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A computational study into the mechanistic insights of base catalysed synthesis of cyclic carbonates from CO_2: Bicarbonate anion as active species

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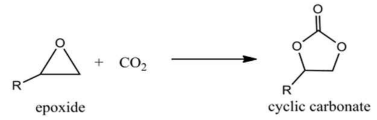
Kuruppathparambil Roshith Roshan,[a] Revi Achuthan Palissery,[b,c] Amal Cherian Kathalikattil,[a] Robin Babu,[a] George Mathai,[b] Hwa-Soo Lee,[d] and Dae-Won Park*[a]

The standalone catalytic potential of common organic bases such as imidazole, pyridine and dimethylaminopyridine (DMAP) for the solvent-free cycloaddition of CO_2 with epoxides yielding five membered cyclic carbonates is reported here. Appreciable conversion of various epoxides with excellent selectivity towards the desired products was materialized in this metal/ halide/hydrogen bond donors/solvent free reaction. The presence of catalytic amounts of water was found significantly advantageous in this base catalyzed chemical fixation of CO_2 and the conversion almost got doubled or tripled under the same reaction conditions. A definitive mechanism for activation of base catalysis is also proposed with the aid of *ab initio* calculations performed at B3LYP/6-31G (d,p) level. Besides, a bicarbonate anion mediated catalytic cycle is also proposed utilizing computational calculations. The possible intermediates and transition states and the related energy constraints of the base alone and base- water catalyzed reaction is deduced and the activation energy obtained was found higher for the former (~30 kcal/mol) than that of the latter (~12 kcal/mol), which rationales the experimental observation of the higher activity of the latter.

Introduction

Exploitation of renewable resources in the chemical industry serves as the key viable approach towards the replacement of at least a part of the present day fossil fuel consumption. A strategic methodology to harness such an opportunity consists of effectively introducing renewable sources in the chemical production chain. In that aspect, CO_2 serves as one of most promising C1 feedstock towards the synthesis of important chemicals including methanol, lactones, oxazolidinones, five and six membered cyclic carbonates, formyl derivatives and biodegradable polymers. Among the aforementioned transformations, the solvent less cycloaddition ring expansion reaction of epoxides with CO_2 yielding five membered cyclic carbonates (Scheme 1) requires special attention owing to the 100% atom economic nature of the reaction as well as due to the wide applicability of cyclic carbonates as electrolytes in Li ion batteries, aprotic solvents, polymer synthesis etc.[1] Since CO_2 is thermodynamically stable and kinetically inert, extensive research has been devoted to the development of efficient catalytic systems to eventuate its cycloaddition with the epoxide moieties. As a result, the library of catalyst systems available for CO_2-epoxide coupling is enriched with homo and heterogeneous catalysts of various types ranging from simple metal oxides [2a], Schiff's bases [2b] and phenols,[2c] to rationally and carefully designed organometallic salen complexes,[3] supported ionic liquid catalysts,[4a-e] and most recently metal organic frameworks.[4f-j] Even though, transition metal catalyzed reactions furnished excellent conversion rates, the demand for materializing metal-free reaction mediums unmasked the potential of hydrogen bonding groups such as hydroxyl, and carboxylic entities to engage in synergistic catalysis with nucleophilic anions to deliver appreciable epoxide-CO_2 conversion.[5] A step further close towards ensuring greener credentials was the finding that, halide ions (nucleophiles), which are otherwise considered hazardous from an environmental point of view, is not a necessity to afford cyclic carbonates from CO_2-epoxide cycloadditions; superbase/cellulose[6a] and alkanolamines[6b] which are completely devoid of any metal or halides are recently reported as promising catalysts for this chemical



Scheme 1 Cyclic carbonate synthesis from CO_2 and epoxides

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[a] School of Chemical and Biomolecular Engineering, Pusan National University, Busan 609-735, South Korea. Email: dwpark@pusan.ac.kr.
[b] Department of Chemistry, Sacred Heart College, Thevara, Kochi 682-013, India.
[c] Bharatiar University, Coimbatore 641046, India.
[d] Department of Chemical Industry, Dong-Eui Institute of Technology, South Korea.

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transformation of CO_2. Although inferior to the metal catalysts in terms of efficiency, these organocatalysts are generally low cost molecules characterized by their inertness towards air and moisture.

Organic bases are most probably the simplest and widely studied homogeneous organocatalysts in the context of chemical fixation of CO_2 owing to their ready availability, low toxicity, economic nature and structural diversity.[1d] Du et al.[7a] reported polymer resins tethered with primary, secondary and tertiary amine groups active as single component catalysts in the synthesis of propylene carbonate at 80 bar CO_2 pressure and 100 °C. Also, in 2004, Sankar et al. reported the catalytic activity of dimethylamino pyridine (DMAP) alone for cyclic carbonate synthesis in CH_2Cl_2 under relatively mild conditions of 4 bar CO_2 and 140 °C.[7b] In agreement with this, Jones and co-workers also reported the catalytic activity of DMAP alone in both homogenous and heterogeneous phases (Scheme 2).[7c]. To elucidate the mechanism behind, several groups have tried to identify the chemical species formed by the reaction between Lewis bases and CO_2, especially DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) and CO_2 using various physico-chemical analytical techniques. Heldebrant et al. reported that, white single crystals of bicarbonate salt of DBU were isolated in the presence of adventitious water[7d] and later, Villers et al. successfully solved the crystal structure of a TBD-CO_2 adduct (TBD=1,5,7-triazabicyclo[4.4.0]dec-5-ene) under strict anhydrous conditions.[7e]

Even though, definitive mechanistic details regarding the base catalyzed CO_2-epoxide cycloaddition were still lacking, more reports on the organic base tethered catalysts were published intermittently.[7f-i] Most recently, Sankar et al. investigated imidazole anchored silica as a heterogeneous catalyst for the synthesis of cyclic carbonates from CO_2 and epoxides where the surface silanol groups supposedly played synergistic catalysis with the base moieties.[7i] However, as per Tsang et al. the synergistic effect of surface silanol groups is just one possible way of accelerating the catalysis and speculated that, the bases alone must be able to catalyze the reaction even with little assistance from hydrogen bonding groups.[7h] Hence we deemed it worthwhile to explore the mechanism underlying in this sort of base alone catalyzed cycloaddition reaction of CO_2 through *ab initio* calculations.

Results and Discussion

The application of theoretical simulations to gather more insights into the mechanism prevailing in a specific organic transformation is an expanding field of research [8]. For the purpose, the cycloaddition of propylene oxide (PO) with CO_2 forming propylene carbonate (PC) mediated by simple organic bases catalysts such as imidazole, pyridine and DMAP, both in the absence and presence of water was experimentally evaluated and was theoretically validated using density functional theory (DFT) study.

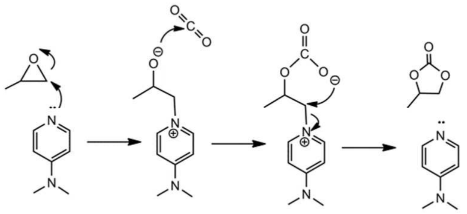
Table 1 displays the catalytic activity exhibited by the various organic bases towards PO-CO_2 coupling. As is generally known, no conversion of PO occurred in the absence of a catalyst (entry 1). But catalytic amounts of imidazole, pyridine and DMAP catalyzed the PO conversion to PC with 28, 34 and 31% yields, respectively at 120 °C, and 12 bar CO_2 pressure in 3 h using 1.2 mol% catalyst amount under solvent free conditions (entries 2, 3, 4). With a double increase in the CO_2 pressure (25 bar), the conversion rates with imidazole, pyridine and DMAP was increased to 63, 77 and 71% respectively (entries 5, 6, 7) where in all cases, the selectivity to PC remained more than 99%. DMAP has earlier been reported to display appreciable conversion rates at similar conditions, but in the presence of CH_2Cl_2.[7b] Surprisingly, the solvent less catalysis of DMAP mediated PC synthesis has never been reported, to the best of our knowledge. Entries 8, 9, and 10 (Table 1) evidenced the highly co-operative role of water in the base catalyzed reaction, in accordance with the literature.[7i] The catalytic activity of bases were increased to more than 90% even at lower CO_2 pressures (12 bar), in the presence of small amounts of water. And delightful it was to observe that, the selectivity to PC was not compromised, which is a key factor in ensuring sustainability of a reaction.

From the literature reports, the mechanism behind this Lewis base alone catalyzed reaction shall be considered to portray the following events. The lone pair of electron from the Lewis base (in here, imidazole, pyridine or DMAP) attacks the least hindered C atom of the epoxide ring forming a new N-C bond. As a result, the epoxide "O" atom attains partial negative charge and makes a nucleophilic attack on the C atom formed leads to ring closure and the lone pair returns to the parent base. To obtain more insightful information about the

Table 1 Catalyst screening test using propylene oxide – CO_2 cycloaddition.

	Catalyst	CO_2 pressure (bar)	PO conversion (%)[a]	PC selectivity (%)[a]
1	-	12	2	-
2	Imidazole	12	28	99
3	Pyridine	12	34	99
4	DMAP	12	31	99
5	Imidazole	25	63	99
6	Pyridine	25	77	99
7	DMAP	25	71	99
8	Imidazole + H_2O	12	91	98
9	Pyridine + H_2O	12	96	99
10	DMAP + H_2O	12	98	99
11	Imidazole + CH_3COOH	12	95	98
12	Pyridine + CH_3COOH	12	94	98

Reaction conditions: PO = 3 mL (42.8 mmol), Catalyst amount = 1.2 mol%, H_2O = 0.6 mol%, CH_3COOH = 0.6 mol% , 120 °C, 3 h, a. Obtained from GC.



Scheme 2 Mechanism of DMAP activated CO_2 cycloaddition [7c]

theoretical plausibility of this mechanism, we utilized DFT with a Gaussian 09 set package and B3LYP correlation functional which simulated the structural and stereochemical aspects of the entities involved and the energy parameters associated with it.

Computational organic chemistry has been increasingly recognized as bridge between theory and experiment in establishing the mechanisms of chemical reactions.[8] Even though quite a handful of studies including ours have reported the quantum mechanical calculations of hydrogen bond donor - halide synergistic catalysis,[5b,f,6b] a similar computational study on a base alone catalyzed CO_2-epoxide cycloaddition has never been done, to the best of our knowledge. Herein we have done two sets of theoretical calculations using the bases (imidazole, pyridine and DMAP) moieties as catalysts in the absence and presence of water (set 1 and 2, respectively).

The activation energy (*Ea*) required for non-catalyzed cycloaddition of PO with CO_2 to produce PC was reported to be around 55–59 kcal/mol, which is too high for the reaction to proceed spontaneously, demanding the need for a catalyst.[5b,f,6b]

Organic bases without water

For imidazole, pyridine and DMAP, the total energy of the system including the catalyst and the substrates (PO + CO_2), were preset to zero. The optimized geometrical arrangement of PO, CO_2 and DMAP forming the reactant complex is shown in Fig. 1a and the diagram showing the relative energy levels associated is illustrated in Fig. 2. The reactant complex gets transformed to a ring opened transition state ($_{DMAP}$ TS-1), which involves the following events, i) the aromatic nitrogen atom on the DMAP interacts with the β C atom of the epoxide via its lone pair of electrons characterized by a bond distance of 1.92 Å., ii) the weakening of the β C-O bond of PO, as is evident from its increase in bond distance from a typical C-O bond (1.43 Å) to 1.95 Å., iii) the linear geometry of CO_2 starts transforming into a bent structure, accelerated by the influence of partial negative charge developed on the epoxide oxygen atom (the bond distance of O_{PO}-C_{CO2} decrease from 2.76 Å to 2.17 Å). The energy value corresponding to $_{DMAP}$TS-1 was obtained as 27.62 kcal/mol. This $_{DMAP}$TS-1 transforms inevitably to its stable intermediate state as a ring opened complex ($_{DMAP}$ Int) with energy of 4.18 kcal/mol. It was found that, the C-N bond between the epoxide β carbon and the DMAP nitrogen (1.48 Å) becomes stronger than its preceeding step (1.87 Å). Also, the O_{PO}-C_{CO2} (1.39 Å) attains a bond length more closely to that of a typical C-O bond. Subsequently, a second transition state was formed ($_{DMAP}$TS-2) wherein, the partial breakage of the C-N bond was witnessed, detaching the DMAP moiety from the epoxide-carbonate complex. Besides, the β carbon atom of the epoxide gets closer with the O atom of CO_2 (the βC_{PO} - O_{CO2})

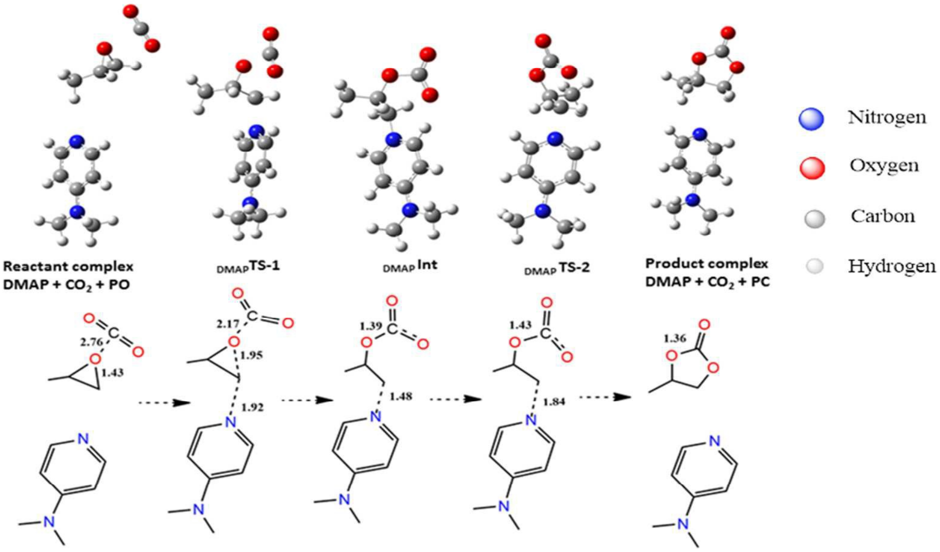


Fig. 1a Optimized structural images of DMAP catalyzed PC synthesis from DFT simulations (Bond lengths are in Å).

drops from 2.83 Å to 2.06 Å), preparing for the final step of cycloaddition. The $_{\mathrm{DMAP}}$TS-2 changes to the product complex forming the product, PC and regenerates the catalyst, imidazole. Thus, altogether, two new bond formations (βC$_{\mathrm{PO}}$-N$_{\mathrm{DMAP}}$ and O$_{\mathrm{PO}}$-C$_{\mathrm{CO2}}$) and a bond breakage (βC-O$_{\mathrm{PO}}$) represents the $_{\mathrm{DMAP}}$TS-1, while one new bond formation (O$_{\mathrm{PO}}$-C$_{\mathrm{CO2}}$) and bond breakage (βC-N$_{\mathrm{DMAP}}$) constitutes the $_{\mathrm{DMAP}}$TS-2. The formation of $_{\mathrm{DMAP}}$TS-1 from the reactant complex required an energy of 27.62 kcal/mol and this step of ring opening is considered to be the rate determining step. This explains the catalytic ability of DMAP, since the E_a required is almost 28 kcal/mol less in comparison to the non-catalyzed reaction (55~57 kcal/mol) . Similar sequence of events befalls with the imidazole and pyridine catalyzed PO-CO_2 cycloaddition (ESI, Fig. S1a, S1b respectively). However, the E_a required for the imidazole catalyst (32.25 kcal/mol, S2, ESI) was a bit higher than that of the pyridine (30.66 kcal/mol) which rationales the higher catalytic activity of the latter compared to the former (Table 1, entries 2-6). Also, the more homogeneous nature of pyridine in the epoxide may have had additional advantages in the initiation of the catalysis. Thus it shall be surmised that, DMAP, pyridine and imidazole propagates the catalytic cycle of PO-CO_2 cycloaddition very much in similar ways and if so this shall account for the numerous DMAP catalyzed CO_2-PO reactions or in general CO_2-epoxide cycloaddition reactions.

The organic bases, in most of the organic transformations of CO_2, has been credited the role of activating CO_2 via carbamate salt formation.[5c,e,6b] Even though this is a viable method of CO_2 activation, it is important to bring to notice that, we were unable to cast out the equilibrium geometries of the stationary points belonging to the intermediates and transition states of a carbamate centered reaction pathway (formed by the interaction of CO_2 with bases) using DFT. In addition, the possibility of CO_2 interacting with the DMAP initially, and the so formed carbamate salt attacking the epoxide ring has been excluded with experimental clarity, by Shi et al. [2c] via ^{1}H NMR studies using deuterated epoxide substrate. Hence, from the theoretical calculations and the literature, we assume that, the Lewis base catalyzed PO-CO_2 cycloaddition occurs as per depicted in Fig. 1a.

Organic bases with water

As shown in Table 1 (entries 8-10), the presence of water had a pronounced effect on the catalytic activity of the Lewis bases employed. The PC yields with imidazole increased from 31 to 91% with the assistance of water, and those of pyridine and DMAP also exhibited significant increment with 96 and 98% PC yield respectively. As mentioned earlier, Heldebrant et al. [7d] has reported that, a bicarbonate salt of the Lewis base is formed readily upon reaction with CO_2 in the presence of water (Scheme 3). DMAP, pyridine and imidazole shall also be considered to form bicarbonate salts with CO_2 in the presence of water. Moreover, the role of bicarbonate ion in the cycloaddition of CO_2 and epoxides are very recently reported by two groups. [7k,l] It has been mentioned elsewhere that, the anion plays the key role in eventuating the epoxide – CO_2 cycloaddition.[1i] Hence, we ought to investigate the possibility of bicarbonate moiety being an active species for eventuating PO-CO_2 cycloaddition via computational methods. The equilibrium geometries of all the stationary points belonging to the reactants, intermediates, transition states and products were optimized by B3LYP function with 6-31 G (d,p) basis set. The energy of the reactant complex (PO + CO_2 + bicarbonate ion HCO_3^-) is taken as zero. The structures of the transition states and intermediates related to the ring-opening and ring-closure process catalyzed by the bicarbonate moiety are plotted in Fig. 1b and the relative energy profile diagram is as shown in Fig. 2. In the reactant complex, the PO

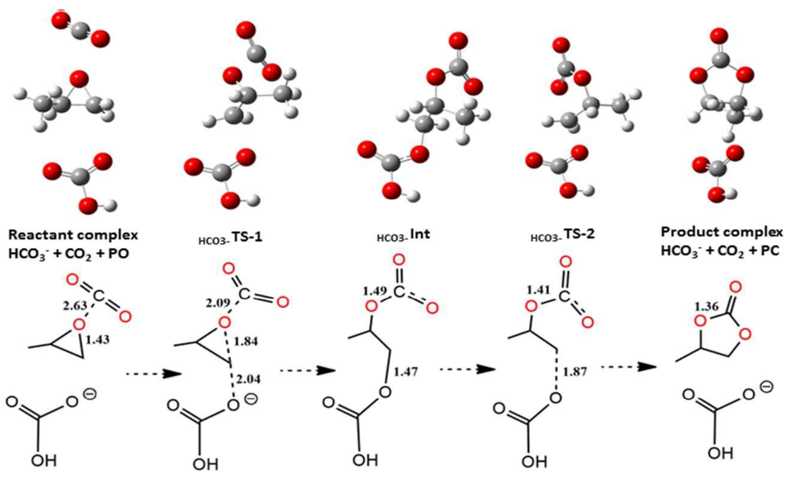
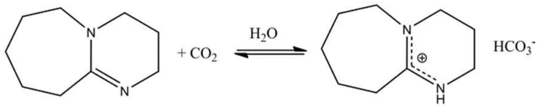


Fig. 1b Optimized structural images of bicarbonate catalyzed PC synthesis from DFT simulations (Bond lengths are in Å).



Scheme 3. The bicarbonate salt of DBU formed by the reaction of DBU with CO_2 and water [7d]

molecule lies between HCO_3^- and CO_2 molecule. At this isolated structure, one of the oxygen atom of HCO_3^- was at a distance of 2.90 Å with the epoxide β carbon, and the epoxide O atom was held at a distance of 2.63 Å from the electrophilic carbon of CO_2. The first transition state $_{HCO3}$TS-1 paved its way to the key step of ring opening of epoxide where, one of the O atom of the carboxylate end of the HCO_3^- starts interacting with the β carbon of the epoxide, leading to the ring opening of the epoxide ring, and concertedly, the partially negative O atom of the epoxide makes a nucleophilic attack on the C atom of CO_2. This step is clearly elucidated by the decrease in bond distance between epoxide O atom and the C atom of CO_2 (2.63 Å to 2.09 Å), as well as between the O atom of HCO_3^- and β C atom of the epoxide (2.90 Å to 2.04 Å). The ring open complex intermediate ($_{HCO3}$Int) follows the transition state $_{HCO3}$TS-1, wherein the carbonate link was formed firmly by the epoxide O atom and the CO_2 molecule. Also, in the rear end, an –OCOOH link gets formed through the reaction of the HCO_3^- anion and the β carbon of the epoxide. In the second transition state, $_{HCO3}$TS-2, the O atom of the CO_2 molecule becomes conformationally more accessible for the ring closure to occur via interaction with the β carbon of PO. Besides, the HCO_3^- moiety loosens its grip over the PO substrate and finally the cycloaddition completes in the next step. As is shown in the relative energy profile diagram for bicarbonate mediated catalysis, the ring opening shall be considered as the rate determining step with activation energy, E_a of 12.34 kcal/mol. This rationales the experimental observation of higher activity of “base + water” system over a “base alone” system where the E_a for the former was only 10 - 13 kcal/mol while that of the latter was in the range of 27 - 33 kcal/mol.

The series of events occurred as calculated from our DFT results are in quite good agreement with those reported by Ema et al.[7k] who used tetrabutylammonium hydrogen carbonate formed insitu from tetrabutyl ammonium hydroxide and CO_2. In the case of Rocha et al.,[7l] N-octyl-N,N-dimethyl-N-(2-hydroxymethyl)ammonium hydrogenocarbonate was chosen as the catalyst for styrene oxide (SO) coupling with CO_2. From the detailed DFT study, they proposed a new reaction mechanism for this catalyst in the SO-CO_2 reaction. The reaction starts with the nucleophilic attack of $HCO3^-$ on the epoxide. A new intermediate (B-HCO_3’)[7l] was obtained as a result of the transfer of hydrogen atom of HCO_3^- to the ring opened epoxide, due to its proximity. Such a prototropy was not found in the DFT calculations done in this work or Ema et al.[7k] The resulting B-HCO_3’ was stabilized by H- bonds of the hydroxyethyl substituent carried by the polar head of the ammonium ion.

In order to confirm the plausibility of this HCO_3^- assisted mechanism proposed in this work (as it is portrayed in the Fig. 1b), we ought to perform a comparative study using acetate (CH_3COO^-) as well, since both acetate and bicarbonate have the same geometrical as well as conformational arrangement with the mere difference of a methyl group substituting the hydroxyl group. The DFT study done with CH_3COO- + PO + CO_2 also followed similar series of events as of bicarbonate

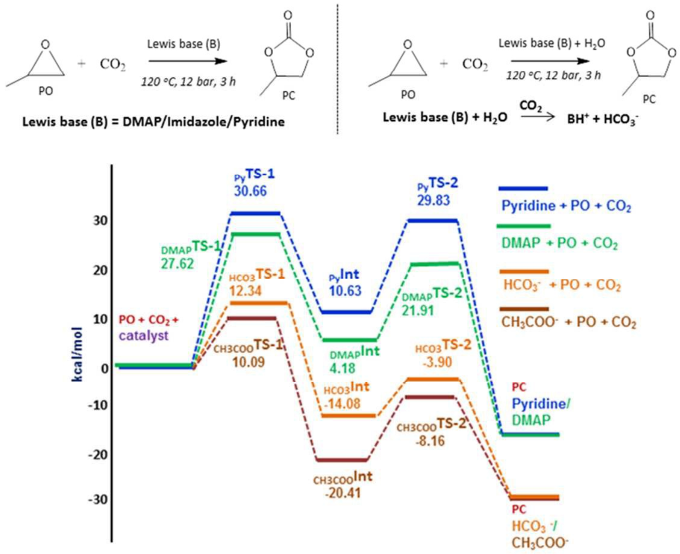


Fig. 2 Relative energy profile diagram from DFT for, DMAP (green), pyridine (blue), bicarbonate (orange), and acetate (brown) mediated PC synthesis. Y –axis = Relative energy.

Table 2 Catalyst activity of Lewis base with water on various

	Epoxide	Yield of cyclic carbonate[a]	
		DMAP alone	DMAP-H_2O
1	Propylene oxide	30	95
2	Styrene oxide	11	56
3	Allylglycidylether	33	91
4	Epichlorohydrin	26	87

Reaction conditions: Epoxide = 42.8 mmol, DMAP = 1.2 mol%, H_2O = 0.6 mol%, 120 ^{o}C, 3 h, 12 bar CO_2 pressure., a. Obtained from GC.

assisted pathway (ESI, Fig. S1b). The ring opening transition state of the acetate catalysis ($_{\mathrm{CH3COO}}$TS-1) had an Ea of 10.09 kcal/mol, and the ring closure transition state ($_{\mathrm{CH3COO}}$TS-2) possessed an E_a of 12.25 kcal/mol. The energy difference among these two steps was insignificant, such that either of them could represent the rate determining step of the reaction. Entry 11 and 12 of Table 1 was conducted to experimentally validate this theoretical prediction. To our delight, we found that, Lewis bases in presence of acetic acid also materialized high yields of PC under the same reaction conditions as that used for base-water system. Thus the DFT calculations clearly elucidated that, the energy values obtained with HCO_3^- and CH_3COO^- catalyzed cycloaddition of PO with CO_2 were significantly less than those obtained with the base alone calculations which in accordance with the experimental observations of this study. The finding that, both the HCO_3^- and CH_3COO^- catalyzed reactions materialized nearly similar catalytic results (experimentally and theoretically), was an indirect proof that, the OH group of the HCO_3^- did not play an important role in the PO-CO_2 cycloaddition with a base catalyst in the presence of water. The role of HCO_3^- in the synthesis of styrene carbonate was also explained by Ema et al, using tetrabutylammonium hydroxide as catalyst. Even though, hydroxyl groups are acclaimed widely for its cooperative catalytic potentials to eventuate the epoxide-CO_2 cycloaddition, [4b,d,f,5b,c,g] they remain much less active than HCO_3^- ion as reported by Rocha et al.[7l] using tetrabutylammium bicarbonate as catalyst in the synthesis of styrene carbonate.

The general scope of the aforementioned catalysis was tested using various commonly employed epoxides and the results obtained are shown in the Table 2. All the terminal epoxides were converted to its corresponding cyclic carbonates in moderate yields with Lewis bases alone and to very high yields with the Lewis base-water binary catalyst system as was observed in the case of PO-CO_2 cycloaddition. Hence, in general, the catalysis by Lewis base (B) alone and Lewis base-water, binary catalyst system shall be elucidated as in Fig. 3.

Conclusions

Thus, the catalytic ability of common Lewis bases such as imidazole, pyridine and dimethylamino pyridine (DMAP) to initiate and materialize the synthesis of five membered cyclic carbonates from epoxide-CO_2 cycloaddition without any hydrogen bond donors or metal species or solvent medium is depicted here. The presence of water greatly enhanced the catalysis of these simple single component catalysts without compromising the selectivity to the desired product. From the DFT calculations, stable intermediates and crucial transition states were identified and initiation of the catalysis was found to occur via the lone pair of electrons on the Lewis base catalysts. No formation of a carbamate salt was found positive in the DFT and that, the ring opened epoxide led to the activation of the CO_2. The presence of bicarbonate moiety being formed on the reaction with water-CO_2-base was found as the key active species leading to the higher activity of base-water systems in epoxide-CO_2 cycloaddition reactions. The carboxylate end of the bicarbonate rendered the catalysis in base-water system and the hydroxyl group takes no part in the catalysis. We expect the results obtained in this study may provide useful clues towards the design of more efficient combinations of cheap, accessible bases with H_2O/CO_2 for CO_2 fixation.

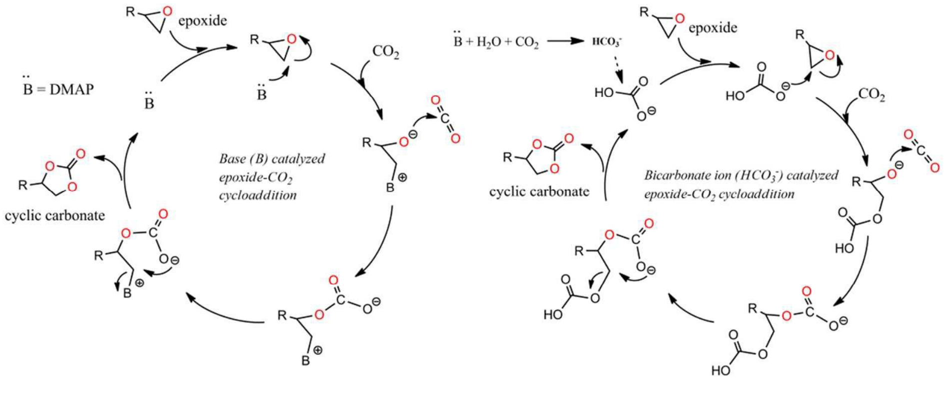


Fig. 3 The catalytic pathway of “base” mediated (left) and “base-water” mediated (right) cycloaddition of epoxides with carbon dioxide forming corresponding cyclic carbonates.

Experimental Section

All the chemicals, including the organic bases and the epoxides (anhydrous, 99.9%) were purchased from Sigma-Aldrich, Korea and were used without any further purification. 99.5% pure CO_2 was purchased from MS Corp., Korea.

Coupling reactions

Propylene carbonate (PC) was synthesized by the coupling reaction between PO and CO_2 in the presence of Lewis bases or Lewis base-water system. All the reactions were carried out in a 60 mL stainless-steel batch reactor with a magnetic stirrer at 600 rpm. In a typical batch reaction process, the catalyst was charged into the reactor containing 42.8 mmol of PO. The reaction was carried out under a preset pressure of carbon dioxide at the specified temperature. After the completion of the reaction, the reactor was cooled to zero degree and the products were identified by a gas chromatograph (Agilent HP 6890 A) equipped with a capillary column (HP-5, 30 m × 0.25 µm) using a flame ionized detector. The product yield was determined by using an internal standard method with biphenyl (0.05 g) as the standard. The product PC (and other cyclic carbonates) was identified by comparing with the authentic sample through GC analysis.

Acknowledgements

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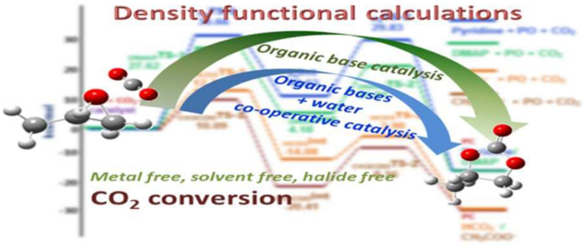

Role of bicarbonate ion as catalyst species in CO_2 fixation via cyclic carbonate synthesis is probed experimentally and validated theoretically