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A Free Energy Landscape of CO₂ Capture by Frustrated Lewis PairsLei Liu,^{*,†,‡,⊥} Binit Lukose,[§] and Bernd Ensing^{*,||}[†]Department of Physics & Earth Sciences, Jacobs University Bremen, Campus Ring 1, 28759 Bremen, Germany[‡]Mulliken Center for Theoretical Chemistry, Institute for Physical and Theoretical Chemistry, University of Bonn, Beringstraße 4, 53115 Bonn, Germany[§]School of Electrical and Computer Engineering, Boston University, Boston, Massachusetts 02215, United States[⊥]Van't Hoff Institute for Molecular Sciences, University of Amsterdam, 1098 XH Amsterdam, The Netherlands

Supporting Information

ABSTRACT: Frustrated Lewis pairs (FLPs) are known for their ability to capture CO₂. Although many FLPs have been reported experimentally and several theoretical studies have been carried out to address the reaction mechanism, the individual roles of the Lewis acid and base of FLPs in the capture of CO₂ are still unclear. In this study, we employed density functional theory (DFT) based metadynamics simulations to investigate the complete reaction path for the capture of CO₂ by the *t*Bu₃P/B(C₆F₅)₃ pair and to understand the roles of the Lewis acid and base. Interestingly, we find that the Lewis acid plays a more important role than the Lewis base. Specifically, the Lewis acid is crucial for the catalytic properties and is responsible for both kinetic and thermodynamics control. The Lewis base, however, has less of an effect on the catalytic performance and is mainly responsible for the formation of a FLP system. On the basis of these findings, we propose a rule of thumb for the future synthesis of FLP-based catalysts for the capture of CO₂.

KEYWORDS: CO₂ capture, frustrated Lewis pairs, metadynamics simulations, free energy surface, Lewis acid, Lewis base

INTRODUCTION

The growing use of fossil fuels has resulted in large amounts of CO₂ being exhausted into the atmosphere, which is considered to be the major reason for global warming.¹ On the positive side, CO₂ is an abundant and renewable carbon source, and it can be reduced to various useful chemicals.² To convert CO₂ into more valuable chemicals, we first need to transfer the gas-phase molecule into the solution or solid-state phase by adsorbing or capturing it. This process is typically accomplished via surface catalysis.³ However, this method is not economically and environmentally friendly due to the introduction of transition-metal centers. Recently, Stephan and co-workers developed a class of reactive complexes, named “frustrated Lewis pairs” (FLPs), which may help to solve the problem.⁴ In these molecules, the Lewis acids and Lewis bases are sterically hindered by the presence of bulky organic substituents, which prevent a neutralization reaction between the two components. As a result, the reactivity of both the Lewis acid and the Lewis base remains in the FLPs, leading to many interesting applications, such as H₂ activation, capture of CO₂ (see Scheme 1) and reduction of CO₂.^{5–12}

Scheme 1. Capture of CO₂ by an Intermolecular FLP, *t*Bu₃P/B(C₆F₅)₃

After the discovery of FLPs, the concept has been expanded to many other systems consisting of P/B or P/N compounds, and all of these pairs have been found to capture CO₂ in a similar fashion. Their interesting properties have also attracted interest from theoretical and computational chemists.^{13–18} Until now, two typical reaction mechanisms have been reported in the literature. Taking the representative FLP *t*Bu₃P/B(C₆F₅)₃ as an example, the first reaction mechanism, which is based on static density functional theory (DFT) calculations, shows that the Lewis acids and bases work in a cooperative way, and the capture of CO₂ by FLPs follows a concerted mechanism—the P–C and B–O bonds are formed simultaneously.¹³ The second reaction mechanism, which is based on ab initio molecular dynamics (AIMD) simulations, shows that the capture of CO₂ by FLPs follows a two-step mechanism.¹⁶ In that work, by analyzing the AIMD trajectories, the authors found out that the P–C bond was formed before the formation of the B–O bond when CO₂ got close to the FLP. However, no studies on the individual roles of the Lewis acid and base have been reported so far. Due to the lack of that knowledge, a targeted experiment or a rational design of a FLP-based catalyst for capture and reduction of CO₂ is not immediately expected.

In this study, we have performed metadynamics simulations based on density functional theory with dispersion corrections

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(DFT-D) to compute the free energy surface (FES) at a finite temperature (i.e., room temperature) and to explore the lowest free energy reaction path for the capture of CO₂ by the prototypical FLP: *t*Bu₃P/B(C₆F₅)₃ (Scheme 1).¹³ By analyzing the FES, we also aim to understand the detailed reaction path, specifically to unravel the individual roles of Lewis acid and base in the capture of CO₂.

RESULTS AND DISCUSSION

We performed AIMD simulations starting from the CO₂–FLP adduct [*t*Bu₃PCOOB(C₆F₅)₃]. We adopted this treatment because the structure of the CO₂–FLP adduct is rigid and has been confirmed by X-ray crystallography measurements and DFT calculations, while the structures of free CO₂ and FLP are unclear because of their complexity.¹³ Hence, in the course of MD simulations, we first followed the CO₂ liberation process, instead of CO₂ capture. On the other hand, we performed relatively long simulations that cover both the CO₂ liberation and capture processes (see Figure S1 for the distances between P, B, C, and O as a function of simulation time). Note that prior DFT calculations show that the capture of CO₂ by FLPs follows a concerted mechanism.^{13,15} The reactants (FLP and free CO₂ molecule) and the CO₂–FLP adduct are connected by only one transition state (TS). In the TS structure, both P–C and B–O distances are around 2.5 Å. This means that C and O start to interact with P and B at nearly the same time. However, AIMD simulations reveal a two-step mechanism.¹⁶ When the CO₂ molecule moves closer to the FLP system, a P–C bond is formed, followed by the formation of a B–O bond. After that, the final CO₂–FLP adduct is formed. The authors concluded this on the basis of the AIMD trajectories. They reported that the P–C bond was formed prior to the B–O bond, and they obtained some structures in which the P–C bond lengths were about 2.0 Å while the B–O distances were around 4.0 Å. However, this conclusion is qualitative, since the complete free energy reaction path was not computed and the roles of the Lewis acid and base were not investigated. Complementary to that, from our metadynamics simulations, we were able to obtain the complete FES for the capture of CO₂ by FLPs (Figure 1), which is more rigorous than the

reaction profile obtained either by static DFT calculations or by AIMD simulations. The FES depicted in Figure 1 shows that the overall reaction mainly has two steps after the entrance of CO₂ into the cavity of FLP (see path I). (1) *Capture of C by the Lewis base center, phosphorus (P)*: when CO₂ molecules move close to the FLP pair, the C of CO₂ attaches to P while O remains free. (2) *Capture of O by the Lewis acid center, boron (B)*: after the capture of C, O of CO₂ attaches to B. As shown in Figure 1, the reaction could also proceed in the opposite way: i.e., O first attaches to B and then C attaches to P (see path III). However, it is apparent that all of the points along this reaction path have high free energies, and the barriers for this path are much higher than that of path I. On the grounds of static DFT calculations, it is commonly believed that the reaction proceeds via a concerted mechanism. Both C and O are captured by FLPs at the same time and pass through a single TS in which P–C and B–O have similar distances (i.e., 2.5 Å). From Figure 1, one could think of such a possibility: i.e., the reactant and the product are directly connected via path II. However, analogous to path III, all points along this reaction path have high free energies, and this will lead to a high energy barrier (see Figure S4 in the Supporting Information). Therefore, the probability of these two paths (paths II and III) will be very low. If the reaction proceeds through path II or III, it would most likely fall back into the reactant, product, or intermediate state (point A, C, or D in Figure 1) and then proceed via path I. Justifying this, we obtained some structures in which both the O–B and P–C bond lengths are about 2.5 Å, at around 20 ps of the simulations, and some other structures in which the P–C distance is about 4 Å while the O–B bond length is about 1.6 Å, at around 25 ps.

In short, the capture of CO₂ by *t*Bu₃P/B(C₆F₅)₃ pair has two steps: first, C attaches to P and then O to B. It is important to point out that the previous AIMD simulation has also reached a similar conclusion.¹⁶ However, the authors attribute this to the explicit presence of solvent molecules in the simulations. Here, we show that the reaction mechanism presented is the nature of the reaction between FLP and CO₂, as it happens despite the absence of solvent molecules in our simulations. Eventually, the role of the solvent is to stabilize the final zwitterionic products, which is a common viewpoint in FLP chemistry.^{19–21} Interestingly, a recent study showed that stabilization from organic solvents can be replaced by the crystal fields when FLP reactions are transferred into the solid state.²²

Now, to understand the individual roles of Lewis acid and base and to systematically design more efficient catalysts in the future, we have calculated the one-dimensional (1D) lowest FES profile (shown in Figure 2) along path I, which is depicted in Figure 1. We note that capture of CO₂ by the *t*Bu₃P/B(C₆F₅)₃ pair has three steps. From A to B is the entrance of CO₂ into the cavity of the FLP. The computed energy barrier of such a step is 11.4 kcal mol^{−1}. Note that a previous study on H₂ activation by FLPs also found a similar energy barrier for the entrance of H₂ into the cavity of FLPs.²³ The second step, from B to C, is the formation of a P–C bond. This step has an energy barrier of 3.3 kcal mol^{−1}, which is one-fourth that of the first step. However, the second step is more thermodynamically favored in comparison to the first step. The computed reaction free energy for the second step is −5.4 kcal mol^{−1}, while it is 9.3 kcal mol^{−1} for the first step. In short, the capture of C by Lewis base (*t*Bu₃P) is an endergonic process with a computed reaction free energy of 3.9 kcal mol^{−1}. It is worth pointing out that B is an unstable intermediate, and the region containing

Figure 1. Two-dimensional free energy surface of the capture of CO₂ by the *t*Bu₃P/B(C₆F₅)₃ pair. The detailed one-dimensional free energy surface of path I is given in Figure 2, and the representative structures along path I are depicted in Figure 3 (energies in kcal mol^{−1}). Notation used: *cn*_{P-C}, the coordination number between P and C; *cn*_{B-O}, the coordination number between B and O. *cn* = 1 indicates a chemical bond, while *cn* = 0 indicates no chemical bond.

TS1, B, and TS2 is relatively flat. Thus, the first and second steps can be treated as one step which is mainly corresponding to the formation of a P–C bond. The third step, from C to D, is the formation of an O–B bond. Unlike the first two steps, the third step is favored by thermodynamics and the computed reaction free energy is $-5.8 \text{ kcal mol}^{-1}$ (the free energy difference between D and C). If we take solvent effects into account, the third step becomes more exergonic (see Table S1 in the Supporting Information). It is important to point out that the formations of both intermediate states (B and C) are endergonic. According to the energetic span model,²⁴ we can define only one energy barrier along the reaction path, $-18.4 \text{ kcal mol}^{-1}$ (free energy difference between TS3 and A), which mainly corresponds to the formation of the O–B bond. In short, the third step, which is the capture of O by B, is a thermodynamically and kinetically controlled step for the capture of CO₂ by the *t*Bu₃P/B(C₆F₅)₃ pair. In other words, the Lewis acid (the B(C₆F₅)₃ molecule) plays a more important role than the Lewis base (the *t*Bu₃P molecule) in the capture of CO₂. This finding is surprising, since it is commonly believed that Lewis acids and bases work in a cooperative way and both components are important for the reactivity of FLPs with CO₂. This is also different from what we have found for the H₂ activation by FLPs, where the Lewis acid is responsible for the thermodynamics while the Lewis base is responsible for the kinetics.²⁵ Our finding suggests that more attention should be paid to the Lewis acid part of FLPs in future studies regarding CO₂ capture. Strong Lewis acids should be selected to make the overall reaction thermodynamically possible (i.e., $\Delta G \leq 0$). On the other hand, the Lewis acids should not be too strong; otherwise, the final products will be too stable (i.e., D in Figure 2) and that will lead to irreversible reactions.²⁶ This will not be

Figure 2. One-dimensional lowest free energy surface of the capture of CO₂ by the *t*Bu₃P/B(C₆F₅)₃ pair (path I in Figure 1). The representative structures are depicted in Figure 3.

suitable for the future utilization of the solution-phase CO₂, such as the reduction of CO₂ into useful chemicals. The kinetics of the reaction suggest that relatively strong Lewis acids are needed to lower the energy barriers.¹⁷ In addition, relatively weak Lewis bases should be selected to have less stable intermediates along the reaction path (i.e., C in Figure 2), which would result in relatively small energy barriers for the second step. However, the Lewis bases should not be too weak; otherwise, the energy barriers for the first step will become too high, which is also not suitable for the overall reaction kinetics.

Geometrical parameters of the four minima and the three TSs are depicted in Figure 3. The structures are denoted as A–D and TS1–TS3, as shown in Figures 1 and 2. Structure A is

the starting point of the reaction. In this structure, the CO₂ molecule is still free, and no interactions have been found between the CO₂ and the *t*Bu₃P/B(C₆F₅)₃ pair. For evidence, the P–C and B–O distances are 3.9 and 4.0 Å, respectively, and the corresponding Wiberg bond orders (WBO) are computed to be 0.0. The distance between the two reactive centers (P and B) is relatively large at 4.7 Å. Note that the angle O–C–O of the CO₂ species is 167.8°, which is slightly smaller than that of a free CO₂ molecule (i.e., 180.0°). In other words, the CO₂ species is bent in structure A, although there are no chemical bonds formed between the CO₂ and FLP. This could be due to the weak interaction between CO₂ and the FLP: CO₂ interacts with crystal fields created by the FLP pair.²³ The next minimum on the potential energy surface is structure B. CO₂ starts to enter the cavity of the FLP. Both P–C and B–O distances become shorter, which are 3.2 and 3.4 Å, respectively. The computed WBO for both P–C and B–O is 0.0, indicating that there are no interactions between CO₂ and the FLP as well in structure B. Afterward, B will arrive at structure C, in which the P–C bond is formed with a length of 2.1 Å and the corresponding WBO is 0.6. In this structure, O is still free, and the B–O distance is about 3.1 Å with a computed WBO of 0.0. Moreover, the angle O–C–O of the CO₂ further decreases to 135.1°. The final minimum of the FES is the CO₂–FLP adduct, which is given as D. In this structure, the CO₂ species is finally bonded to the FLP with P–C and B–O distances being 1.9 and 1.6 Å, respectively. The O–C–O angle of the CO₂ species is again decreased to 130.4°. The computed corresponding WBO shows a chemical bond characteristic of P–C and B–O bonds (both are 0.8). In general, the geometrical parameters of the TSs stay between their neighboring stationary points. For example, TS1, which connects the structures A and B, has a shorter P–C distance than that in A but longer than that in B (3.9 Å > 3.4 Å > 3.2 Å). Similar trends have been also found in the case of TS2. However, the distance between B and O remains almost constant with deviations under 0.3 Å. This trend also applies for TS3, which corresponds to the capture of O by B. The distance between P and C remains nearly the same for C, TS3, and D, with a change of only 0.2 Å, while the distance between B and O gradually decreases from 3.1 to 1.6 Å. Interestingly, the greatest change in the O–C–O angle happens when C is captured by P (from 172° to 135°); in the following step, i.e., capture of O by B, the change will be only about 5°.

To gain deeper insight into the reaction mechanism, we have plotted the frontier molecular orbitals (including the highest occupied molecular orbital, HOMO, and the lowest unoccupied molecular orbital, LUMO) and performed natural population analysis (NPA) for the important structures along the reaction path I—structures A, C, and D (see Figure 4). In structure A, the HOMO is located on the Lewis base component (the *t*Bu₃P molecule) and it has large contributions from the lone pair electrons of P. The LUMO is located on the Lewis acid component (the B(C₆F₅)₃ molecule), and it mainly consists of the empty orbitals of B. The frontier molecular orbitals indicate no orbital interactions between the FLPs and the CO₂ in structure A. This is consistent with the geometric parameters depicted in Figure 3, where the distances between CO₂ and two reactive centers (P and B) are too large (ca. 4 Å). When the reaction arrives at structure C, the plotted orbitals indicate that there are some orbital interactions between C and P. For example, the HOMO of structure C shows that the C accepts the lone pair electrons of P. There are also some charges

Figure 3. Representative structures of stationary points along path I (see Figures 1 and 2) for the capture of CO₂ by the *t*Bu₃P/B(C₆F₅)₃ pair obtained from metadynamics simulations with selected distances given in Å and Wiberg bond orders in parentheses. Hydrogen atoms are omitted for clarity. Color legend: P, yellow; B, pink; C, black; F, green.

Figure 4. Highest occupied molecular orbitals (HOMOs), lowest unoccupied molecular orbitals (LUMOs), and natural charges for selected atoms of the important structures provided in Figure 3. An isosurface value of 0.02 was used for the plot of molecular orbitals. Color legend: P, yellow; B, pink; C, black; F, green; H, white.

transferred from C to P. In structure A, P and C are positively charged with partial charges of 0.68 and 0.96 e, respectively. In structure C, the partial charge of P increases to 1.01 e while the partial charge of C decreases to 0.66 e. The LUMO of structure C is almost identical with that of structure A, which mainly consists of empty orbitals of B. Moreover, there is no change in the partial charge of B. When the reaction arrives at structure D, B finally bonds to O, indicated by the HOMO of structure D, and more charge transfer is seen from B to CO₂, and subsequently to P. The partial charge of P is 1.32 e in structure D, while it is 1.01 e in structure C. The partial charge of B

decreases to 0.68 e, while it is about 0.83 e when the distances between O and B are large (ca. 4 Å in the cases of structure A and C). It is interesting to point out that the charges of the whole CO₂ molecule are almost the same (about −0.60 e) in the cases of structures C and D. This finding indicates that the CO₂ molecule acts as a “bridge” for the charge transfer from B to P. For a comparison, the H₂ molecule functions similarly to CO₂ and H₂ mediates the charge transfer from Lewis acid to base during its activation by FLPs.^{26–28}

CONCLUSIONS

In this study, the capture of a CO₂ molecule by the *t*Bu₃P/B(C₆F₅)₃ frustrated Lewis pair is revisited by density functional theory (DFT) based metadynamics simulations. The obtained lowest free energy reaction path is more eventful than has been explained in the literature so far, which was obtained by static DFT calculations and AIMD simulations. Importantly, our study has revealed for the first time the separate roles of the Lewis acid and base in the FLP. Specifically, the capture of CO₂ by the *t*Bu₃P/B(C₆F₅)₃ pair has two steps after the entrance of CO₂ into the cavity of the FLP: capture of C by P, followed by capture of O by B. It is commonly believed that the roles of Lewis acid and base centers are the same—capturing CO₂ in a cooperative way and having equal contributions. Thus, modifications of either Lewis acid or base have the same effects on the reactivity between FLPs and CO₂. However, our findings derived from metadynamics simulations are in contrast with that. First, the overall reaction can be viewed as a pseudo-one-step process. Along the reaction path, the highest free energy barrier corresponds to the capture of O by B, indicating that this step is the rate-determining step. The formation of B–O is strongly exergonic, while the formation of P–C is endergonic. In short, the Lewis acid component (B(C₆F₅)₃) plays a more important role than the Lewis base component (*t*Bu₃P) in the capture of CO₂ by FLPs. The Lewis acid

component is responsible for both thermodynamic and kinetic control. The overall thermodynamics is determined by the strength of the Lewis acids, and the overall reaction rate is determined by the strength of the Lewis acids as well. As a rule of thumb, we suggest that future synthetic studies on the FLP or FLP-based system for activation of CO₂ should choose strong Lewis acids to make the reaction thermodynamically possible. In addition, the combination of a strong Lewis acid and a weak Lewis base should be selected to make the reaction kinetically feasible. We believe that the presented conclusions are key to the rational design of FLP-based catalysts for the activation of CO₂.

COMPUTATIONAL DETAILS

We performed all calculations similarly to those described by us in an earlier study.²⁵ In short, density functional theory (DFT) calculations were performed for both geometry optimizations and ab initio molecular dynamics simulations (AIMD) using the CP2K program.²⁹ We used the PBE density functional³⁰ augmented with the Grimme D3 dispersion correction³¹ and the Gaussian plane-wave (GPW) basis set.³² The valence orbitals were expanded in the DZVP-GTH Gaussian basis set, while an auxiliary plane-wave basis set up to the kinetic energy cutoff of 250 Ry was used to describe the valence electron density. The core electrons were replaced by pseudopotentials.³² To avoid spurious interactions due to the periodicity of the plane-wave basis, we used the Martyna–Tuckermann technique³³ and a large 20 × 20 × 20 Å unit cell. We first optimized the FLP–CO₂ adduct at the aforementioned DFT level of theory and then performed AIMD simulations. The AIMD simulations were done using the NVT ensemble, with the temperature set at 300 K by making use of a CSVR (canonical sampling through velocity rescaling) thermostat³⁴ with a time constant of 500 fs. The MD time step was 0.5 fs and the simulations ran for 35 ps in total.

For the metadynamics simulations, we used two collective variables (CVs) to bias the making and breaking of bonds between the P, B, C, and O, in practice: (1) the coordination between the P and C, cn_{PC} , and (2) the coordination between the B and O, cn_{BO} . Quadratic walls were used to avoid the sampling of uninteresting parts of the configuration space. For example, the distance between P and B was limited to be less than 4.5 Å, and the P–C and B–O distances were restricted to be at most 4.0 Å. The Gaussian bias potentials were initially spawned every 25 time steps, with a height of 0.25 kcal mol^{−1} and width of 0.15. After 20 ps of metadynamics simulation, the height was reduced to 0.10 kcal mol^{−1} and the deposit interval to 50 MD steps. The trace_irc program was used to compute the minimum free energy path (1D FES in Figure 2 of path I).³⁵

Natural population analysis (NPA) was performed at the PBE/def2-SVP³⁶ level of theory. Wiberg bond orders (WBOs)³⁷ and frontier molecular orbitals were computed at the PBE/def2-SVP level. The molecular orbitals were plotted with VESTA (visualization for electronic and structural analysis) software³⁸ with isosurface values of 0.02. The COSMO-RS (conductor-like screening model for real solvents) solvation model^{39,40} was used to compute the solvation free energies with toluene as the solvent. All the above calculations were done by employing Turbomole software^{41,42} and were single-point calculations based on the structures obtained from the metadynamics simulations.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.7b04072.

Additional information on DFT calculations, metadynamics simulations, and the Cartesian coordinates of the seven structures depicted in Figure 3A (PDF)

Movie of molecular dynamics simulations at 300 K (MPG)

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Notes

The authors declare no competing financial interest.

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