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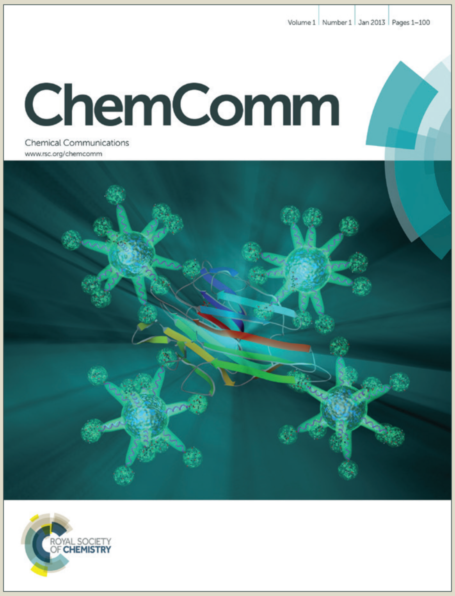

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The unprecedented catalytic activity of alkanolamine CO_2 scrubbers in the cycloaddition of CO_2 and oxiranes: A DFT endorsed study

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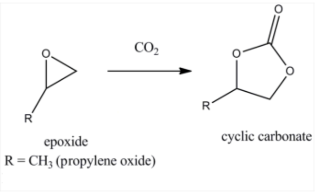
A novel application of alkanolamines, the widely employed CO_2 scrubbers in catalyzing the insertion of CO_2 into epoxides generating cyclic carbonates with excellent yields and selectivity via the synergistic activity of hydroxyl and amine groups is unravelled along with computational studies.

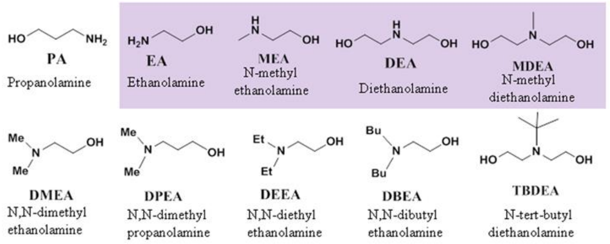
Even the most optimistic speculations have made it clear that, the atmospheric CO_2 concentration will rise beyond 450 ppm before the midcentury which will monotonically compromise the heat budget of our planet.[1a] To mitigate this unwelcomed CO_2 burden, amine scrubbing using alkanolamines such as ethanolamine (EA), diethanolamine (DEA), N-methylethanolamine (MEA) etc has been identified as the state of art technique or the only effective robust methodology available and will probably remain the technology of choice for CO_2 captured from coal-fired power plants in 2030.[1b-e]

However, the near inexhaustible abundance of CO_2 along with its easy availability, non toxic and non flammable nature has steered in brought about dynamic scientific research to engage CO_2 as a renewable C1 feedstock to replace the currently employed toxic $COCl_2$ and CO. The cycloaddition of CO_2 with epoxides offers a promising mode of five-membered cyclic carbonate syntheses on the grounds of its 100% atom economic nature and resource utilization. Cyclic carbonates are quite useful industrial products especially as aprotic solvents, electrolytes for Li ion batteries, intermediates for polymer synthesis, etc. [2a-i] Numerous catalyst systems of various genres such as ionic liquids,[3a,b] metal oxides,[3c,d] modified molecular sieves,[3e,f] supported catalysts,[3g-k] and metal organic frameworks[3l-o] have been successfully deployed in the trials to materialize CO_2-epoxide coupling at ambient reaction conditions. The mechanistic insights furnished through this wide catalytic spectrum and the seminal works on organometallic catalysts[4a-e] attested that, a binary catalytic system including a Lewis acidic metal site (Co, Zn, Al, etc.) and a highly nucleophilic anion with good leaving ability (Br^- and I^-) represents the ideal catalytic motif for an effective CO_2-epoxide coupling. Also, from previous works including the authors of this study,[5a-e] the catalysts equipped with functional groups such as hydrogen bonding groups (-OH, -NH_2, -COOH) and halide anions which are capable of activating epoxides and CO_2 synergistically, also have delivered new dimensions to this field. Hence, in a broader sense, cyclic carbonate synthesis through the CO_2-oxirane coupling is not a naive synthetic route, but the catalysts involved have always lodged metallic centers and/or halide anions. Therefore, the development of a metal and halide free catalysis is imperative from a green chemistry view point. Recently, Sun et al.,[6a] reported a cellulose/superbase system for cyclic carbonate synthesis which to date is the first report on a metal and halide free CO_2 chemical fixation. This work investigates the catalyzing potential of alkanolamines for Scheme 1, foreseeing the possible synergistic catalysis by amine and hydroxyl groups. After all, considering the fact that, alkanolamines (Scheme 2) are produced in colossal amounts worldwide as scrubbers for CO_2 removal, we envisaged that the possibility of exploiting the same for CO_2 fixation via solvent-less cyclic carbonate synthesis is considerably appealing. Density functional theory (DFT) is also applied to have theoretical insights about the mechanism prevailed in this metal and halide free synthesis of cyclic carbonates.



Scheme 1 Cyclic carbonates from CO_2 and epoxides

Propylene oxide (PO) was used as the model substrate to explore our anticipation of the catalytic properties of alkanolamines. As can be seen, while the common organic bases such as ethylamine and propylamine alone hardly furnished any appreciable propylene



Scheme 2 Alkanolamines used in this work (Shaded are the most commonly employed amine CO_2 scrubbers)

carbonate (PC) yield, the addition of a small amount of water boosted the catalysis to nearly 43% and 48% PC yield, respectively (entries 1,2 Table 1). Similar results were furnished by the common 2^0 and 3^0 amines and N-heterocycles (entries 3-8), displaying the promising synergistic catalysis of amine and hydroxyl groups but in a way considerably higher than the 1^0 amine/water mixture. It has been reported elsewhere that, [5,6a] while hydroxyl groups can initiate the epoxide ring opening, the amine groups are capable of activating the otherwise inert CO_2 molecule. The control tests done with water alone (without any amine) and dibutylether/Me_3N (which has no free hydroxyl group) furnished apparently no significant product yield, while methanol/Me_3N procured 71% yield of PC, which further validated the unambiguous synergism between -OH group and amine moieties (see footnote, Table 1).

Intrigued, the authors extended this study to alkanolamines (Scheme 2), which possess the hydroxyl and amine moieties in the same molecular unit and found them even more promising because of its higher selectivity towards PC (Table 2). While ethanolamine (EA) achieved a 50% yield of PC, N-methylethanolamine (MEA) procured a higher yield of 71% followed with N,N'-dimethylethanolamine (DMEA) furnishing even better PC yields of 82% with more than 99% PC selectivity (entries 9-11). N,N'-dimethylpropanolamine (DMPA), another disubstituted alkanolamine with a higher alkyl chain attained 91% PC yield maintaining 99% selectivity (entry 12). However, with increase in bulkiness of alkyl substituent on the N atom, the catalytic rate was found declining (entries 13-15), positively attributable to the hindrance of the lone pair on the N atom in attacking the electrophilic centre of CO_2. The almost negligible PC yield found with N-tert-butyldiethanolamine (entry 15), another sterically crowded alkanolamine, further supplemented the crucial role of the amine "nitrogen" in this synergistic catalysis. To notice, the widely employed amine CO_2 scrubbers, EA, MEA, DEA, and, MDEA manifested impressive PC yields with high PC selectivity (entries 9,10,17,18) displaying a similar synergistic profile. Since DMPA served the best catalysis, parameter studies to identify the optimum conditions were conducted and concluded that 120 ^{o}C, 1 MPa, and 3 h offer the best catalysis with a catalytic amount of 0.8 mol% (S1, ESI). Promising is the fact that, the above mentioned alkanolamines, DMPA and DMEA catalyzed the PO-CO_2 cycloaddition to an extent similar to that accomplished with ionic liquid catalysts (with halide anions) but under lower pressures most likely due to the higher CO_2 affinity of the former (S2, ESI,). In fact, this appears to be the first report of a homogeneous halide and metal free catalyst found effective in cyclic carbonate synthesis purely utilizing the synergistic catalysis between -OH and amine groups alone.

Table 1 Catalytic activity of amines & amine/H_2O in propylene carbonate (PC) synthesis

Entry		Catalyst	PC Yield [Sel] %[a]	
			Without H_2O	With H_2O
1	1^0	Ethylamine	-	43 [95]
2		Propylamine	-	48 [96]
3	2^0	Diethylamine	4 [67]	56 [97]
4		Dipropylamine	3 [76]	55 [98]
5	3^0	Me_3N	4 [52]	79 [85]
6		Et_3N	8 [66]	77 [87]
7	N-hetero cycle	Pyridine	7 [80]	84 [96]
8		Imidazole	3 [81]	78 [97]

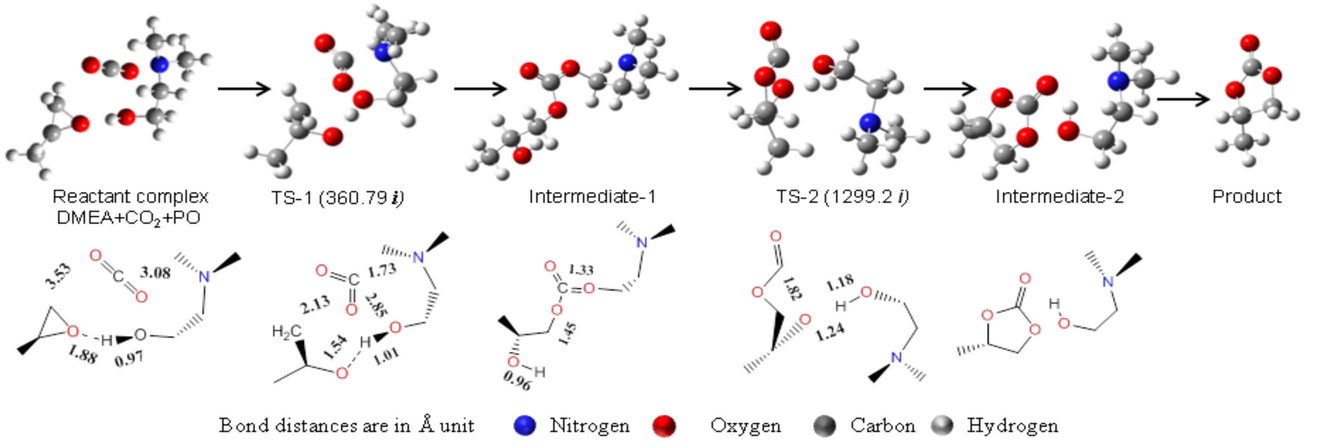
Reaction conditions: Catalyst amount 0.8 mol%, PO 42.8 mmol, 120 ^{o}C, 1 MPa, 3 h., [a]from GC analysis with toluene as internal standard. Sel- selectivity, H_2O = 1.1 mmol
H_2O alone : PC yield = 0%,
Dibutylether/Me_3N (0.8 mol% each) : PC yield = 4 %,
Methanol/ Me_3N (0.8 mol% each) : PC yield [Sel] = 71 [95]%.

Table 2 Catalytic activity of alkanolamines in PC synthesis

Entry	Catalyst	PC Yield [Sel]%[a]
9	Ethanolamine (EA)	50 [99]
10	N-Methylethanolamine (MEA)	71 [99]
11	N,N-dimethylethanolamine (DMEA)	82 [99]
12	N,N-dimethylpropanolamine (DMPA)	91 [99]
13	N,N-diethylethanolamine (DEEA)	64 [99]
14	N,N-dibutylethanolamine (DBEA)	11 [99]
15	N-tert-butyldiethanolamine (TBDEA)	6 [99]
16	Propanolamine (PA)	47 [99]
17	Diethanolamine (DEA)	61 [99]
18	Methyldiethanolamine (MDEA)	76 [99]

Reaction conditions: Catalyst amount 0.8 mol%, PO 42.8 mmol, 120 ^{o}C, 1 MPa, 3 h., [a]from GC analysis with toluene as internal standard. Sel- selectivity. (Shaded region represents the activity of the most commonly employed amine CO_2 scrubbers)

In previous studies conducted by the authors along with some other pioneering works, [5b-e] the synergistic catalysis of the hydroxyl groups (OH) with halide ions (I) in cyclic carbonate synthesis have been corroborated using density functional simulations and energy calculations. However, the synergism between -OH groups and amine groups has never been explored before using computational methods. Hence, with the objective of harnessing more intuitive insight into the mechanism behind this amine-hydroxyl propagated cycloaddition, we employed DFT using Gaussian 09 set package with B3LYP correlation functional for the energy calculations. The activation energy (Ea) required for non-catalyzed cycloaddition of PO with CO_2 to produce PC has been reported previously to be around 55-59 kcal/mol[6b-e] which is too high for the reaction to proceed spontaneously, demanding the need for a catalyst. Since DMEA and DMPA achieved the highest PC yields (entry 11 and 12) among the employed alkanolamines, they were chosen for DFT simulations. For both DMEA and DMPA, the total energy of the system including the catalyst and the substrates were preset to zero. The optimized geometrical arrangement of PO, CO_2 and DMEA forming the reactant complex is as shown in Scheme 3. A transition state (TS-1) with imaginary frequency of 360.79*i* cm^{-1} and activation energy (E*a*) of 37.5 kcal/mol found its origin from the reactant complex. This



Scheme 3 The Gauss view images of the DMEA-PO-CO_2 interactions from the DFT simulations. Dotted lines indicate hydrogen bonding interactions. (TS- transition state, *i* – imaginary frequency of the TS)

E*a* is comparable to those reported for other catalysts which were effective under similar reaction conditions,[6b-f] thus verifying the appropriateness of the chosen optimized structures of this study. The transition from reactant complex to TS-1 produce the following events; a) ring opening of the epoxide via breakage of *β*C-O bond in PO, b) strengthening of the hydrogen bonding interaction between 'O *(epoxide)* and 'H' *(DMEA)* from 1.88 Å in reactant complex to 1.54 Å, c) CO_2 becomes more closer to the catalyst via amine groups as evidenced by the decrease in C-N bond distance from 3.08 Å to 1.73 Å whereby the geometry of CO_2 molecule transforms from linear to bent structure, luring one of the "O" atom (of CO_2) closer to the carbocation centre (*β*C) of the ring opened in PO. Additionally, the TS-1 drops to a stable intermediate, Int-1 (-22.3 kcal/mol) where a hydrogen transfer occurs from hydroxyl group of alkanolamine (DMEA) to the ring opened epoxide oxygen which complies with the H-abstraction reported by H. Sun et al.[6c] The CO_2 molecule gets tethered between epoxide and the catalyst via two new C-O covalent bonds viz., βC_{PO} - O_{CO2} (1.35 Å) and C_{CO2} – O_{DMEA} (1.33 Å). Int-1 is stabilized over TS-1 by 59.8 kcal/mol and the reason behind this stabilization could be reasonably credited to the aforementioned H-transfer and carbonate linkage. Subsequently TS-2 (20.3 kcal/mol) is formed, wherein the H atom detaches from the 'O' atom of the epoxide and reverts back to its parent location on the catalyst. Cycloaddition occurs in the next step forming another stable intermediate (Int-2, -36.5 kcal/mol) which ultimately rendered the desired, PC. The catalysis with DMPA also propagates via the same mechanistic pathway as of DMEA. The E*a* for DMPA was found to be 40 kcal/mol (Fig S3, ESI), quite similar to the value obtained for DMEA (37.5 kcal/mol) while the catalytic activity was found to be higher with DMPA. This could possibly be accounted for on the basis of the higher stabilization of Int-1 of DMPA (-30 kcal/mol) than compared to the -22.3 kcal/mol for DMEA Int-1.

Aspired from the experimental and computational evidences, a plausible mechanism of the 3^0-alkanolamine scrubber catalyzed PO-CO_2 cycloaddition could be portrayed as in S4 (ESI)**.** The hydroxyl group of the catalyst (DMEA) forms a hydrogen bond with the epoxide oxygen, whereby the latter becomes more vulnerable to ring opening. Concertedly, the activation of CO_2 occurs via the nucleophilic attack of the lone pair on nitrogen atom of the catalyst. The low activity of the N-crowded amino alcohols clearly elucidates the exigency of the above step in the catalysis (entries 14, 15). A reversible proton transfer from the catalyst hydroxyl group to the epoxide "O" occurs, leaving an oxy anion at the rear end of the amino alcohol catalyst. This oxy anion makes a nucleophilic attack on the C atom of CO_2 and a carbonate linkage is formed by the catalyst, CO_2 and ring opened propylene oxide. In case of 2^0 and 1^0-alkanolamines, hydrogen atom from the amine group may get a hydrogen bond with this oxyanion, which would hinder its nucleophilic attack on the CO_2 molecule. It is surmised that this is reason for the lower activities of 1^0 and 2^0-alkanolamines compared to the 3^0 analogues. In the final step, the hydrogen atom of the ring opened epoxide reverts to its destination, regenerating the amino alcohol catalyst, while cycloaddition furnishes the cyclic carbonate. The alkanolamine catalysts materialized promising catalysis for a series of terminal epoxides as indicated in S5 (ESI) while the conversion rates for internal epoxides were quite low, most probably attributable to the steric factors.

Conclusions

In conclusion, a novel application of alkanolamines as a metal and halide free catalyst in the solvent-less synthesis of cyclic carbonates besides their CO_2 absorption capability is revealed. 3^0-alkanolamines are found to be more efficient for CO_2-epoxide cycloaddition. The computational studies elucidate probable interactions among propylene oxide-CO_2-catalyst entities, which go in hand with the experimental evidences and are suggestive of the concerted action of amine and hydroxyl groups on carbon dioxide and epoxide (respectively) in the critical transition state complex. Since alkanolamines exhibit a catalytic activity profile similar to the well known ionic liquids, and are produced in large quantities worldwide, it can be concluded that the findings in this study would be of industrial relevance for an important process like CO_2 fixation.

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