Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


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

# Supporting Information

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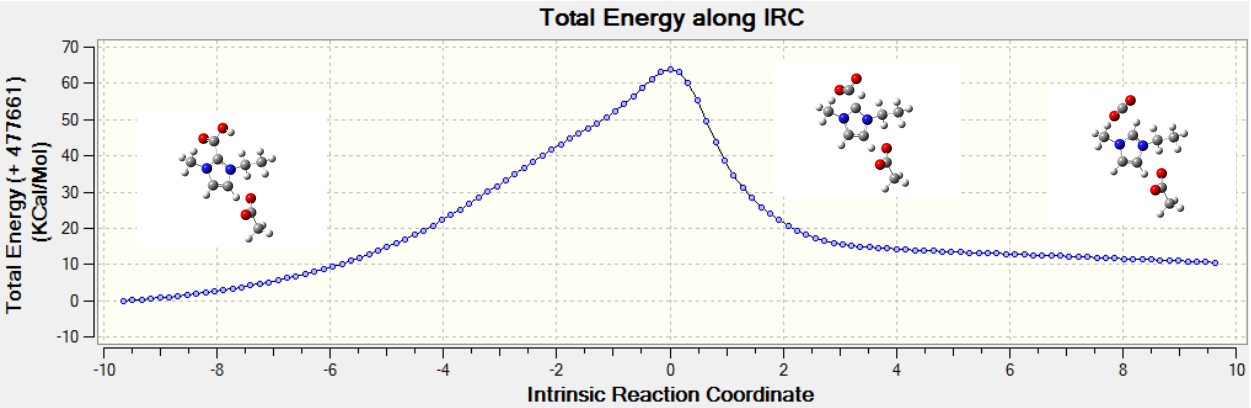



Figure S1: Energy profile for a possible direct reaction between $EMIM^+Ac^-$ IL and $CO_2$. The energy barrier is about 267 kJ/mol.

Table S1: Calculated energies [a] for species involved in carbene formation and carboxylate steps in Figure S2 at different calculation levels.

| Species | Relative Energies | | |
|---|---|---|---|
| | B3LYP/6-31+G(d,p) | PBE0/cc-PVTZ | PCM[b] |
| I + $CO_2$ | 0 | 0 | 0 |
| TS-I + $CO_2$ | 7.9 | 1.9 | 34.4 |
| II + $CO_2$ | 4.5 | -3.3 | 40.3 |
| III + HAc | 53.7 | 47.2 | 84.5 |
| TS-II + HAc | 60.4 | 54.8 | 91 |
| IV + HAc | 18.5 | 10.9 | 11.5 |

[a] Energies in unit of kJ/mol. [b] With a dielectric constant of 30.

Table S2: Interactions between different fragments in imidazolium acetate stabilization step, $E_{c-a}$ interactions between cation and anion of imidazolium acetate ILs, and $E_{stab}$ the energy gained from stabilization step at B3LYP/6-31+G(d,p) level. [a,b]

| Ionic liquids | Interactions | | | $E_{c-a}$ | $E_{stab}$ |
|---|---|---|---|---|---|
| | $E_{int}$ | $EMIM^+ \cdots$ Carboxylate | $Ac^- \cdots HAc$ | | |
| DMIM $^+$ Ac $^-$ | -605.8 | -137.8 | -174.9 | -431.9 | -173.9 |
| EMIM $^+$ Ac $^-$ | -598.6 | -134.0 | -173.8 | -426.4 | -172.2 |
| PMIM $^+$ Ac $^-$ | -595.0 | -132.0 | -173.7 | -423.9 | -171.1 |
| BMIM $^+$ Ac $^-$ | -592.6 | -131.4 | -172.8 | -422.3 | -170.3 |
| EEIM $^+$ Ac $^-$ | -589.7 | -128.9 | -174.1 | -420.7 | -169.0 |

[a] Energy in unit of kJ/mol. [b] BSSE correction is considered.

Table S3: Interactions between different fragments in imidazolium acetate stabilization step, $E_{c-a}$ interactions between cation and anion of imidazolium acetate ILs, and $E_{stab}$ the energy gained from stabilization step at B3LYP-D3/6-31+G(d,p) level. [a,b]

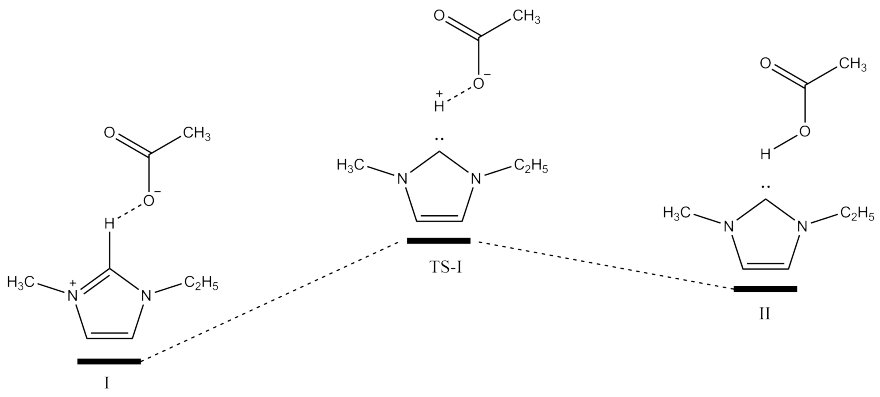
| Ionic liquids | Interactions | | | $E_{c-a}$ | $E_{stab}$ |
|---|---|---|---|---|---|
| | $E_{int}$ | $EMIM^+ \cdots$ Carboxylate | $Ac^- \cdots HAc$ | | |
| DMIM $^+$ Ac $^-$ | -643.2 | -152.0 | -177.7 | -445.1 | -198.1 |
| EMIM $^+$ Ac $^-$ | -624.7 | -150.4 | -173.1 | -440.1 | -184.6 |
| PMIM $^+$ Ac $^-$ | -622.7 | -149.2 | -173.0 | -438.0 | -184.7 |
| BMIM $^+$ Ac $^-$ | -629.2 | -150.0 | -176.3 | -436.6 | -192.6 |
| EEIM $^+$ Ac $^-$ | -620.8 | -147.2 | -173.0 | -435.4 | -185.4 |

[a] Energy in unit of kJ/mol. [b] BSSE correction is considered.

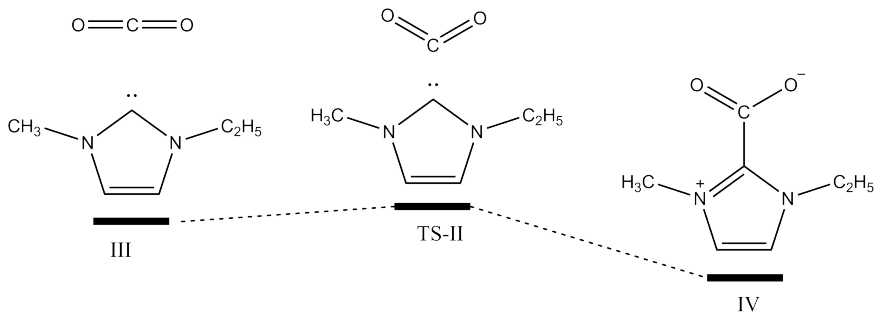
Table S4: Calculated reaction energy changes [a] for $Emim^+Ac^- \rightarrow$ Carbene+HAc in solvated model by ONIOM and QM methods.

| ONIOM and | Energy Change | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| QM Methods | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | Average |
| PBE0/cc-pVTZ:UFF | -11.9 | -5.1 | 0.2 | -0.8 | 0.5 | -0.3 | -0.1 | -1 | 2.3 |
| PBE0/cc-pVTZ:$UFF_E$ [b] | -14.9 | -6.0 | 5.9 | -11.5 | -14.5 | -4.0 | -11.9 | -11 | -8.5 |
| PBE0/cc-pVTZ:Dreiding | -9.5 | -4.6 | 2.2 | -1.3 | 0.4 | 1.4 | -0.4 | -1.5 | -1.7 |
| PBE0/cc-pVTZ:$Dreiding_E$ [b] | -12.5 | -5.5 | 7.9 | -12.0 | -14.6 | -2.3 | -12.2 | -11.5 | -7.8 |
| PBE0/cc-pVTZ:RHF/STO-3G | 112.5 | 71.2 | 67.3 | 12.3 | 27.5 | 6.1 | 28.3 | 8.9 | 41.8 |
| PBE0/cc-pVTZ:RHF/3-21G | 91.6 | 56.0 | 57.2 | 9.8 | 12.8 | 6.1 | 19.9 | 8.2 | 32.7 |
| PBE0/6-31+G(d,p) | 78.4 | 53.5 | 57.1 | 12.3 | 19.4 | 4.3 | 21.8 | 10.2 | 32.1 |

[a] Energy in unit of kJ/mol. [b] Subscript E donates electronic embedding.




(a) carbene formation step




(b) carboxylate step

Figure S2: Reaction profile of carbene formation and carboxylate for $EMIM^{+}Ac^{-}$. Detailed data are listed in Table S1.

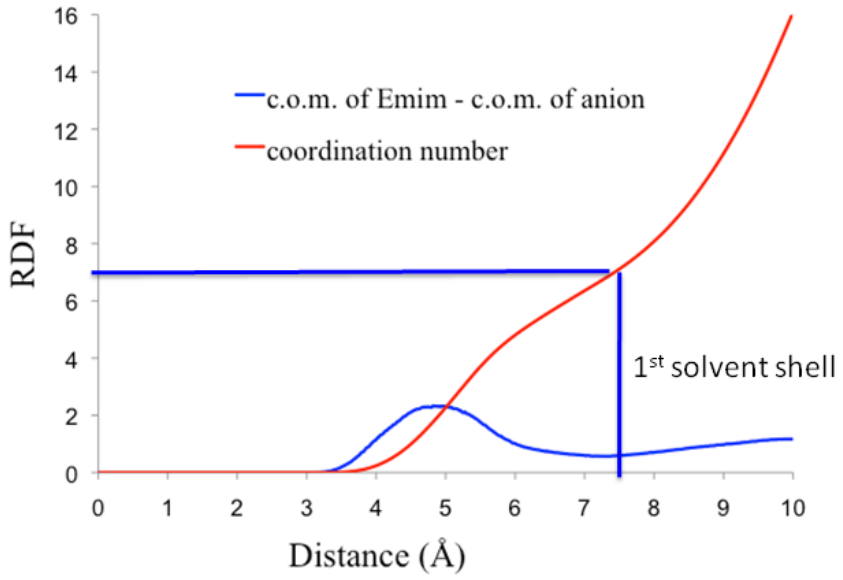



Figure S3: Radial distribution function (blue line) and integrated coordination number (red line) with respect to the center of mass (c.o.m.) of $EMIM^+$ cation and the center of mass (c.o.m.) of $Ac^-$ anion. The first solvent shell is at a distance of $\sim 7.5$Å, with a coordination number of 7.

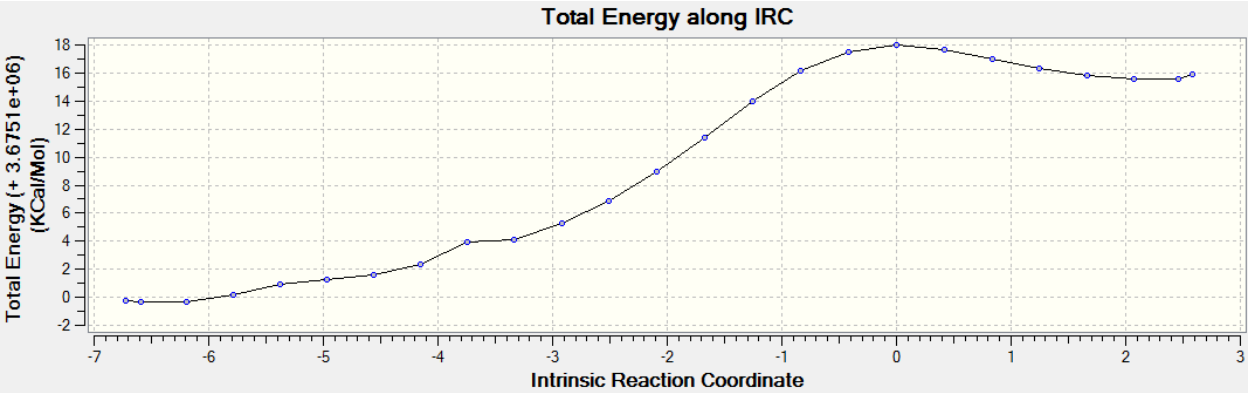



Figure S4: Energy profile for direct reaction between $EMIM^+Ac^-$ IL and $CO_2$ in solvated model. The energy barrier is about 96.6 kJ/mol.

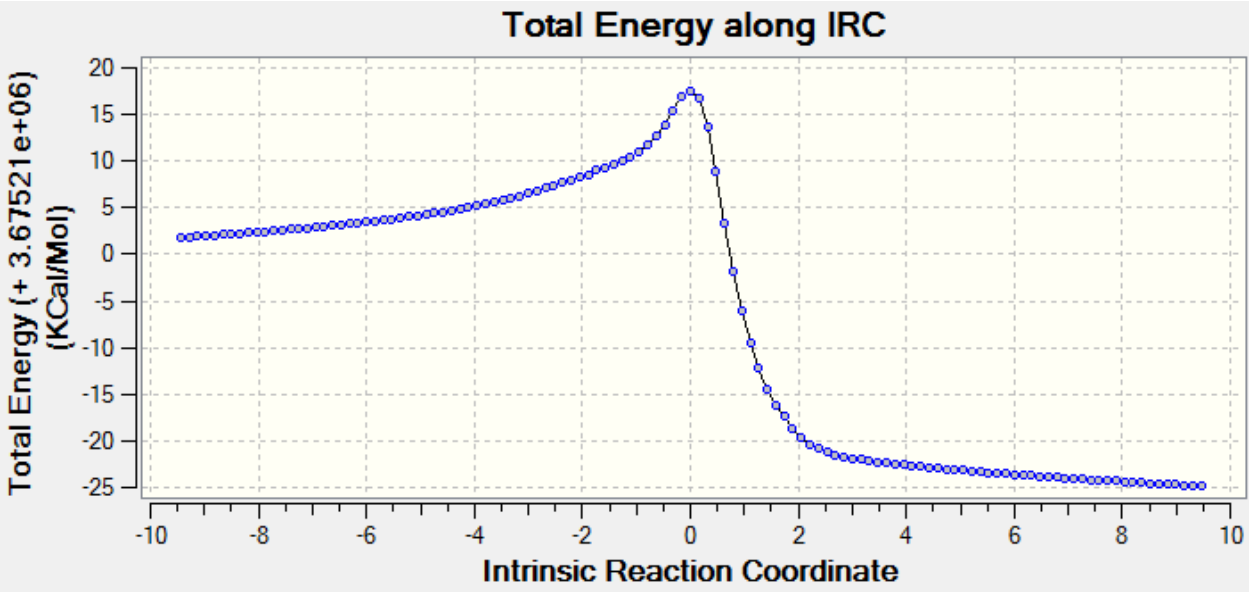



Figure S5: Energy profile for the first step of our proposed mechanism between $EMIM^+Ac^-$ IL and $CO_2$ in solvated model. The energy barrier is about 66.1 kJ/mol.

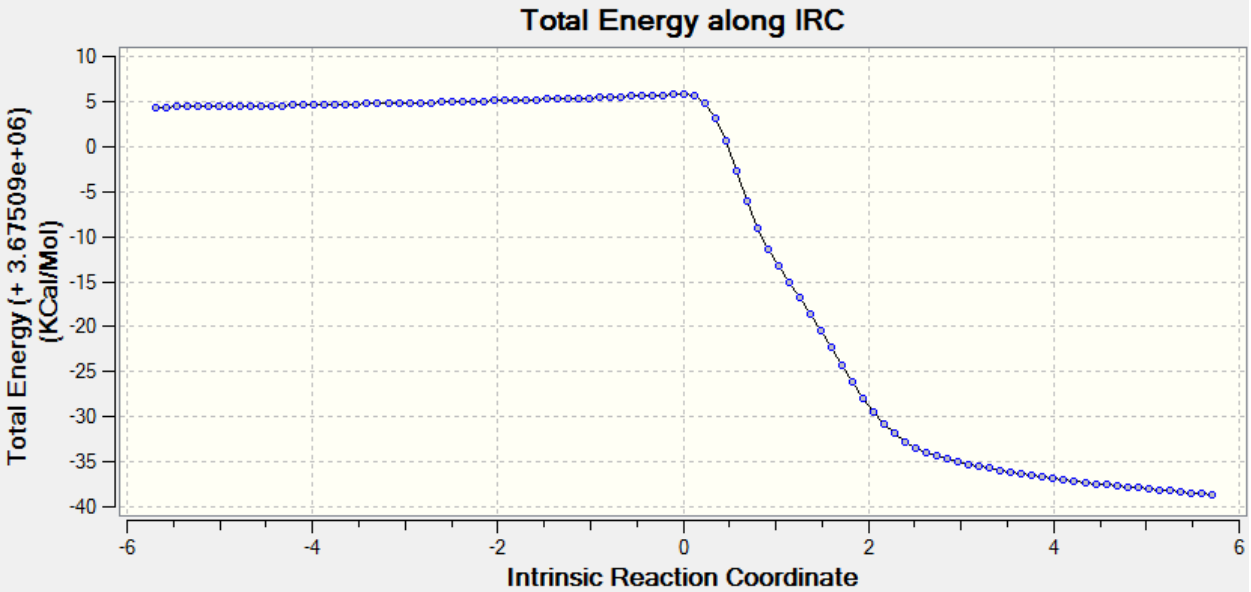



Figure S6: Energy profile for the second step of our proposed mechanism between $EMIM^+Ac^-$ IL and $CO_2$ in solvated model. The energy barrier is about 6.0 kJ/mol.