PCCP

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/pccp

Understanding the Mechanism of CO_2 Capture by 1,3 Di-substituted Imidazolium Acetate Based Ionic Liquids

James X. Mao,[†] Janice A. Steckel,[‡] Fangyong Yan,[¶] Nilesh Dhumal,[¶] Hyung Kim,[¶] and Krishnan Damodaran*,[†]

†*Department of Chemistry, University of Pittsburgh, Pittsburgh, Pennsylvania 15260*
‡*National Energy Technology Laboratory, P.O. Box 10940, Pittsburgh, Pennsylvania 15236*
¶*Department of Chemistry, Carnegie Mellon University, Pittsburgh, Pennsylvania 15213*

E-mail: damodak@pitt.edu
Phone: 412-624-8403. Fax: 412-624-8611

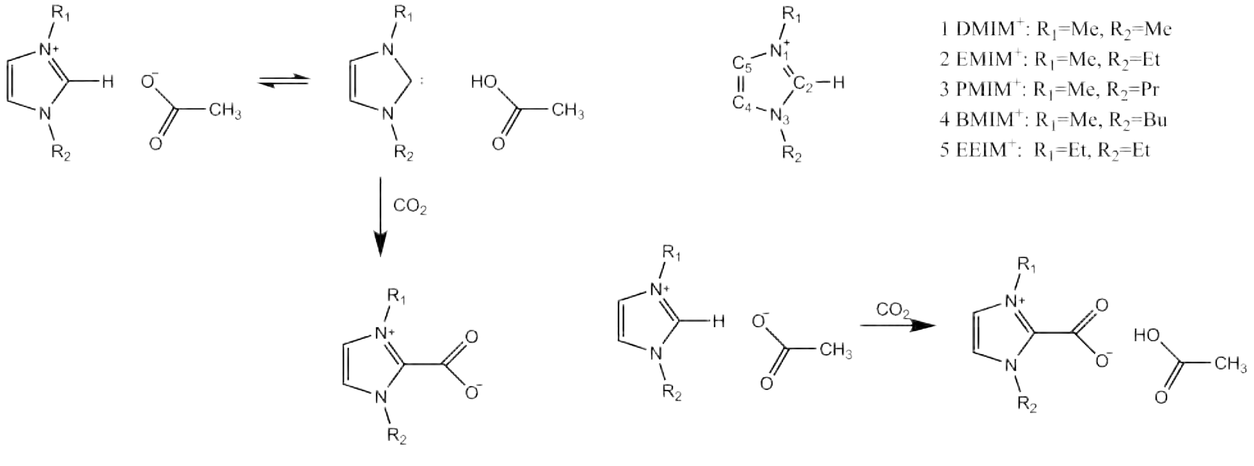
Abstract

Efficient CO_2 capture by ionic liquids need a thorough understanding of underlying mechanisms of CO_2 interaction with ionic liquids, especially when it involves chemisorption. In this work we have systematically investigated the mechanism of CO_2 capture by 1,3 di-substituted imidazolium acetate ionic liquids using Density Functional Theory. Solvent effects are analyzed using QM/MM and QM/QM approaches with the help of molecular dynamics simulations and ONIOM methods. Investigation of different stepwise mechanisms show that CO_2 could be involved in the first step of the reaction mechanism, also a new two-step mechanism is proposed. The final stabilization step is analyzed and pointed out to be responsible for important experimentally-observed features of the reaction.

Introduction

Room-temperature ionic liquids (RTILs) are salts that are liquid below 100 °C. They are largely comprised of ions and short-lived ion pairs, and possess some very attractive characteristics such as negligible vapor pressure, wide electrochemical window, and good thermal stability. These interesting properties have promoted them in a wide variety of applications, and among them using RTILs for gas separation has gained more and more attention in recent years, particularly in the area of CO_2 capture for climate change mitigation.

For most RTILs which were studied as media for CO_2 capture, anions of RTILs play a central role.[1,2] Acidic CO_2 is captured by interacting with the basic anion through physical interaction (physisorption of CO_2). While in 2005, to explain the absorption of CO_2 in 1-butyl-3-methylimidazolium acetate ($BMIM^+Ac^-$), Maginn[3] proposed that a possible chemical reaction might occur between $BMIM^+$ cation and CO_2 molecule in which the imidazolium cation is carboxylated by CO_2. A possible mechanism was proposed as well, in which the proton at the C(2) position of the imidazolium ring (atom numbering scheme refers to Figure 1) is abstracted by the acetate ion to form a carbene species in first step, followed by a reaction between CO_2 and carbene (Scheme I, Figure 1). However, this chemisorption mechanism was critisized by Shiflett *et al.* since the presence of produced acetic acid could not be detected,[4] although they agreed the formation of a 1 CO_2:2 IL molecular complex in the solution.



Scheme I

Scheme II

Figure 1: Possible mechanism schemes for the carboxylation of imidazolium acetate by CO_2.

In 2011 Gurau *et al.* reported a crystalline product after introducing CO_2 into RTIL 1-ethyl-3-methylimidazolium acetate ($EMIM^+Ac^-$).[5] The single-crystal X-ray structure of this solid product clearly showed the formation of 1-ethyl-3-methylimidazolium-2-carboxylate. In 2012 Besnard *et al.* reported their investigations of the reaction between $EMIM^+Ac^-$ and CO_2 in a series of publications.[6–8] Through their excellent work the formation of carboxylate (1-butyl-3-methylimidazolium-2-carboxylate) was put in evidence clearly via Raman, IR, and NMR spectroscopies. They noted that the presence of acetic acid was only detected after the introduction of CO_2, and since the formation of carbene in dense phase is questionable, it was concluded the triggering of this reaction is CO_2, and a different reactive scheme was proposed, in which CO_2 is involved in the first step to avoid the formation of carbene (Scheme II, Figure 1). After Besnard *et al.*'s work the occurence of carboxylation reaction between imidazolium cation and CO_2 in these systems is clear. Soon Shiflett *et al.* agreed the chemisorption mechanism and reported another supporting example in which 1-ethyl-3-

ethylimidazolium acetate ($EEIM^+Ac^-$) was carboxylated by CO_2.[9]

Although now it is clear that imidazolium acetate-based RTILs attract CO_2 via chemisorption reaction, different imidazolium acetate-based RTILs present quite different experimental observations.[5,6,9] The reaction mechanism should be elucidated in more detail to understand the chemisorption process. In this work, DFT methods were employed to further investigate the chemisorption reaction mechanism.

Calculation Details

DFT calculations were performed using the Gaussian 09[10] and Firefly[11] program at PBE0/cc-pVTZ[12–15] and B3LYP-D3/6-31+G(d,p)[16–20] levels. All geometries were fully optimized, followed by analytical frequency calculations to ensure that no imaginary components existed for minima and only one negative frequency for transition states. Transition states were further characterized by mimicking the unique imaginary frequency to confirm their relaxations to correct corresponding local minima. The basis set superposition error (BSSE)[21] was corrected for all interaction calculations using the counterpoise method.[22,23]

To address the solvent effects, we developed a method by combining quantum mechanics (QM) and classical molecular mechanics (MM). The QM/MM schemes includes four steps.

The first step is to obtain a liquid phase of 100 ion pairs of ionic liquid molecules at 298 K using molecular dynamics (MD) simulations. The MD simulations were conducted using a parallel version of Gromacs 4.5.4.[24] All simulations were conducted in the isothermal-isobaric ensemble (NPT) at 1 bar using a Nosé-Hoover thermostat[25,26] and an isotropic Parrinello-Rahman barostat[27] with relaxation times of 1 and 5 ps, respectively. During the simulation a fully relaxed model and a time step of 1.5 fs were used. The force field for cation is taken from Lopes et al.,[28] and anion from the OPLS force field.[29] The simulations employed periodic boundary conditions in cubic boxes, and run at a time scale of 30 ns, with 10 ns equilibration and 20 ns production. In the production phase, we calculated the densities of ionic liquids.

The simulated density is 1.120 g/cm^3, compared well to the experimental density[30] of 1.101 g/cm^3. By this comparison we confirmed in this step that the MD simulations are capable of finding a reasonable number of solvent molecules in a finite volume in liquid state.

The second step is to obtain a reasonable solvation environment for each species (reactant, transition state, and product). For each species optimized in the gas phase QM calculations, 100 pairs of surrounding ILs were added respectively to build MD structures. MD simulations were run at 298 K using these structures. The simulation setup is the same as the first step, except that simulations were run in the canonical ensemble (NVT). During the simulations, central QM structures were fixed and only 100 pairs of cations and anions were allowed to move. The MD simulations were run for 10 ns equilibrium and 20 ns production respectively for each structure built from the three species (reactant, transition state, and product).

The third step is to extract solvated structures from MD simulations. A solvated structure includes the central QM species and nine closest neighbor ionic liquid pairs. Since the radial distribution function from MD simulation showed a coordination number of 7 for cation and anion (Figure S3), nine closest IL pairs are considered enough to include the first solvation shell and provide a reasonable solvation environment for the central QM species for further calculations. To account for a reasonable sampling, eight solvated structures were extracted randomly from MD simulations' 20 ns production session for further investigation.

In final step, ONIOM calculations[31] were carried out for each solvated structure. In these calculations, the nine ionic liquid solvent molecules were fixed and treated at relative low computational level. The central species, which were QM optimized structures in gas phase, were optimized again in QM level with the nine solvent molecules around. In this way the reaction energy profiles were rebuilt in solvation environment. The results were averaged for the eight solvated structures to account for sampling in liquid state.

Results and Discussion

Carboxylation Reaction Scheme

To investigate carbene formation scheme (Scheme I, Figure 1), DFT calculations were performed at PBE0/cc-pVTZ level (results at other levels are quite similar and provided in Table S1 of Supporting Information) for five different imidazolium acetate-based RTILs which have been reported experimentally studied (Figure 1). The calculations showed low energy barriers for both carbene formation and subsequent carboxylation: the barriers are about 3 and 7 kJ/mol, respectively. (Detailed data are presented in Tables 1 and 2). These low energy barriers suggest that the mechanism proposed by Maginn seems quite feasible.

Table 1: Calculated energies [a,b] for species involved in the carbene formation step in Figure 1.

Ionic Liquids	Relative Energies		
	Cation··· Acetate	Transition State	Carbene··· Acetic Acid
$DMIM^+Ac^-$	3.5	5.8	0
$EMIM^+Ac^-$	2.6	5.4	0
$PMIM^+Ac^-$	2.0	5.1	0
$BMIM^+Ac^-$	0.4	5.0	0
$EEIM^+Ac^-$	1.6	5.1	0

[a] Energies in units of kJ/mol, and relative to products. [b] Calculated at PBE0/cc-pVTZ level.

Table 2: Calculated energies [a,b] for species involved in the carboxylation of the carbene depicted in Figure 1.

Ionic Liquids	Relative Energies		
	CO_2··· Carbene	Transition State	Carboxylate
$DMIM^+Ac^-$	32.8	40.8	0
$EMIM^+Ac^-$	36.6	43.9	0
$PMIM^+Ac^-$	37.4	44.3	0
$BMIM^+Ac^-$	37.7	44.5	0
$EEIM^+Ac^-$	39.8	46.5	0

[a] Energies in unit of kJ/mol, and relative to products. [b] Calculated at PBE0/cc-pVTZ level.

However, this two-step mechanism was not without critics,[4] for the reason that the stability of a carbene in a dense phase is questionable, and that experimentally the presence of acetic acid was only detected after the introduction of CO_2 into the IL.[8] (Hypothetically, if the proton is abstracted from the cation by the anion in step 1, this should be possible without the presence of the CO_2.)

An alternative mechanism (Scheme II, Figure 1) to account for these observation is that in which CO_2 directly reacts with the cation. There is a possibility that the reaction could proceed via a concerted, single-step mechanism. In a concerted reaction, the processes of proton transfer (from the imidazolium cation to the acetate anion) and CO_2 bonding (to the imidazolium ring) would happen at the same time. A great deal of effort was spent trying to locate such a transition state. No transition state related to the concerted reaction could be found from our efforts. From collision theory it is well known that the probability of an elementary reaction which simultaneously involves three chemical species (here they refer to a cation, an anion, and a CO_2 molecule) is negligible. However, we were able to successfully locate a transition state for a direct reaction between CO_2 and $EMIM^+$. The intrinsic reaction coordinate (IRC) calculation from the transition state shows that the associated energy barrier is around 300 kJ/mol (see Figure 2). A similar result (an energy barrier of 303 kJ/mol, Figure S1 in Supporting Information) was achieved while an acetate anion was placed beside $EMIM^+$, showing a simple stabilization from the anion is not enough to lower the energy barrier of this reaction scheme. To account the effects from more solvent molecules, a bigger sphere of influence must be considered.

Solvent Effects

With method described in Computational Details section, the reaction energy profile of both Scheme I and II for $Emim^+Ac^-$ were rebuilt to investigate the influence from solvent effects for reaction mechanism.

For step one (carbene formation) of Scheme I, the surrounding solvent molecules were

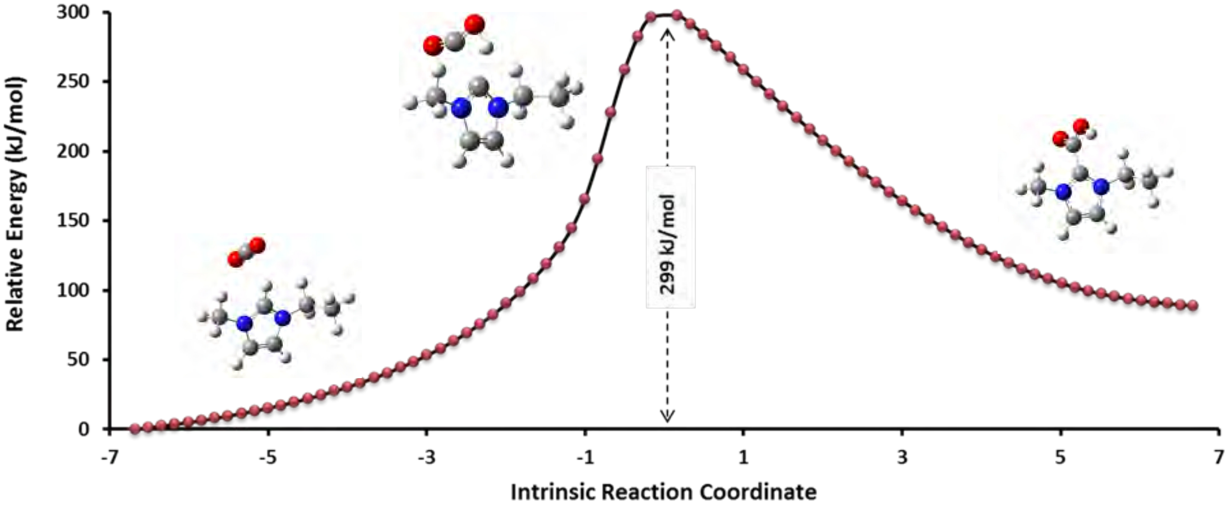


Figure 2: Energy profile for a direct reaction between $EMIM^+$ and CO_2.

first treated at different calculation levels (Table 3) to observe the validity of the method. Full QM calculations for both central species and surrounding solvent molecules at PBE0/6-31+G(d,p) level showed a dramatic change of reaction energy profile from the one in gas phase. In gas phase, the product (carbene-acid) is slightly favored than reactant (cation-anion) by 2.6 kJ/mol, with an energy barrier of 5.4 kJ/mol (Table 1). However, the full QM calculations using solvation structures showed there is no reaction at all: the transition state of the reaction disappears (for solvated structures, "transition state" structure is always more stable than carbene form), and the reactant (cation-anion) becomes much more stable than product (carbene-acid) by 32.1 kJ/mol (Table 3). Since the presence of carbenes in neat imidazolium acetate-based RTILs has not been directly detected in any spectroscopic method, full QM calculations using solvation model seems to correctly account for the solvent effect which stabilizes the cation-anion form significantly.

While full QM calculations are too expensive for further investigations in this study, ONIOM calculations[31] were affordable and expected to deliver similar results as full QM calculations. In ONIOM calculations, the central species (where reaction occurs) were still treated at QM level, while the surrounding solvent molecules were treated at relatively low computational level (Table 3) to reduce computational cost. It was found the reaction energy profiles are similar to gas phase energy profile when solvent molecules were treated at Molecular Mechanics level, showing carbene-acid form is more stable than cation-anion form. Turning on electronic embedding to include interactions at QM level makes not much difference. However, while solvent molecules were treated at Quantum Mechanics level (RHF/STO-3G or RHF/3-31G), the results are close to full QM calculations. The result of ONIOM(PBE0/cc-pVTZ:RHF/3-21G) calculations is almost the same as full PBE0/6-31+G(d,p) calculations. Although ONIOM(QM/MM) failed to produce solvent effects in ionic liquids as showed above, ONIOM(QM/QM) is capable of accounting for the solvent effect. The rest of the solvated model ONIOM calculations in this study were carried out at ONIOM(PBE0/cc-pVTZ:RHF/3-21G) level.

Table 3: Calculated reaction energy changes [a,b] for $Emim^+Ac^- \rightarrow$ Carbene+HAc in solvated model by ONIOM and QM methods.

Method	Energy Change
PBE0/cc-pVTZ:UFF	-2.3
PBE0/cc-pVTZ:UFF_E[c]	-8.5
PBE0/cc-pVTZ:Dreiding	-1.7
PBE0/cc-pVTZ:$Dreiding_E$[c]	-7.8
PBE0/cc-pVTZ:RHF/STO-3G	41.8
PBE0/cc-pVTZ:RHF/3-21G	32.7
PBE0/6-31+G(d,p)	32.1

[a] Energy in unit of kJ/mol. [b] Each energy change is an average from calculations of eight solvated structures (Table S4 in Supporting Information). [c] Subscript E donates electronic embedding.

Although these calculations indicate the carbene form is not favored energetically in solution, we should not conclude carbene is not accessible in neat imidazolium acetate-based RTILs. Indeed, although the presence of carbenes in imidazolium acetate-based RTILs has never been directly detected in any spectroscopy method, it was believed they were accessible.[32,33] Ab initio molecular dynamic simulations also showed that the presence of carbenes in pure $EMIM^+Ac^-$ is inherent,[34] and adding CO_2 to ILs facilitates the accident of carbenes formation.[35]

In another side, by using the solvated structures, we found the energy profile of Scheme

II change significantly: the energy barrier drops from 300 kJ/mol to 96 kJ/mol (Figure S3 in Supporting Information). This huge change implies the solvent effects could help the direct reaction between CO_2 and cation. A more interestingly observation is that structures similar to transition state in Scheme II (Figure 2) is not stable in gas phase (can only be saddle point but not minimum). However, we found they can be stable (as energy minimum) with the solvent molecules aside in our solvated structures (Figure 3). Since both the reaction mechanisms proposed in the literature (Scheme I and II) has their own limitations, we propose a more probable mechanism (Scheme III, Figure 4) which is an outcome of our solvated model calculations. For this new mechanism scheme, a two-step reaction profile was successfully built and confirmed with $Emim^+Ac^-$, with energy barriers of 66 kJ/mol for first step and 6 kJ/mol for second step respectively (Figure S5 and S6 in Supporting Information). Although the energy barrier (66 kJ/mol) seems still high, considering that carbene formation is no longer a reaction in solvated model, and our model only estimates the solvent effects with nine solvent molecules, this energy barrier should be further lowered in a real system and the mechanism is more feasible than carbene formation mechanism. According to our calculations, both the steps of Scheme III are exothermic processes with energy releases of 177 kJ/mol and 186 kJ/mol for first and second step respectively (Figure S5 and S6 in Supporting Information), which can provide the energy to overcome the reaction barrier. The surrounding solvent molecules help to stabilize the resulting structure in first step, and remove hydrogen atom from the structure in second step.

Stabilization After Carboxylation

A careful review of reported experimental results brings up one interesting question. It is well known that in many RTILs, the nature of anion plays a central role for solubility of CO_2 via physical interactions between anions and CO_2,[1,2] and there is every reason to expect CO_2 to interact with the acetate ion in imidazolium acetate-based RTILs. Molecular dynamics simulations[36] predicted the existence of CO_2-acetate complexes, and the binding energy be-

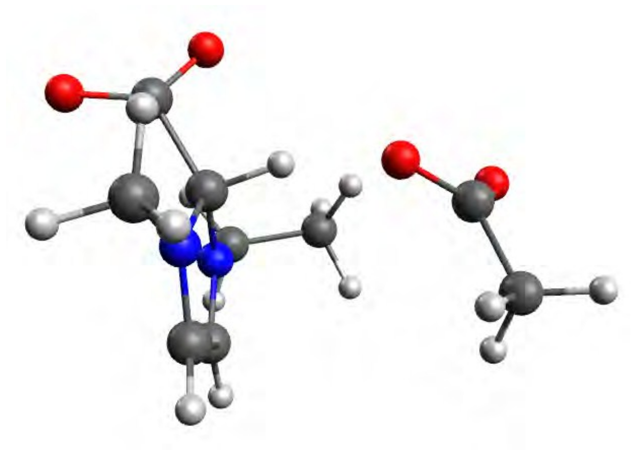


Figure 3: Intermediate structure in our proposed mechanism (Figure 4). It is not stable in gas phase, but stable in solvated model. The surrounding solvent molecules are not shown for clarity.

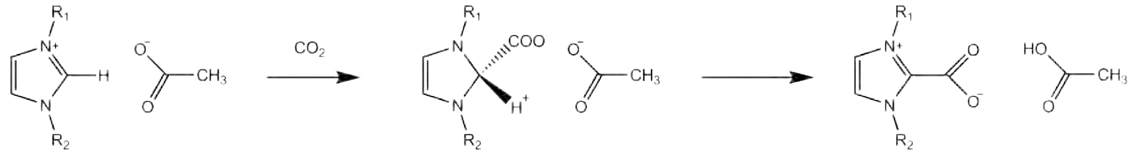


Figure 4: A new possible reaction mechanism scheme (Scheme III) for the carboxylation of imidazolium acetate by CO_2.

tween CO_2 and the acetate ion were estimated to be -44 kJ/mol by ab initio calculations.[36,37] Thus it is worth investigating whether competition between the anion (physisorption) and the cation (chemisorption) plays a role in CO_2 capture in imidazolium acetate ILs.

Ab initio calculations reveal that the CO_2 is near-linear in the lowest-energy acetate-CO_2 complex.[37] (However, CO_2 that has formed a carboxylate with the cation is, of course, highly distorted from linearity.) A characteristic feature of linear CO_2 in Raman spectra is the presence of Fermi dyad peaks, which have been observed with diluted CO_2 in many organic and ionic liquids.[38,39] The presence of uncomplexed or weakly-complexed linear or near-linear CO_2, therefore, should be accompanied by the observation of the Fermi dyad signature. Interestingly, for CO_2 in imidazolium acetate-based RTILs, the Fermi dyad signature is not initially observed and can only be observed after the mole fraction of CO_2 reaches about 1/3.[7] This observation can be explained if we assume that while the CO_2 is diluted, all the CO_2 reacts to form a carboxylate (and becomes non-linear). After the 2:1 IL:CO_2 stoichiometry has been reached, additional CO_2 molecules remain uncomplexed or form weak complexes with the anion, and the Fermi dyad is observed. So the interesting question is why the carboxylation reaction appears to occur with a 2:1 IL:(CO2) ratio while reaction mechanism suggests one CO_2 requires only one IL molecule to form the carboxylate.

We were inspired by the reported crystal structure of the solid products from the CO_2-$EMIM^+Ac^-$ reaction.[5] The crystal structure shows that the products of the carboxylation step, which are carboxylate and acetic acid, interact with a cation and an anion of the ionic liquid respectively to form a large complex. The interactions between the fragments of this large complex could provide sufficient stabilization to stop the chemisorption process. To investigate these interactions, we optimized similar complexes for the five ILs studied in this work. Each complex contains an imidazolium cation, an acetate anion, a carboxylate and an acetic acid. The optimized minimum energy structure for the complex formed by $EMIM^+Ac^-$ is shown in Figure 5 as an example. Significant interactions between different fragments of the complex are listed in Table 4.

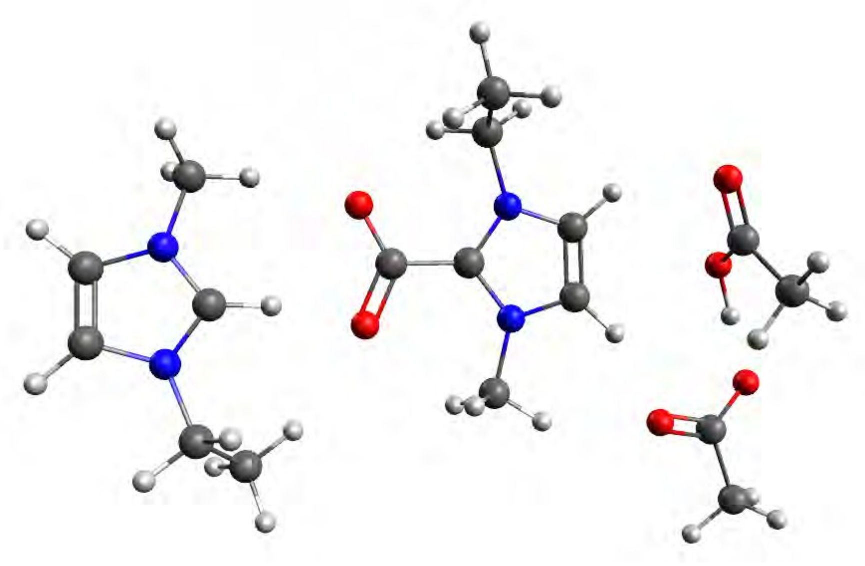


Figure 5: A complex containing an EMIM$^+$ cation, an imidazolium-2-carboxylate, an acetate anion, and an acetic acid molecule optimized at the PBE0/cc-pVTZ level.

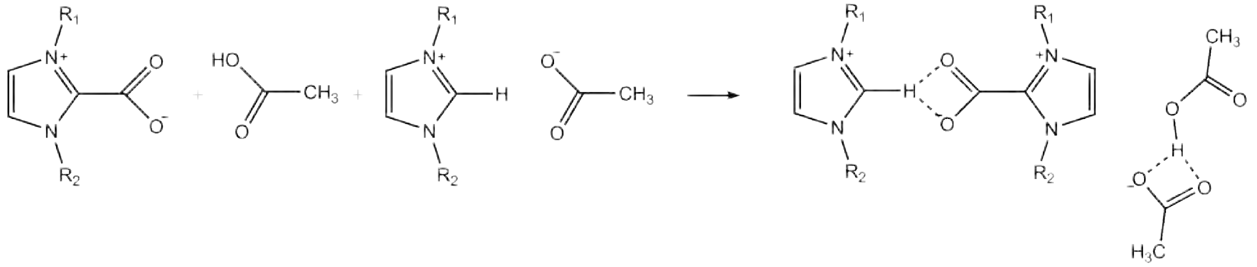


Figure 6: Stabilization of the carboxylation reaction products by an imidazolium-acetate ion pair

Table 4: Interactions between different fragments in imidazolium acetate stabilization step [a,b,c]

Ionic liquids	Interactions		
	E_{int}	Cation$^+ \cdots$ Carboxylate	Ac$^- \cdots$ HAc
DMIM $^+$ Ac $^-$	-623.5	-141.2	-180.9
EMIM $^+$ Ac $^-$	-614.6	-137.1	-178.7
PMIM $^+$ Ac $^-$	-610.6	-135.2	-177.9
BMIM $^+$ Ac $^-$	-611.0	-134.4	-179.5
EEIM $^+$ Ac $^-$	-605.8	-132.0	-178.7

[a] Energy in unit of kJ/mol. [b] BSSE correction is considered. [c] Calculated at PBE0/cc-pVTZ level.

As shown in Figure 6, the stabilization step involves the establishment of two strong interactions. One is an interaction between the carboxylate and a cation and the other is an interaction between the acetic acid and the acetate anion. These interacting pairs are arranged to form a large complex. The interaction energy (E_{int}), therefore may be calculated as energy gained from the formation of the complex:

$$E_{\mathrm{int}} = E_{\mathrm{complex}} - (E_{\mathrm{carbox}} + E_{\mathrm{HAc}} + E_{\mathrm{EMIM^+}} + E_{\mathrm{Ac^-}})$$

where E_{complex}, E_{carbox}, E_{HAc}, $E_{\mathrm{EMIM^+}}$, and $E_{\mathrm{Ac^-}}$ are the total energies of the complex, the carboxylate, acetic acid, the EMIM$^+$ cation, and the acetate anion respectively.

To form the complex, each CO_2 molecule requires an ion pair to react with and another ion pair to stabilize the products. Once the mole fraction of CO_2 reaches 1/3, no more free ion pairs are available to stabilize the carboxylation products and the chemisorption stops, which is in accordance with the reported experimental results.[7] Therefore, with the stabilization energy gained in this step, it can be the key to control the whole process of the chemisorption reaction.

Summary

In this work, we investigated the CO_2 capture mechanism of 1,3 di-alkyl imidazolium acetate based ionic liquids using DFT and ONIOM calculations. The two existing mechanisms were investigated and compared in both gas phase and solvated phase. A new two-step reaction mechanism that overcomes the limitations of the reported mechanisms was proposed. We also demonstrated qualitatively that the stabilization step can account for important, experimentally-observed features of the reaction of CO_2 with cations in imidazolium-based ILs. However, although these calculations provide extremely valuable insight into the mechanism of CO_2 absorption, there are questions that still remain. From our calculated data it is difficult to rationalize certain experimental observations, for example the state of the final complex (for $EMIM^+Ac^-$ it is solid, while for $BMIM^+Ac^-$ and $EEIM^+Ac^-$ it is liquid) or the reversibility of CO_2 capture (reported as reversible for $EEIM^+Ac^-$ and irreversible for $BMIM^+Ac^-$).[5,6,9] While we have carried out these calculations on a series of ILs, (see tables 1, 2, 4), our results do not clarify the underlying differences in the reaction of CO_2 with this series of ILs. We believe the stabilization step needs a further study, probably via molecular dynamics simulations, to consider larger influence of bulk system, and the study could provide a full understanding of the experimental observations. Any further study aiming at tuning the reaction rate or assessing the reversibility of the reaction of CO_2 with imidazolium acetate-based ILs should include the proposed new mechanism and a description of the stabilization step described herein.

Acknowledgement

This technical effort was performed in support of the National Energy Technology Laboratory's ongoing research in CO_2 Capture under the RES contract DE-FE0004000. The authors would like to thank Dr. Nilesh Dhumal for his valuable advices and help throughout the research.

Supporting Information Available

Table of optimized geometries in the form of Gaussian archive entries. This material is available free of charge via the Internet at `http://pubs.acs.org/`.

Notes and References

(1) Cadena, C.; Anthony, J. L.; Shah, J. K.; Morrow, T. I.; Brennecke, J. F.; Maginn, E. J. Why Is CO2 So Soluble in Imidazolium-Based Ionic Liquids? *Journal of the American Chemical Society* **2004**, *126*, 5300–5308.

(2) Bhargava, B.; Balasubramanian, S. Probing anioncarbon dioxide interactions in room temperature ionic liquids: Gas phase cluster calculations. *Chemical Physics Letters* **2007**, *444*, 242–246.

(3) Maginn, E. J. Design and evaluation of Ionic liquids as novel CO_2 absorbents. *Quarterly Technical Report to DOE, January-March* **2005**,

(4) Shiflett, M. B.; Kasprzak, D. J.; Junk, C. P.; Yokozeki, A. Phase behavior of carbon dioxide + [bmim][Ac] mixtures. *Journal of Chemical Thermodynamics* **2008**, *40*, 25–31.

(5) Gurau, G.; Rodríguez, H.; Kelley, S. P.; Janiczek, P.; Kalb, R. S.; Rogers, R. D. Demonstration of Chemisorption of Carbon Dioxide in 1,3-Dialkylimidazolium Acetate Ionic Liquids. *Angewandte Chemie, International Edition* **2011**, *50*, 12024–12026.

(6) Besnard, M.; Cabaço, M. I.; Chávez, F. V.; Pinaud, N.; ao, P. J. S.; ao A. P. Coutinho, J.; Danten, Y. On the spontaneous carboxylation of 1-butyl-3-methylimidazolium acetate by carbon dioxide. *Chemical Communications* **2012**, *48*, 1245–1247.

(7) Cabao, M. I.; Besnard, M.; Danten, Y.; Coutinho, J. A. P. Carbon Dioxide in 1-Butyl-3-methylimidazolium Acetate. I. Unusual Solubility Investigated by Raman Spectroscopy and DFT Calculations. *Journal of Physical Chemistry A* **2012**, *116*, 1605–1620.

(8) Besnard, M.; Cabaço, M. I.; Fabián Vaca Chávez, N. P.; ao, P. J. S.; ao A. P. Coutinho, J.; Mascetti, J.; Danten, Y. CO2 in 1-Butyl-3-methylimidazolium Acetate. 2. NMR Investigation of Chemical Reactions. *Journal of Physical Chemistry A* **2012**, *116*, 4890–4901.

(9) Shiflett, M. B.; Elliott, B. A.; Lustig, S. R.; Sabesan, S.; Kelkar, M. S.; Yokozeki, A. Phase Behavior of CO2 in Room-Temperature Ionic Liquid 1-Ethyl-3-Ethylimidazolium Acetate. *ChemPhysChem* **2012**, *13*, 1806–1817.

(10) Gaussian 09, Revision A.1, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2009.

(11) Alex A. Granovsky, Firefly version 8.0.0, www http://classic.chem.msu.su/gran/firefly/index.html.

(12) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Physical Review Letters* **1996**, *77*, 3865–3868.

(13) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Physical Review Letters* **1997**, *78*, 1396–1396.

(14) Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *The Journal of Chemical Physics* **1999**, *110*, 6158–6170.

(15) Thom H. Dunning, J. Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen. *Journal of Chemical Physics* **1989**, *90*, 1007–1023.

(16) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy

formula into a functional of the electron density. *Physical Review B: Condensed Matter and Materials Physics* **1988**, *37*, 785–789.

(17) Becke, A. D. Density-functional thermochemistry. III. The role of exact exchange. *Journal of Chemical Physics* **1993**, *98*, 5648–5652.

(18) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *Journal of Chemical Physics* **2010**, *132*, 154104.

(19) Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self-Consistent Molecular-Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *Journal of Chemical Physics* **1972**, *56*, 2257–2261.

(20) Hariharan, P. C.; Pople, J. A. The influence of polarization functions on molecular orbital hydrogenation energies. *Theoretical Chemistry Accounts* **1973**, *28*, 213–222.

(21) Jansen, H. B.; Ros, P. Non-empirical molecular orbital calculations on the protonation of carbon monoxide. *Chemical Physics Letters* **1969**, *3*, 140–143.

(22) Boys, S. F.; Bernardi, F. The Calculation of Small Molecular Interactions by the Differences of Separate Total Energies. Some Procedures with Reduced Errors. *Mol. Phys.* **1970**, *19*, 553–566.

(23) Szczesniak, M. M.; Scheiner, S. Correction of the Basis Set Superposition Error in SCF and MP2 Interaction Energies. The Water Dimer. *J. Chem. Phys.* **1986**, *84*, 6328–6335.

(24) Berk Hess, D. v. d. S., Carsten Kutzner; Lindahl, E. GROMACS 4: Algorithms for Highly Efficient, Load-Balanced, and Scalable Molecular Simulation. *Journal of Chemical Theory and Computation* **2008**, *4*, 435–447.

(25) Nosé, S. A molecular dynamics method for simulations in the canonical ensemble. *Molecular Physics* **1984**, *52*, 255–268.

(26) Hoover, W. G. Canonical dynamics: Equilibrium phase-space distributions. *Physical Review A: Atomic, Molecular, and Optical Physics* **1985**, *31*, 1695–1697.

(27) Parrinello, M.; Rahman, A. Polymorphic transitions in single crystals: A new molecular dynamics method. *Journal of Applied Physics* **1981**, *52*, 7182–7190.

(28) José N Canongia Lopes, J. D.; Pádua, A. A. Modeling ionic liquids using a systematic all-atom force field. *Journal of Physical Chemistry B* **2004**, *108*, 2038–2047.

(29) Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids. *Journal of the American Chemical Society* **1996**, *118*, 11225–11236.

(30) Kumelan, J.; Kamps, A. P.-S.; Tuma, D.; Maurer, G. Solubility of H-2 in the ionic liquid [hmim][Tf2N]. *Journal of Chemical and Engineering Data* **2006**, *51*, 1364–1367.

(31) Svensson, M.; Humbel, S.; Froese, R. D. J.; Matsubara, T.; Sieber, S.; Morokuma, K. ONIOM: A Multilayered Integrated MO + MM Method for Geometry Optimizations and Single Point Energy Predictions. A Test for DielsAlder Reactions and Pt(P(t-Bu)3)2 + H2 Oxidative Addition. *Journal of Physical Chemistry* **1996**, *100*, 19357–19363.

(32) Kelemen, Z.; Hollóczki, O.; Nagyc, J.; Nyulászi, L. An organocatalytic ionic liquid. *Organic and Biomolecular Chemistry* **2011**, *9*, 5362–5364.

(33) Rodríguez, H.; Gurau, G.; Holbrey, J. D.; Rogers, R. D. Reaction of elemental chalcogens with imidazolium acetates to yield imidazole-2-chalcogenones: direct evidence for ionic liquids as proto-carbenes. *Chemical Communications* **2011**, *47*, 3222–3224.

(34) Brehm, M.; Weber, H.; Pensado, A. S.; Stark, A.; Kirchner, B. Proton transfer and polarity changes in ionic liquidwater mixtures: a perspective on hydrogen bonds from ab

initio molecular dynamics at the example of 1-ethyl-3-methylimidazolium acetatewater mixturesPart 1. *Physical Chemistry Chemical Physics* **2012**, *14*, 5303–5044.

(35) Hollóczki, O.; Firaha, D. S.; Friedrich, J.; Brehm, M.; Cybik, R.; Wild, M.; Stark, A.; Kirchner, B. Carbene Formation in Ionic Liquids: Spontaneous, Induced, or Prohibited? *Journal of Physical Chemistry B* **2013**, *117*, 5898–5907.

(36) Shi, W.; Myers, C. R.; Luebke, D. R.; Steckel, J. A.; Sorescu, D. C. Theoretical and Experimental Studies of CO2 and H2 Separation Using the 1-Ethyl-3-methylimidazolium Acetate ([emim][CH3COO]) Ionic Liquid. *Journal of Physical Chemistry B* **2012**, *116*, 283–295.

(37) Steckel, J. A. Ab Initio Calculations of the Interaction between CO2 and the Acetate Ion. *Journal of Physical Chemistry A* **2012**, *116*, 11643–11650.

(38) Besnard, M.; Cabao, M. I.; Talaga, D.; Danten, Y. Raman spectroscopy and ab initio investigations of transient complex formation in CO2-benzene mixtures. *Journal of Chemical Physics* **2008**, *129*, 224511.

(39) Cabaço, M. I.; Besnard, M.; Danten, Y.; Coutinho, J. A. P. Solubility of CO2 in 1-Butyl-3-methyl-imidazolium-trifluoro Acetate Ionic Liquid Studied by Raman Spectroscopy and DFT Investigations. *Journal of Physical Chemistry B* **2011**, *115*, 3538–3550.

Graphical TOC Entry