

Review on the Chemical Conversion of Carbon Dioxide with Aziridine by Using Catalysts: Environmentally Friendly Accesses to Cyclic Carbamates

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Abstract: Carbon dioxide produced by means of human matters to do is one of the essential contributions accountable for the greenhouse effect, which is enhancing the Earth's climate. From the viewpoint of green chemistry and sustainable development, it is of exquisite magnitude to synthesize chemical substances from CO₂ as C1 source with the aid of C-N bond formation. Therefore, post-combustion CO₂ catch and its conversion into excessive value-added chemical substances are crucial components of today's inexperienced industry. Chemical fixation of carbon dioxide (CO₂), which is much less high-priced and renewable carbon source, is turning into greater and greater important. The improvement of each new reactions and new catalysts is wished to overcome the kinetic and thermodynamic balance of CO₂. Organic and steel catalysts with unique and high-quality endeavor and selectivity have been developed for a wide variety chemical conversions of CO₂. On the different hand, carbon dioxide is a ubiquitous, cheap, abundant, non-toxic, non-flammable and renewable C1 source. Among CO₂ usages, this evaluate pursuits to summarize and discuss the advances in the response of CO₂, in the synthesis of cyclic carbonates, carbamates, and urea.

Keywords: Aziridine, Carbon Dioxide, Cyclic Carbamate, Ionic Liquids

1. Introduction

The combustion of fossil fuels are although the most substantially used energy grant whilst produces giant quantities of waste gases. Among them, carbon dioxide is one of the predominant gasoline to blame for the greenhouse influence [1]. This is related barring delay or in a roundabout way to human activities such as the use of fossil fuels and deforestation. As one of the integral contributors to undesired local weather change and environmental destruction, excessive CO₂ emissions have significantly affected our world in spite of it being a quintessential material for existence and many industrial processes [2]. In order to mitigate these worldwide problems, feasible options for reducing CO₂ emissions are being carried out such as the growing of smooth and renewable power sources (such as

wind power, solar, geothermal, nuclear and hydropower energy) participation, in addition to the strength storage [3] and proceed to be luxurious relative to ordinary fossil gasoline primarily based energy [4, 5], so due to the above troubles it is greater to use fossil gas based totally absolutely electricity source for the world strength demand and conversion of CO₂ into useful fuels/chemicals for utilization is an beautiful answer that reduces greenhouse consequences and furnish tremendous energy sources [2].

In the final decade, tons attention now not only due to the truth of world warming alternatively also due to the fact of the attainable use of CO₂ as a safe, considerable, renewable and cheaper C1 source for the formation of treasured chemicals [6]. Utilization of CO₂ as an ideal C1 constructing block turns into a hot and promising discipline in every tutorial and industrial respects. A large variety of benefits

promoted the vast and deep lookup on catalytic conversion of CO₂ into chemical compounds (C-O, C-N and C-C bond construction) and fuels [7], however, CO₂ conversion however faces many challenges due to its thermodynamic steadiness ($\Delta G^\circ \sim -394$ kJ/mol) and kinetic inertness. Consequently, most of the regarded lookup used quite reactive substrates and/or severe response prerequisites to set off CO₂, limiting the utility of such methods.

In particularly, the catalytic coupling of CO₂ with energy-rich substrates, such as epoxides and aziridines, to generate polycarbonates/polycarbamates [8]. Among a number of feasible transformations, the atom-economic synthesis of cyclic carbamates from aziridines and CO₂ has been of terrific interest every industrially and academically. A variety of catalytic structures has been currently developed that efficiently promote the incorporation of this molecule into fee added chemical substances such as quinazoline-2,4(1H,3H)-diones, azoles, 2-alkynoates, urethanes, and carbonates. Among these transformations, synthesis of 1, 3-oxazinan-2-one derivatives the use of CO₂ as building. As a part of my continuing critiques on chemical fixation of CO₂ into beneficial products and new methodologies in natural synthesis [9], the usage of aziridine for their transformation into five-member heterocyclic rings such as oxazolidinonesin (Figure 1).

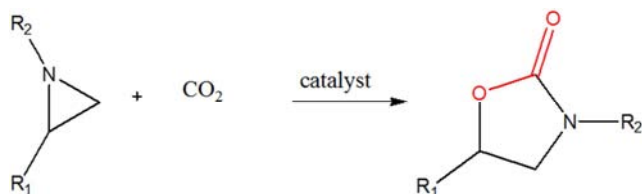


Figure 1. Carboxylation of aziridine with CO₂ [9].

In particular, 2-oxazolidinones are found in chiral auxiliaries (with 4-substitution) and in extraordinary antibiotics such as Linezolid and Tedizolid (with 3-aryl,5-alkyl substitution pattern), whereas aryl-fused six-membered rings are current in some HIV-battling antiretrovirals and N-methyl-D-aspartate (NMDA) receptor antagonists [10]. Conventionally, these cyclic carbamates are synthesized the use of phosgene or CO, which are hazardous and environmentally unfriendly, have been avoided, and instead, CO₂ was once once built-in as C1 beneficial useful resource into cyclic carbamate is formed [11].

Over the past three decades, CO₂ has emerged as an desire to phosgene and isocyanates in carbamate synthesis. Syntheses of β -oxoalkyl carbamates by using means of three-component coupling of CO₂, secondary amines and propargyl alcohols have passed through an explosive growth in current years [12]. This new web page of carbamate synthesis affords quite a few advantages, such as: 1) unhazardous by-products; 2) excessive atom economy; 3) ease of managing and 4) lower priced and easy establishing materials and many more [13]. There is giant model in the mechanism of the response between an aziridine and carbon dioxide, and extensive types of catalysts have been used, and some evaluations exist of

catalyst-free reactions [14].

This overview focuses on the cycloaddition of CO₂ to aziridines the use of catalysts, alongside with natural bases, ILs and supported catalysts. Catalytic device for the chemical conversion of carbon dioxide with aziridine: Environmentally benign accesses to cyclic carbamates as properly as the related response mechanism are discussed.

2. Thermodynamics of CO₂

The thermodynamics archives suggests that the CO₂ conversion response tends to be endergonic with the O/C ratio of the merchandise shaped less than two. On the contrary, the reaction tends to be exergonic when CO₂ is stored in its 4 oxidation country with a wide variety of O/C ratios in the products, such as carbonates or urea. The CO₂ is inert due to the reality it exists in the most oxidized state of carbon, and its chemical conversions are thermodynamically unfavorable. This steadiness consequently constitutes a predominant obstacle in placing up industrial procedure for its conversion. Hence, a huge input of energy, optimized response conditions and very energetic catalysts are required for any CO₂ conversion into beneficial merchandise with industrial appeal. It need to be stated however, that any chemical conversions are pushed thru versions in Gibbs free energy between the reactants and merchandise of a chemical reaction, as given with the resource of the Gibbs–Helmholtz relationship (Eq (1)):

$$\Delta G = \Delta H - T\Delta S \quad (1)$$

Most CO₂ conversion processes under a standard condition have positive values of the Gibbs free energy change ($\Delta G > 0$), meaning that the conversion reactions are non-spontaneous [15].

2.1. Cyclic Carbamates

Carbamates are greatly employed in agricultural chemistry, medicinal chemistry, and polyurethane preparation. In particular, cyclic carbamates (2-oxazolidinones, 2-oxazinanones) are the core constructions of many treasured drugs. The manufacturing of substituted 2-oxazolidinones with the aid of potential of coupling of CO₂ with aziridines is each other reaction which lets in the chemical fixation of CO₂ with one hundred percent atom efficiency. While regioselectivity is no longer a bother with epoxides, due to the reality the oxygen atoms are indistinguishable, the synthesis of oxazolidinones regularly presents mixture of regioisomers. The most placing distinction with the mechanism of epoxides is the higher nucleophilicity of the nitrogen, which supply raise a zwitterionic intermediate [1].

The reaction of carbon dioxide with aziridines as properly as with propargyl alcohols has been broadly reviewed in the previous years. However, in the closing two years a large manufacturing of search for articles on this theme has seemed in the literature and some are summarized in this review. The

normally widespread mechanism for the response of aziridine and carbon dioxide described at Figure 2 [1].

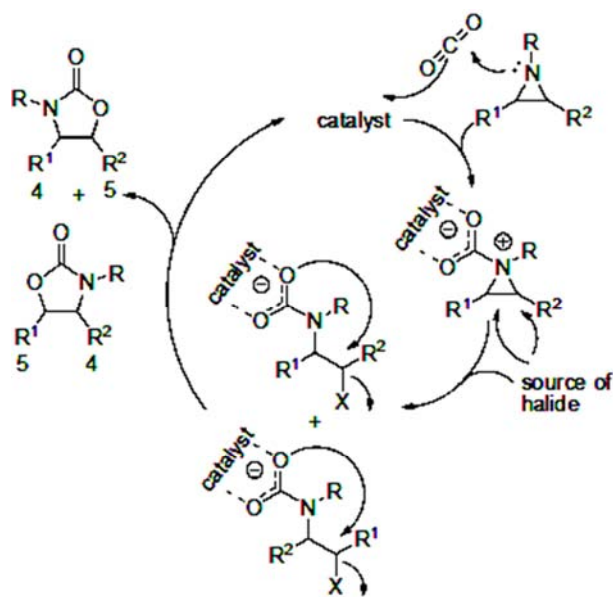


Figure 2. A simplified mechanism of the addition of CO₂ to aziridines [1].

2.2. Cycloaddition of Aziridines with CO₂

Aziridine, the nitrogenous analogue of epoxide is one of the most critical convenient heterocycles, which is decided in a extensive variety of natural merchandise and biologically energetic pills [16]. This heterocycle is additionally one of the broadly ordinary and versatile intermediates in the synthesis of a number kinds of nitrogen-containing compounds [17]. One very fascinating and promising artificial software of aziridines includes the coaching of 2-oxazolidinone derivatives thru the coupling with CO₂. However, solvent-free reactions had been almost omitted. In this section, we present the existing day literature on cycloaddition of CO₂ to aziridines underneath neat conditions. These lead to the formation of substituted 2-oxazolidinones in a green and best atom monetary approach (all the atoms current in the beginning components are modern-day in the product) [14].

2.3. Ionic Liquid Catalyzed Reactions

Ionic liquid catalyzed synthesis of oxazolidin-2-one

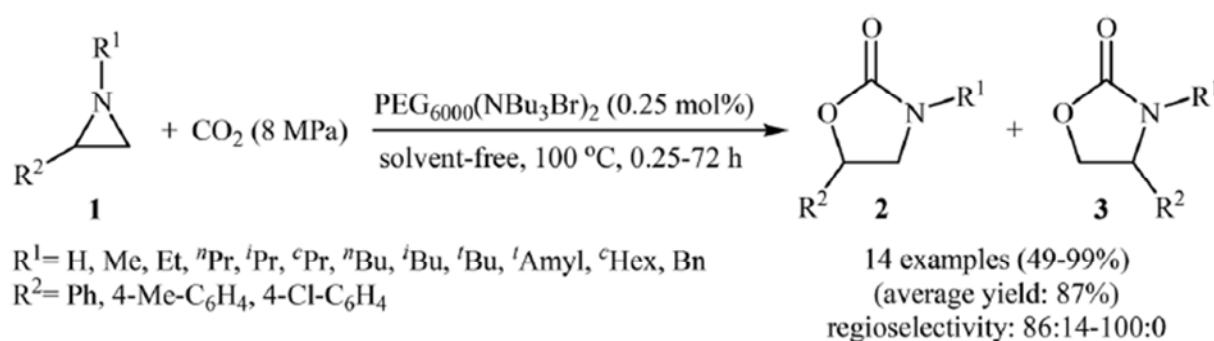


Figure 3. PEG₆₀₀₀(NBu₃Br)₂-catalyzed fixation of CO₂ with 2-arylaziridines [19].

derivatives with the aid of cycloaddition of CO₂ to aziridines underneath solvent-free conditions was once developed for the first time by way of L.-N. He and co-workers in 2008 [18]. They confirmed that cure of 1-alkyl-2-arylaziridines 1 with CO₂ (8 MPa) in the presence of 0.25 mol% of PEG6000(-NBu₃Br)₂ at 100°C underneath solvent-free condition, resulted in 5-aryl-2-oxazolidinones two in average to notable yields, alongside with small portions of the 4-aryl-oxazolidinone 3 facet merchandise (Scheme 3). The outcomes tested that the regiochemical impact of the response was once once strongly established on the nature of the R₂ crew on the beginning material. If R₂ is an aryl group, product two is favored, whereas if R₂ is an alkyl group, product three is favored. It is cited that 1,2-diphenylaziridine did not take part in this cycloaddition response and hence no other N-aryl aziridines had been examined in the protocol. The contrast of the catalytic endeavor of PEG6000 (NBu₃Br)₂ with unsupported quaternary ammonium (Bu₄NBr) and the help (PEG6000) set up its most pleasurable comparability with them in phrases of product yield. In addition, this catalyst displayed higher activity than the handy bodily combination of Bu₄NBr and PEG6000 beneath the same conditions. Interestingly, the recycling take a seem to be at installed that the catalyst ought to be recovered via centrifugation and reused for numerous instances besides any huge loss in the catalytic activity. Mechanistically, this PEG6000(NBu₃Br)₂-catalyzed response is believed to proceed thru a coordination- ring opening-cyclization sequential manner (Scheme 2). Shortly afterwards, the equal lookup team discovered that 1-butyl-4 aza-1-azoniabicyclo [2.2.2] octane bromide ([C₄DABCO]Br) could also correctly catalyze the cycloaddition of CO₂ to aziridinesunder solvent-free stipulations. Thus, in the presence of 1 mol% of [C₄DABCO]Br at 90°C, the response of the same set of 1-alkyl-2-arylaziridines 1 with CO₂ (6 MPa) furnished the anticipated 5-aryl-2-oxazolidinones two with yield vary from 6% to 92%. The consequences validated that the effectivity of this response used to be structured on the steric outcomes of the alkyl substituent at the nitrogen atom. While substrates bearing a plenty less sterically hindered R₁ (e.g., Me, Et, nPr) gave the favored merchandise in applicable yields, the cumbersome alkyl group (e.g., iPr, tBu) substituted aziridinesafforded unsatisfactory yields [19].

In 2011, Bhanage and colleagues brought a novel polymer supported 1-(2,3-dihydroxypropyl)-imidazolium bromide (PSDHPIMBr) catalyst for 2-oxazolidinones synthesis from CO₂ and aziridines under solvent-free condition. The hybrid gadget exhibited a excessive catalytic recreation and reusability for cycloaddition of 1-alkyl-2-arylaziridines **4** with CO₂ (5 MPa) underneath solvent-free stipulations

(Figure 3). The cycloaddition was once carried out at room temperature for 3–12 h and afforded the favored 5-aryl-2-oxazolidinones **5** in reasonable to nearly quantitative yields. Very recently, Luo and Ji alongside with their co-workers designed and synthesized a novel imidazolium-based ionic liquid functionalized zinc porphyrin (IL-ZnTPP) as one of the most versatile catalysts known for this response [20].

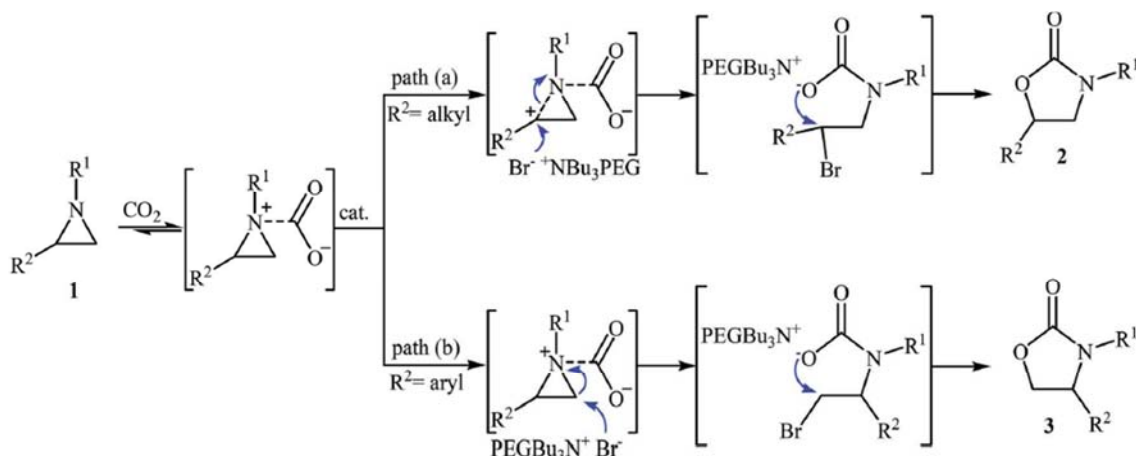


Figure 4. Mechanistic proposal for the reaction [20].

Liu's group developed an efficient catalytic gadget the use of DBN as organocatalyst and LiI as an additive below atmospheric stress of CO₂ in toluene to catalyze the coupling of CO₂ with aziridines giving 2-oxazolidinones (Scheme 5). The system used to be tolerated by means of a quantity of N-alkyl aziridines bearing various useful

corporations in alkyl terminal position, however N-to-sylaziridines did not undergo the coupling reaction probably due to the much less nucleophilic exercise of the nitrogen. In addition, the formation of the DBN-CO₂ was proposed to be the intermediate of the catalytic cycle (Scheme 6) [22].

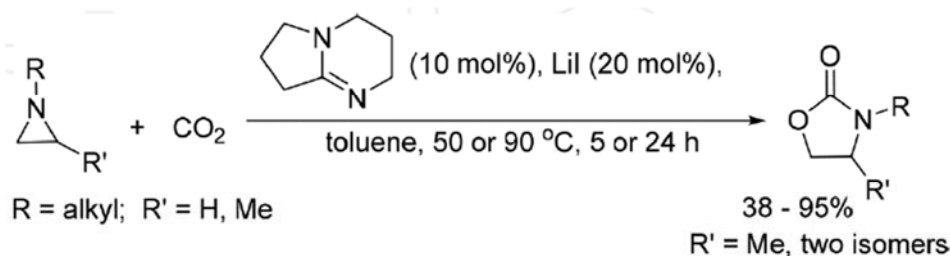


Figure 5. Synthesis of 2-oxazolidinones from CO₂ and aziridine catalyzed by DBN [22].

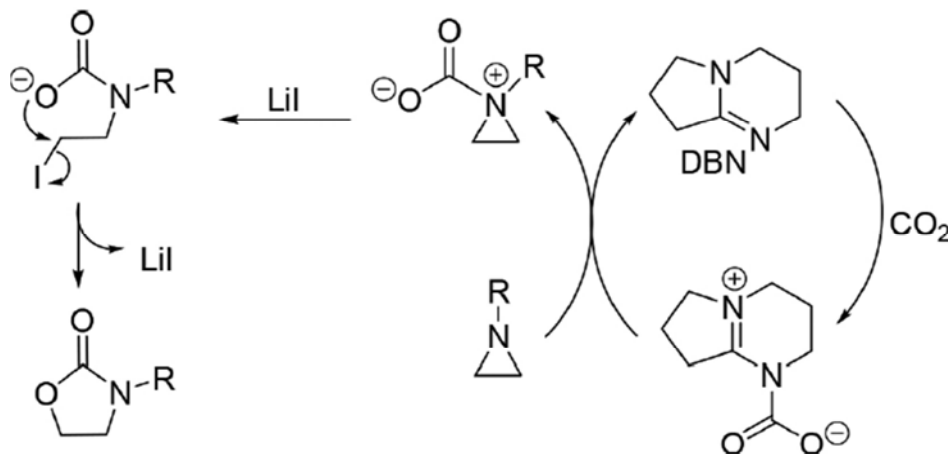


Figure 6. Proposed mechanism in the synthesis of 2-oxazolidinones from CO₂ and aziridines catalyzed by DBN [22].

2.4. Organocatalyzed Reactions

Jiang and co-workers investigated the software of α -amino acids as hydrogen bond donor catalysts for the fixation of CO_2 onto aziridines. They tested quite a few naturally occurring α -amino acids for the benchmark cycloaddition of CO_2 (8 MPa) to N-propyl-2-phenylaziridine underneath solvent-free conditions. After optimization, it was observed

that the use of 0.6 mol% of L-histidine as the catalyst gave the quality results. Examination of the scope of the response published that a variety of 1-alkyl-2-arylaziridines **7** bearing both electron-donating and -withdrawing businesses afforded the 5-aryl-2-oxazolidinone derivatives **8** in honest to top notch yields along with hint quantities of 4-aryl-2-oxazolidinone **9** side merchandise (Scheme 7) [21].

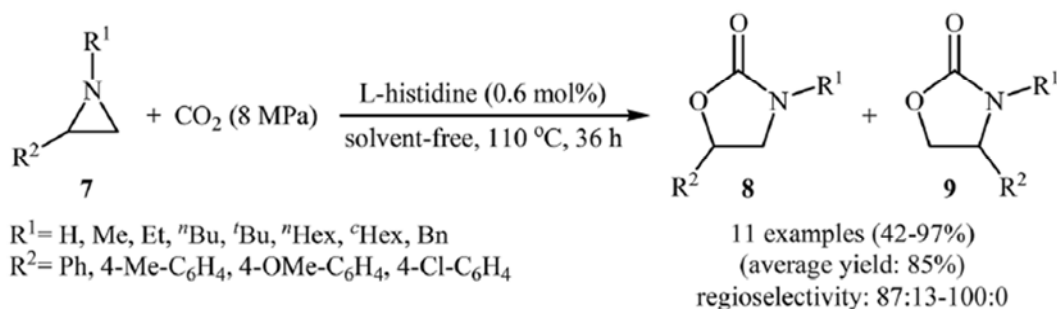


Figure 7. L-Histidine-catalyzed cycloaddition of CO_2 with 1-alkyl-2-arylaziridines **7** [21].

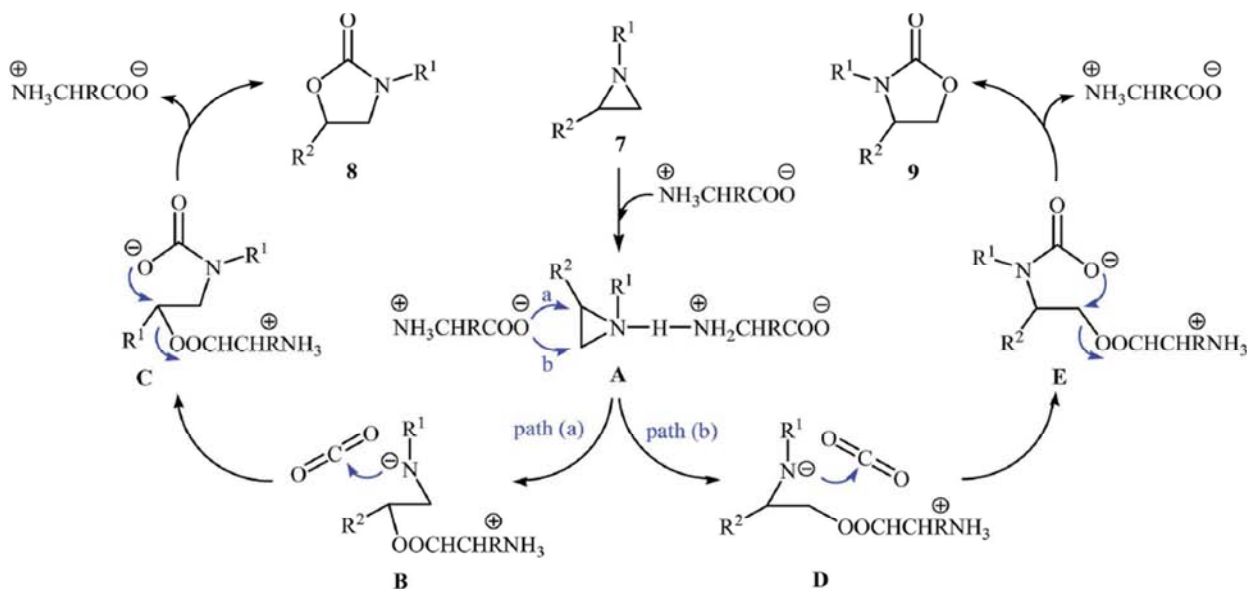


Figure 8. Mechanism that accounts for the formation of 2-oxazolidinones **8** and **9** [21].

2.5. Reaction of CO_2 and N-benzylaziridine Catalyzed by NHC-CO_2 or Free NHC

The response mechanism in the presence of NHC-CO_2 adduct used to be studied. As mentioned in the literatures, NHC-CO_2 adduct is now not very thermodynamically stable. Under immoderate temperature and the existence of epoxides, the decomposition of NHC-CO_2 adduct can be occurred with the release of the free NHC and CO_2 , in specific for NHC-CO_2 adduct bearing giant steric substituents on the nitrogen atom of the imidazolium ring. Both NHC-CO_2 adduct and the launched free NHC would maybe be the catalytic energetic thing for the chemical fixation of CO_2 . Free NHC performs the position as the catalyst precursor to set off the ring-opening of the aziridine

with the insertion of CO_2 , main to the formation of the energetic intermediate. Compared with the response catalyzed via way of the substrate N-benzylaziridine, the strength barrier of the ring-opening step mediated via using free NHC is reduced from 36.0 to 32.6 kcalmol⁻¹, owing to the greater nucleophilicity of free NHC as desirable as the stabilization from the t-Bu crew substituted on the nitrogen atom of the imidazolium ring. Once the full of life intermediate is generated, it can easily react with the extra of N-benzylaziridine and CO_2 by means of the usage of overcoming the lower free power barrier of 27.2 kcal mol⁻¹, which selectively gives the liked cycloaddition product and suppresses the era of the byproduct oligome. The fused-ring NHCs may be the larger effective catalysts for the chemical fixation of CO_2 with aziridines [23].

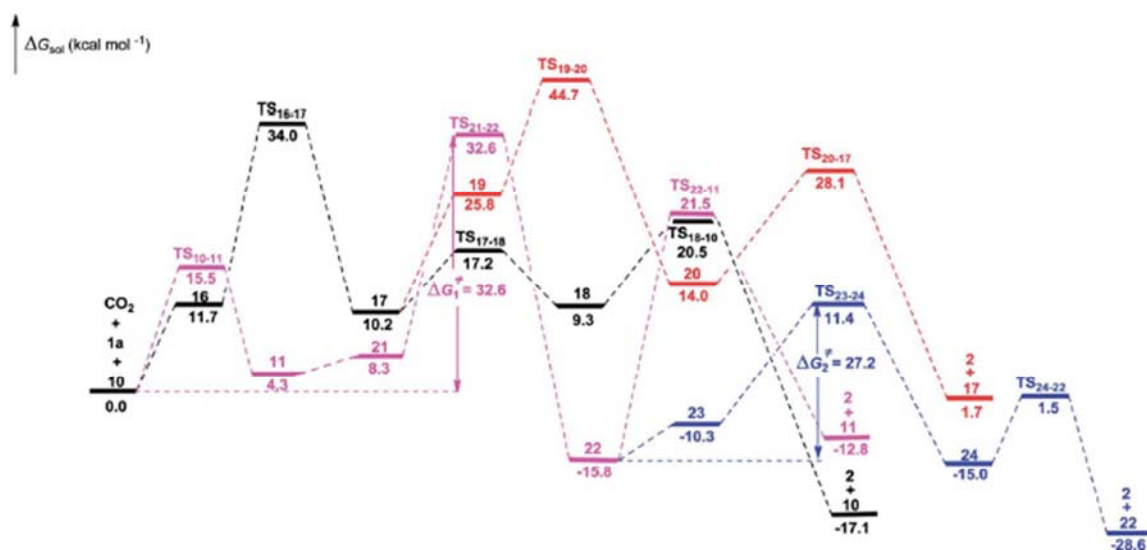


Figure 9. Potential energy profile for cycloaddition of 1a and CO₂ catalyzed by NHC–CO₂ adduct and free NHC, respectively [23].

2.6. Catalytic Effect of Other NHCs

To compare the catalytic effect between 11 and other NHCs, more free NHCs were selected to catalyze the cycloaddition response of 1a with CO₂ in the existing

theoretical simulation (Figure 10). The calculated nucleophilicity indexes of the free NHCs as properly as the corresponding activation free energies in the two ring opening steps are summarized in Table 1.

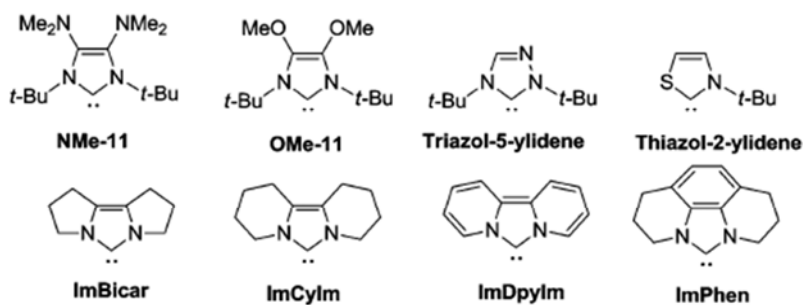


Figure 10. The selected free NHCs in the cycloaddition of 1a and CO₂ [22].

Table 1. Global nucleophilicity *N* (eV) for the selected free NHCs and the corresponding activation free energy (kcal mol⁻¹) in the ring opening steps [23].

| System | <i>N</i> | Δ <i>G</i> ₁ [#] | Δ <i>G</i> ₂ [#] |
|-------------------|----------|--------------------------------------|--------------------------------------|
| 11 | 3.6 | 32.6 | 27.2 |
| NMe-11 | 4.1 | 32.0 | 29.6 |
| OMe-11 | 3.9 | 32.9 | 28.5 |
| Triazol-5-ylidene | 3.2 | 34.3 | 28.1 |
| Triazol-2-ylidene | 3.2 | 32.2 | 27.3 |
| ImBicar | 3.7 | 28.9 | 26.9 |
| ImCylm | 3.9 | 26.6 | 29.2 |
| ImDpylm | 4.7 | 29.3 | 26.9 |
| Imphen | 3.6 | 28.8 | 24.2 |

2.7. The Cycloaddition of CO₂ to Aziridine 1a Catalyzed by Nb(OEt)₅/TBAI

The mechanism considered is represented through the steps of aziridine ring-opening at the phenyl-substituted methine carbon atom through skill of the cooperative action of Nb(OEt)₅ and TBAI, CO₂ insertion and ring-closure to have adequate money the preferred product. This mechanism is analogous to that common for the synthesis of cyclic carbonates from CO₂ and epoxides. Following the formation of intermediate A by coordination of Nb(OEt)₅ by the nitrogen atom of the aziridine, its ring-opening proceeds through C–N bond cleavage by means of capacity of the nucleophilic assault of the iodide anion on the carbon atom bearing the phenyl ring and requires an electrical energy barrier of 10.0 kcal/mol (the whole power barrier for the step of ring-opening is subsequently 14.3 kcal/mol) [24].

The insertion of CO₂ in the Nb–N bond of the ring-opened intermediate B was once discovered to be exceptionally electrical energy demanding, with a barrier of 30.1 kcal/mol

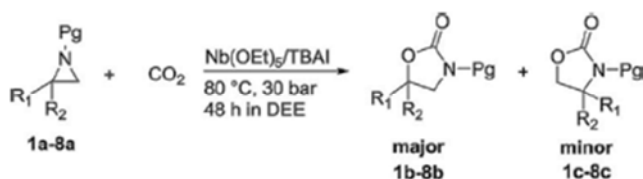


Figure 11. Cycloaddition of CO₂ to several aziridines catalyzed by Nb(OEt)₅/TBAI [24].

and essential to intermediate C. The upper response barrier is located at 31.3 kcal/mol for the step of CO₂ insertion that, therefore, represents the cost figuring out step of the process [25]. This barrier is everyday with the experimentally located requirement of at least 60°C for a sizable alternatively slow conversion of the substrate. The step of ring-opening used to be decided to be 2.6 kcal/mol higher in energy than for the critical regioisomer since, electronically, the NBO value on them ethylene carbon is lower through potential of 0.182 e, for this reason less electrophilic [26, 27]. Switching to the NbCl₅/TBAI system, no qualitative versions have been observed, but, quantitatively, the corresponding transition state A → B regarded greater facile with a barrier of 6.6 clearly kcal/mol. This barrier was significantly higher for the aziridine ring opening at the methylene carbon (9.9 kcal/mol) for this purpose explaining the high-quality regioselectivity positioned for this catalyst (Table 1, Entry 7). However, the CO₂ insertion step grew to become much larger difficult with a barrier of 37.7 kcal/mol (thus 7.6 kcal/mol higher in strength with appreciate to the corresponding barrier for Nb(OEt)₅). This observation, ordinary with the difference in catalytic activity observed experimentally, suggests the

importance of the steric trouble at niobium core to facilitate the insertion of CO₂ by favoring the Nb-N bond cleavage. Indeed, when Nb(OEt)₅ is used as a catalyst, this distance elongates by means of 0.128 Å with admire to the case of NbCl₅. At the identical time the distance between the nitrogen atom and the carbon atom of CO₂ is 0.197 Å shorter for Nb(OEt)₅. Also for the case of NbCl₅, the cooperativity via the usage of a 2nd niobium atom in the step of CO₂ insertion was observed to be disfavored, but entirely by way of 1.3 kcal/mol. Last, the response profile was recalculated the usage of Nb(OMe)₅/TBAI as a catalyst to understand, and at the same time, take away the plausible noise due to the alkyl chains, which would perchance rotate freely at the experimental conditions. Apart from other minimal strength differences in the calculated pathway with admire to Nb(OEt)₅, the charge identifying barrier for the step of CO₂ insertion increased by 2.6 kcal/mol in the case of Nb(OMe)₅; the B → C transition kingdom shows a N••C distance that is 0.167 Å shorter than for the case of NbCl₅ but nevertheless 0.030 Å longer than for Nb(OEt)₅. This fashion confirms the importance of the steric hassle at the niobium middle in facilitating the step of CO₂ insertion [28].

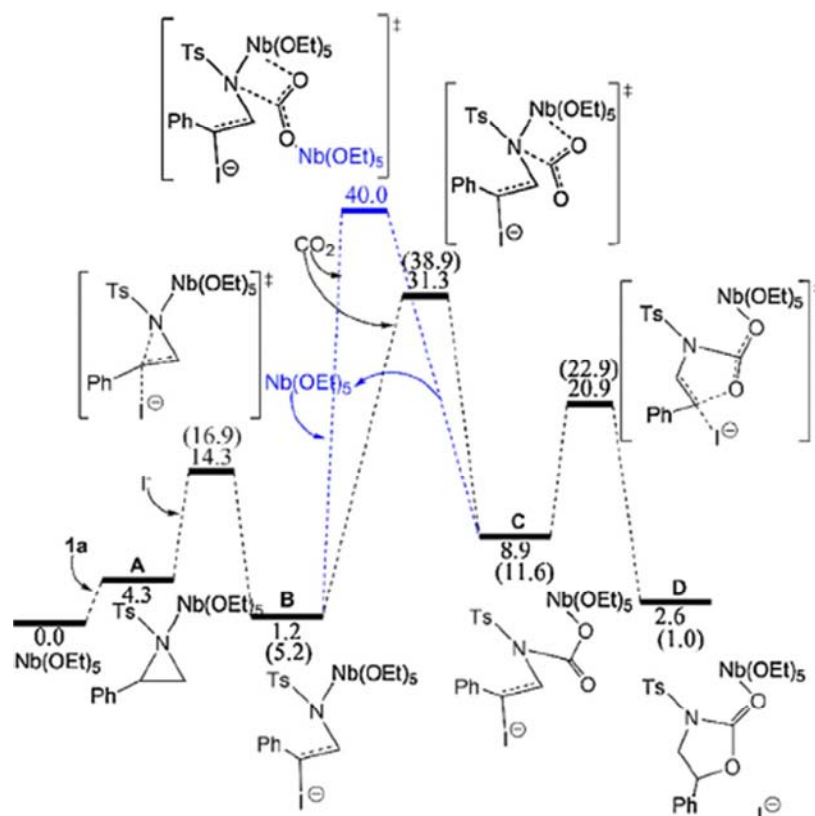


Figure 12. Energy profile for Reaction mechanism of the cycloaddition of CO₂ to aziridine 1a catalyzed by Nb(OEt)₅/TBAI [28].

3. Conclusion

Carbon dioxide is no longer completely one of the waste gases accountable for the greenhouse effect, then again additionally inexpensive, safe, nontoxic, non-flammable, and renewable C1 resource for producing value-added natural

compounds. One of the most promising and environmentally pleasant methodologies in this region is the direct synthesis of cyclic carbamate (2 oxazolidinone) the usage of CO₂ as phosgene or CO replacement. However, due to the thermodynamic inertness of carbon dioxide require excessive extent of activation electricity to convert fee introduced cyclic carbamate (2 oxazolidinone) barring catalyst. As

verified in this review, in modern years, several catalytic structures have been developed that ought to efficiently catalyze the incorporation of CO₂ into two oxazolidinones. Interestingly, most of these catalysts ought to be except troubles recovered and reused for a range of response runs barring observable loss of their catalytic endeavor and yield, imparting extra sustainable procedures for the chemical fixation of CO₂. Thus, there is on the other hand similarly need for the discovery of novel and besides a doubt environment friendly catalytic systems, which can allow the CO₂-based 2-oxazolidinone synthesis underneath milder conditions.

Conflicts of Interest

All the authors do not have any possible conflicts of interest.

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