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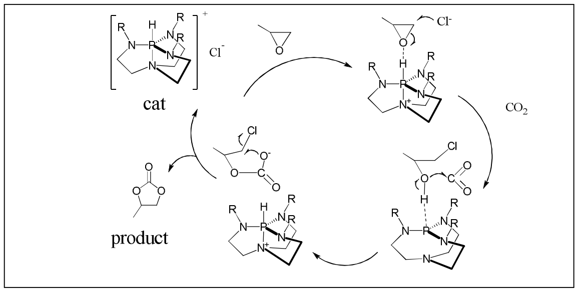
The activity of azaphosphatranes, a novel type of non-metal and solvent-free catalysts for the synthesis of cyclic carbonates from epoxides and CO_2, is unraveled by DFT calculations.



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Communication

Intermolecular Proton Transfer in Cyclic Carbonate Synthesis from Epoxide and Carbon Dioxide Catalyzed by Azaphosphatranes: A DFT Mechanistic Study

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Azaphosphatranes were reportedly efficient and metal-free catalysts for CO_2 fixation to epoxides, however, its mechanism remains unclear. DFT investigations reveal that intermolecular proton transfer is essential for the reaction while the CO_2 insertion into the P−N bond of the catalyst will result in catalytic deactivation.

The utilization of carbon dioxide (CO_2) is a possible strategy for reducing the CO_2 emission into the atmosphere as it could contribute to cycling carbon by mimicking nature that makes thousands of compounds from atmospheric CO_2. The utilization of CO_2 consists of four categories, namely conversion to useful chemicals, conversion to fuels, enhanced biological utilization and technological utilization that may not require CO_2 conversion.[1] The conversion CO_2 to useful chemicals is of growing interest for CO_2 management and sustainable development,[2, 3] and it has been a long-standing goal for chemists, since CO_2 is an abundant, inexpensive and nontoxic renewable C1 resource.[4-6] Although there are some pathways that can convert the CO_2 to useful chemicals,[7] only a few were applied in industrial synthetic processes, because the CO_2 is thermodynamically very stable and the activation requires high energy substrates or electroreductive processes. The cylcoaddition of CO_2 to epoxides to produce five-membered cyclic carbonates (PC) is one of the utilization of CO_2 in industrial syntheses.[8-10] This is due to that the cyclic carbonates are low-energy target molecules whose formation does not require high-energy substrates. The synthesis of cyclic carbonates from CO_2 and epoxides has therefore become a promising alternative to overcome the thermodynamics.

The synthesis of PC in industrial scale is usually carried out using Lewis acid or base catalysts, which require high temperatures and pressures. The conditions have limited the process in terms of energy and economics. As the utilization of PC is substantially increased due to that the PCs are widely used as electrolyte components in lithium batteries, polar aprotic solvents, and intermediates in the production of pharmaceuticals and fine chemicals,[11, 12] new commercially viable catalysts and processes which can be operated under atmospheric pressure and close to room temperature are required to minimize the energy costs of the PCs production. Many efforts have been made to study the catalytic systems for the production of PC. Most of the catalysts are metal complexes.[13-16] Besides metal compounds, bromine,[17] KI,[18, 19] N-Heterocyclic compounds,[20-22] and ionic liquids,[23-27] were also reported to be effective in production of PCs. However, in most of these cases, additives or cocatalysts as well as organic solvents are usually required.

Recently, Chatelet and his coworkers reported that azaphosphatranes, also known as Verkade's superbases,[28-35] can serve as single-component, metal-free organocatalysts for the production of PCs from CO_2 and styrene oxide at atmospheric pressure and the temperature of 80~100 °C.[36] They also proposed a mechanism in which CO_2 was activated via insertion into P−N bond of catalyst. However, their mechanism seems contradict with their kinetic observations that the catalysts with bulky P−N bond protecting group exhibit high catalytic activity. Two questions naturally arise: whether the CO_2 insertion is essential for the catalytic reaction? Which property of the catalyst is related to the catalytic activity?

In this contribution, we theoretically investigated the reported reaction[36] with simplified model (see **Chart 1**.) at 100 °C, 1 atm, and in toluene solution. The structures of catalyst and its derivatives were shown in **Chart 2**. All geometries of minima and transition states were optimized at B3LYP/6-31G(d) theoretical level for gas phase molecules. For all molecules, the electronic energy ($E_{electron}$) was improved by a single-point calculation at B3LYP/6-311++G(2d,p) level. For an intermediate or transition states, the Gibbs energy in gas phase (G_{gas}) was calculated as equation (1):

$$G_{gas} = E_{electron} + E_{dispersion} + ZPE + G_{correct,gas} \qquad (1)$$

where the empirical dispersion correction ($E_{dispersion}$) was calculated using Grimme's D3 parametrization,[37] the zero-point vibrational energy (ZPE) and thermal corrections to Gibbs energy ($G_{correct,gas}$) were calculated via frequencies analysis using 6-31G(d) basis set and with the harmonic frequencies scaled by a factor of 0.9614.[38] The Gibbs energy in solution phase (G_{sol}) was calculated as equation (2):

$$G_{sol} = G_{gas} + G_{correct,sol} \qquad (2)$$

Where the solvent effect ($G_{correct,sol}$) was estimated by a continuum solvation model SMD.[39] All calculations were carried out using Gaussian 09 software package.[40]

For the catalyst **C1a**, the Gibbs energy profiles for this catalytic reaction were depicted in **Fig. 1**. The reaction starts with the epoxide ring-opening step in which the secondary carbon of **1** is attacked by chloride, whilst the phosphonium of **C1a** supplies a proton to the ring-opened **1** to stabilize the intermediate **3**. This elementary step is exothermic in gas phase ($\Delta_r G_{gas}$ = -9.08 kcal mol^{-1}) while endoenergic in solution by $\Delta_r G_{sol}$ =0.94 kcal mol^{-1}. The energy barriers for this step are 35.27 and 26.90 kcal mol^{-1} in gas phase and in solution, respectively. In intermediate **3**, the O−H bond of **1** points towards to the P atom of **C1a** resulting in a short O−H…P (the distance between H and P is 2.43Å).

The secondly elementary step is CO_2 addition which starts with the approaching of CO_2 to ring-opened **1**. When the C atom of CO_2 gets close to the O atom of ring-opened **1,** the transition states **TS3-4** formed. In this stage, the C···O distance is 1.75 Å indicating no covalent bond is formed, whilst the O−H bond is enlongated to 1.37 Å and the H···P distance is decreased to 1.59 Å. This addition reaction has a large barrier ($\Delta^{\ddagger}G_{gas}$ = 30.97, $\Delta^{\ddagger}G_{sol}$ = 28.32 kcal mol^{-1}). However, the reverse reaction has an extremely small barrier ($\Delta^{\ddagger}G_{sol}$ = 9.79 kcal mol^{-1}). In adduct **4**, the C−O bond has been formed between **1** and CO_2, whilst the proton returns to the P atom of **C1a**. The formation of **4** is an endothermic process whether in gas phase or in solution.

The last elementary step is the conversion from **4** to **2** in which the carbonate group attacks the secondary carbon of the ring-opened epoxide followed by the chloride leaving and lactone ring closure. After the separation of cyclic carbonate and azaphosphatrane, the catalyst is regenerated and the catalytic cycle is completed. This step requires a relatively low barrier ($\Delta^{\ddagger}G_{gas}$ = 14.85, $\Delta^{\ddagger}G_{sol}$ = 9.48 kcal mol^{-1}), and it is an exothermic reaction. Among the three steps, the CO_2 addition is the rate determining step. The intermolecular proton transfer is completed in the first two steps of the catalytic reaction.

In order to test the role of the catalyst, the objective reaction was investigated using the same method but with the absent catalyst, see page S4-S5, (ESI†). Without the catalyst, actually a proton donor, the epoxide ring-opening step cannot occur due to the highly reactive oxide anion in the ring opened intermediate. After CO_2 addition to the ring-opened epoxide, the following ring-closure step for the formation of cyclic carbonate requires releasing the proton. Thus, the intermolecular proton transfer is required by the reaction. The protonated phosphonium moiety of the catalyst is the active site which acts as a proton transfer station in the catalytic cycles.

The P−N bond is reportedly sensitive to CO_2, which has been approached to CO_2 capture.[41] The catalyst **C1a** is able to be converted to a tricyclic phosphorylcarbamate structure (**C2a**) via insertion of CO_2 into the P−N bond. The CO_2 insertion into the catalyst **C1a** was subsequently investigated to evaluate its influence on the catalytic reaction. **Fig. S2a** and **S3a** (ESI†) present the Gibbs energy profiles of the CO_2 insertion into acidic and basic form of **C1a**, respectively. According to the DFT calculations, the basic form of **C1a** is more sensitive to CO_2 insertion than its acidic form. The computed activation barrier ($\Delta^{\ddagger}G_{gas}$ = 37.26 , $\Delta^{\ddagger}G_{sol}$ = 32.78 kcal mol^{-1}) for the CO_2 insertion into P−N bond is relatively higher than the barrier for the rate determining step of the objective reaction catalyzed by **C1a**, it is also within a realistic range for a reaction occurring at 100 °C. Thus, the CO_2 insertion into the basic form of **C1a** is a side reaction.

The formation of **C2a** through CO_2 insertion into **C1a** is endothermic by about 35 kcal mol^{-1} (as shown in Fig. 2) which indicated the process is not thermodynamically allowed. However, we still investigated the catalytic activity of **C2a** to reveal the structure-activity relationship of azaphosphatranes. The Gibbs energy profiles for this reaction were depicted in **Fig. 2**. The catalyst **C2a** obviously lowers the barrier of the first step compared with **C1a**, nevertheless, it significantly heightens the barriers for the remaining steps. Thus, the catalytic activity of **C2a** is lower than **C1a**. The intermolecular proton transfer in the catalytic reaction with **C2a** is also different from **C1a**. In the epoxide ring-opening step, the proton transfers from **C2a** to epoxide, thus the intermediate **5** becomes stable. In this stage, the newly formed O−H bond of **1** points towards to the catalyst's carbonyl O atom instead of P atom. In the CO_2 addition step, the proton shifts to the carboxyl of the CO_2 adduct rather than the catalyst during the production of **6**. The proton returns to the catalyst until the last step. These differences in the intermolecular proton transfer cycle imply that CO_2 insertion into the P−N bond reduces the alkalinity of the azaphosphatrane. Furthermore, the catalytic activity may be related with the alkalinity of the catalyst.

To reveal the relationship between the catalytic activity and the alkalinity of the catalysts, a series azaphosphatranes were theoretically investigated. The proton affinity, see **Table S1** (ESI†), was firstly calculated since it can reflect the alkalinity of the base. Among the three analogs (**C1a** ~ **C1c**), **C1b** is the most protophilic azaphosphatrane and followed by **C1c** and **C1a**. The order of the calculated proton affinities is in good agreement with the reported catalytic activity (**C1b** > **C1c** > **C1a**).[36]

On the other hand, the ionization state of an azaphosphatrane, which can greatly change the catalytic reaction pathway, is primarily determined by the alkalinity. Thus, the ionization states of a series azaphosphatranes (see **Table 1**) were theoretically investigated. Under the reaction condition, the superbase **C1a** almost entirely exists in its acidic form indicated by an ionization degree of 99.8%. However, it completely changes to the basic form after CO_2 insertion indicated by an extremely low ionization degree of <0.001% for **C2a**. The deprotonation of the active site will result in the alteration of catalytic reaction pathway, because the catalyst can no longer serve as a proton transfer station which is required by the catalytic process. We carefully explored the possible reaction paths with the basic form of **C2a** as catalyst. However, no realistic one was found. These results suggest that **C2a**, the CO_2 insertion product of **C1a**, is hard to be yielded under the reaction conditions. Unfortunately, **C2a** almost entirely exists in its basic form which is inactive, even it has been yielded. Thus, the CO_2 insertion into **C1a** will result in deactivation of the catalyst.

Given the observations from the present DFT calculations and reported precedents,[42-44] we proposed the reaction mechanism which is illustrated in **scheme 1**. The epoxide ring breaks by the nucleophilic attack of the chloride at the secondary carbon of **1**. The ring-opened epoxide is stabilized by capture of proton from the azaphosphatrane. The consequent attack of the ring-opened **1** by CO_2 at the resultant alcohol moiety leads to the formation of CO_2 adduct, whilst the catalyst is regenerated by recapture of proton from CO_2 adduct. Subsequent ring-closure forms the product **2**. There is an equilibrium existing between the acidic and basic form of azaphosphatranes. Although the basic form is not dominated compared with the acidic form, the insertion of CO_2 to the basic form will result in a displacement of the equilibrium to the left which cause the consumption of the catalyst. The present mechanism can explain the thermodynamic observations reported by Chatelet and his coworkers that **C1a** deactived in a few hours but **C1b** and **C1c** did not under the same condition.[36] It is probably due to that the bulky substituents in **C1b** and **C1c** act as protecting groups avoiding CO_2 insertion into the P−N bond of the catalyst. This was also confirmed by the calculations results (**Fig. S2b, S2c** and **S3b** (ESI†)). Chatelet *et al* also proposed a reaction mechanism in which the CO_2 is activated via insertion into P−N bond of azaphosphatrane and subsequently attacked by ring-opened expoide compound to yield the final product through a ring-closure step.[36] Their mechanism seems contradict with their kinetic observations, while those observations are in good agreement with the present mechanism proposed based on our DFT calculations. According to the present mechanism, the chloride of **C1a** acts as a nucleophile to attack and break the epoxide ring, while the protonated azaphosphatrane, the cation part of **C1a**, acts as a proton transfer center to facilitate the following cyclic carbonate production. We think that an appropriate nucleophile, such as chloride or bromide but not confined to halogens, and an adequate base which is protonated and insensitive to carbon dioxide can serve as a catalyst for cyclic carbonate synthesis. This needs to be confirmed by further experimental and theoretical studies. However, it supplies us with an idea of the design of catalysts for cyclic carbonate synthesis.

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Conclusions

We successfully elucidated the intermolecular proton transfer mechanism for the synthesis of cyclic carbonates from epoxides and CO_2 catalyzed by azaphosphatranes. To answer the forementioned two questions: the catalytic activity is strongly related with the alkalinity of catalyst. The CO_2 insertion into P−N bond of catalyst is not essential for the catalytic reaction but will result in deactivation of catalyst. This will open an avenue to the design of metal-free catalysts toward production of cyclic carbonates from epoxides and CO_2.

Notes and references

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† Electronic Supplementary Information (ESI) available: computational details, electronic energies, corrections to Gibbs free energy and Cartesian coordinates. See DOI: 10.1039/b000000x/

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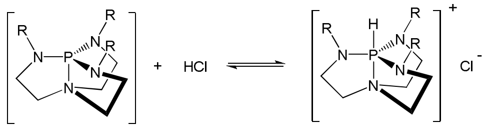
Table 1 The ionization states of azaphosphatranes



species	$\Delta_r G_{sol}$/kcal mol^{-1}	equilibrium constant	ionization degree
C1a	-11.12	3.27×10^{6}	100%
C1b	-13.36	6.67×10^{7}	100%
C1c	-11.33	4.33×10^{6}	100%
C2a	12.42	5.29×10^{-8}	<0.001%
C2b	2.57	3.11×10^{-2}	3.0%

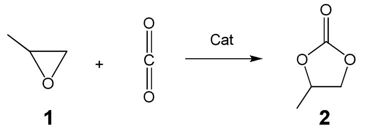


Chart 1 Formation of cyclic carbonate from epoxide and carbon dioxide.

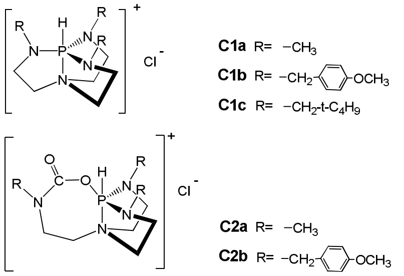
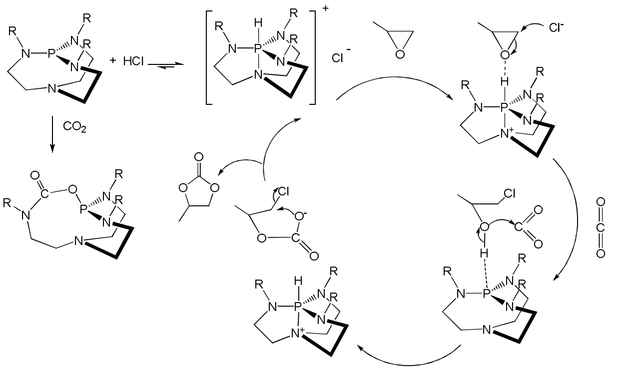


Chart 2 Structure of catalysts and their derivatives



Scheme 1 Catalytic cycles calculated for cyclic carbonate synthesis catalyzed by azaphosphatranes.

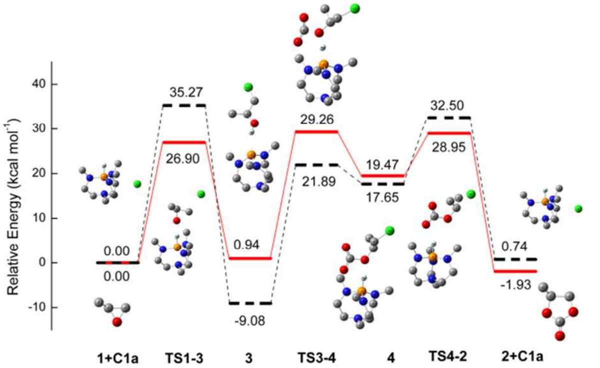


Fig. 1 B3LYP/6-31G(d) optimized structures for cyclic carbonate synthesis from epoxide and carbon dioxide catalyzed by **C1a**. Hydrogens are omitted for clarity except for the one at catalyst's active site. The energy sum of **1**, **C1a** and CO_2 is the reference (0.00). Other relative energies were calculated according the law of Mass Conservation and with respect to the reference. - - - $\Delta_r G_{gas}$, —— $\Delta_r G_{sol}$. Color code: C, gray; P, orange; Cl, green; O, red; N, navy-blue; H, light-blue.

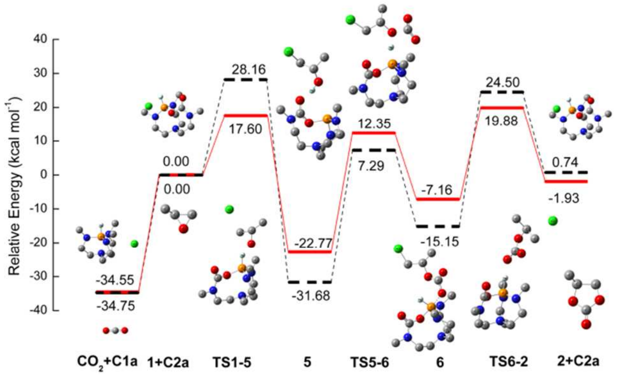


Fig. 2 B3LYP/6-31G(d) optimized structures for cyclic carbonate synthesis from epoxide and carbon dioxide catalyzed by **C2a**. Hydrogens are omitted for clarity except for the one at catalyst's active site. The energy sum of **1**, **C2a** and CO_2 is the reference (0.00). Other relative energies were calculated according the law of Mass Conservation and with respect to the reference.- - - $\Delta_r G_{gas}$, —— $\Delta_r G_{sol}$. Color code: C, gray; P, orange; Cl, green; O, red; N, navy; H, lightblue.