing a monomolecular and bimolecular ring-opening step, DFT calculations show a clearly lower energy and shorter distance between activated CO_2 and epoxide in a bimolecular complex intermediate (-23.6 *vs.* -8.01 kcal mol⁻¹ and 2.93 *vs.* 5.34 Å, Fig. S10†) which hence seems to be the most likely scenario. Finally, the cyclic carbonate is formed by an intramolecular ring-closing step and it is separated from the catalyst.

Conclusions

In summary, for the preparation of cyclic carbonates from CO_2 and epoxides, we have applied simple organocatalysts bearing diamine and carboxylic acid functional groups. These organocatalysts are easily prepared with high yields and no need for any catalytic process or purification. Using these compounds as catalysts for cycloaddition reactions of CO_2 to terminal epoxides, high yields (92–99%) and selectivities (99%) were achieved without the use of any metals, halides or other additives. The high catalytic activity of simple diamine/carboxylic acid based organocatalysts is due to the synergy between COOH and diamine groups with the abilities of hydrogenbonding interactions and CO_2 activation *via* carbamate formation, respectively. The proposed reaction mechanism of this transformation is supported by ¹H, ¹³C NMR, FT-IR and DFT studies, in which the ring-opening of epoxide by hydrogenbonding interactions plays a key role. This method provides a green alternative to the preparation of cyclic carbonates including CO_2 -based ones that often involve metals, halides, phosgene and its equivalents. As simple modifications in the structure of the catalysts lead to improvements in the catalytic activity, it is envisioned that the development of related materials in future works can be effectively used for similar reactions.

Conflicts of interest

There are no conflicts to declare.

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