## Supporting Information

## $\mathrm{CO}_{2}$ capture in ionic liquid 1-alkyl-3-methylimidazolium acetate: A concerted mechanism without carbene

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## S1 Supplementary tables

Table S1. IP and IP/CO ${ }_{2}$ mixture densities ${ }^{\text {a }}$

| IP and $\mathrm{IP} / \mathrm{CO}_{2}$ mixture | Density $\left(\mathrm{g} / \mathrm{cm}^{3}\right)$ |
| :---: | :---: |
| 8 IP | 1.080 |
| $8 \mathrm{IP}+1 \mathrm{CO}_{2}$ | 1.115 |
| $8 \mathrm{IP}+2 \mathrm{CO}_{2}$ | 1.100 |
| $8 \mathrm{IP}+16 \mathrm{CO}_{2}$ | 1.133 |
| $12 \mathrm{IP}+6 \mathrm{CO}_{2}$ | 1.019 |
| $2 \mathrm{IP}+40 \mathrm{CO}_{2}$ | 1.006 |

${ }^{\text {a) }}$ All system densities are obtained by classical MD simulations in the NPT ensemble at 298 K and 1 bar. For ab initio MD simulations in the $N V T$ ensemble at 298 K , classical MD configurations whose densities are arbitrarily close to the average densities of the $N P T$ ensemble are used as starting structures.

Table S2. Energy barrier $E_{a}$ along the C2-Cc coordinate and activation free energy ${ }^{\text {a) }}$

| System | $E_{a}{ }^{\text {b) }}$ | Activation free energy ${ }^{\text {b }}$ |
| :---: | :---: | :---: |
| $2 \mathrm{IP}+40 \mathrm{CO}_{2}$ | $\sim 12.5$ | $\sim 8-9$ |

${ }^{\text {a) }}$ Energy units: kcal/mol.
${ }^{\text {b) }}$ Obtained by integrating the mean force (Fig. S5) from $2.4 \AA$ A to $3.9 \AA$
${ }^{\text {c) }}$ Determined as the difference of $E_{a}$ and the zero-point energy of C2-H2 stretching vibration of EMI ${ }^{+}$.

## S2 Classical molecular dynamics simulations for IP and IP/CO2 mixture.

The pure IL and the $256 \mathrm{IP}+64 \mathrm{CO}_{2}$ mixture were annealed from 600 K to 298 K in steps of 50 K in the $N P T$ ensemble at 1 bar, while the $256 \mathrm{IP}+512 \mathrm{CO}_{2}$ mixture was annealed from 400 K . At each annealing step, the systems were annealed for 4 ns and equilibrated for another 4 ns . At 298 K , the systems were equilibrated for 6 ns , followed by a 6 ns production run, from which radial distribution functions (RDFs) were calculated. Classical MD results thus obtained (Fig. S1) show a very good agreement with ab intio

MD results in Fig. 2, indicating that the latter are reliable despite their small system size and short simulation time.

## S3 $\quad \mathrm{CO}_{2}$ geometry and charge variations in the $\mathbf{1 2} \mathbf{I P}+\mathbf{6} \mathrm{CO}_{\mathbf{2}}$ system.

For the C2-Cc distance between $2.7 \AA$ to $4 \AA$, the average value of the Oc-Cc-Oc angle remains unchanged at $172^{\circ}-173^{\circ}$ with the maximum value of $180^{\circ}$ (Fig. S3). This indicates that $\mathrm{CO}_{2}$ mainly retains a linear geometry away from the cation. Nonetheless, the minimum value of the Oc-Cc-Oc angle reaches $156^{\circ}$, revealing that there is significant bending of $\mathrm{CO}_{2}$ in some cases. This is due to interactions of $\mathrm{CO}_{2}$ with Oa of $\mathrm{OAc}^{-}$. As $\mathrm{CO}_{2}$ approaches the C 2 site of $\mathrm{EMI}^{+}$ more closely, its geometry becomes progressively more bent. The electron density migration to $\mathrm{CO}_{2}$ and the resulting increase in $\mathrm{C} 2-\mathrm{Cc}$ interactions (cf. Fig. S2) are responsible for this geometry change. The $\mathrm{Oc}-\mathrm{Cc}-\mathrm{Oc}$ angle shows a rather abrupt change near the $\mathrm{C} 2-\mathrm{Cc}$ distance of $2.1 \AA$. This is caused by transfer of H 2 from the C 2 site of $\mathrm{EMI}^{+}$to one of the Oa sites of $\mathrm{OAc}^{-}$.

## S4 Constrained ab inito simulation results for the $2 \mathrm{IP}+40 \mathrm{CO}_{2}$ system.

As shown in Figs. S6 and S7, the 2:40 system composed of 2 IPs and $40 \mathrm{CO}_{2}$ molecules (corresponding to a dense $\mathrm{CO}_{2}$ environment) exhibits back proton transfer in contrast to the 12:6 system in Figs. 5 and S4. This is ascribed to the relatively large C2-Cc distance, which yields weak C2-Cc interactions when proton transfers. For example, the mean force between C 2 and Cc at $2.38 \AA$ subsequent to proton transfer is close to 0 (Fig. S5). This means that at this separation, the driving force to form a chemical bond between C 2 and Cc following proton transfer is on average not strong. Thus, when the constraint on the $\mathrm{C} 2-\mathrm{Cc}$ distance is removed after proton transfer, in some cases, $\mathrm{CO}_{2}$ approaches the C 2 site rapidly and forms a carboxylate compound but in other cases, $\mathrm{CO}_{2}$ moves away and proton transfers back to the C 2 site quickly. The energy cost for $\mathrm{CO}_{2}$ approach within $2.4 \AA$ of $\mathrm{EMI}^{+}$was found to be $\sim 12.5 \mathrm{kcal} / \mathrm{mol}$ (cf. Table S2 and Fig. S5).

## S5 Supplementary figures



Fig. S1 Classical MD results for radial distribution functions at 298 K . (a) Distributions of C2 (solid) and H 2 (dashed) of $\mathrm{EMI}^{+}$around Oa of $\mathrm{OAc}^{-}$. (b) Distributions of Cc, carbon atom of $\mathrm{CO}_{2}$, around C 2 (solid) of $\mathrm{EMI}^{+}$and Oa (dashed) of $\mathrm{OAc}^{-}$. The results for the $256 \mathrm{IP}+64 \mathrm{CO}_{2}$ and $256 \mathrm{IP}+512 \mathrm{CO}_{2}$ mixture systems are shown in blue and red, respectively, while those of neat IL (256 IPs) are displayed in black.


Fig. S2 $\mathrm{CO}_{2}$ charge variations with the $\mathrm{C} 2-\mathrm{H} 2$ distance (blue circles) and $\mathrm{Oc}-\mathrm{Cc}-\mathrm{Oc}$ angle (red squares) in the $12 \mathrm{IP}+6 \mathrm{CO}_{2}$ system at 298 K . The C2-Cc distance is fixed at $2.1 \AA$.


Fig. S3 Oc-Cc-Oc angle of $\mathrm{CO}_{2}$ at different $\mathrm{C} 2-\mathrm{Cc}$ distances in the $12 \mathrm{IP}+6 \mathrm{CO}_{2}$ system. The maximum and minimum values of the fluctuating $\mathrm{Oc}-\mathrm{Cc}-\mathrm{Oc}$ angle are shown in red circles and green triangles, respectively, while its average values are marked as black squares.


Fig. S4 Time evolution of $\mathrm{CO}_{2}-\mathrm{EMI}^{+}-\mathrm{OAc}^{-}$conformation with the $\mathrm{C} 2-\mathrm{Cc}$ distance fixed at $2.09 \AA$ in the $12: 6$ mixture: (a) C2-H2 (blue) and H2-Oa (black) distances; (b) average $\mathrm{Cc}-\mathrm{Oc}$ distance of $\mathrm{CO}_{2}$; (c) $\mathrm{Cc}-\mathrm{C} 2-\mathrm{N} 3$ (black), $\mathrm{Cc}-\mathrm{C} 2-\mathrm{Q}$ (blue) and $\mathrm{Oc}-\mathrm{Cc}-\mathrm{Oc}$ (red) angles. Q is the mid-point of N1 and N3 of imidazolium cations. (d) Time evolution of the $\mathrm{C} 2-\mathrm{Cc}$ (green) and average $\mathrm{Cc}-\mathrm{Oc}$ (red) distances with the constraint on the $\mathrm{C} 2-\mathrm{Cc}$ distance removed after $\mathrm{EMI}^{+}$-to- $\mathrm{OAc}^{-}$proton transfer. The arrow marks the point of the constraint removal.


Fig. S5 Mean force between C 2 of $\mathrm{EMI}^{+}$and Cc of $\mathrm{CO}_{2}$ in the $2 \mathrm{IP}+40 \mathrm{CO}_{2}$ system.


Fig. S6 Time evolution of $\mathrm{CO}_{2}-\mathrm{EMI}^{+}-\mathrm{OAc}^{-}$conformation with the $\mathrm{C} 2-\mathrm{Cc}$ distance fixed at $2.38 \AA$ in the 2:40 mixture: (a) $\mathrm{C} 2-\mathrm{H} 2$ (blue) and $\mathrm{H} 2-\mathrm{Oa}$ (black) distances; (b) average Cc-Oc distance of $\mathrm{CO}_{2}$; (c) $\mathrm{Cc}-\mathrm{C} 2-\mathrm{N} 3$ (black), $\mathrm{Cc}-\mathrm{C} 2-\mathrm{Q}$ (blue) and $\mathrm{Oc}-\mathrm{Cc}-\mathrm{Oc}$ (red) angles. Q is the mid-point of N 1 and N 3 of imidazolium cations. (d) Time evolution of the $\mathrm{C} 2-\mathrm{Cc}$ (green) and average $\mathrm{Cc}-\mathrm{Oc}$ (red) distances with the constraint on the $\mathrm{C} 2-\mathrm{Cc}$ distance removed after $\mathrm{EMI}^{+}$-to- $\mathrm{OAc}^{-}$proton transfer. The arrow marks the point of the constraint removal.


Fig. S7 Time evolution of $\mathrm{CO}_{2}-\mathrm{EMI}^{+}-\mathrm{OAc}^{-}$conformation with the $\mathrm{C} 2-\mathrm{Cc}$ distance fixed at $2.50 \AA$ in the 2:40 mixture: (a) $\mathrm{C} 2-\mathrm{H} 2$ (blue) and $\mathrm{H} 2-\mathrm{Oa}$ (black) distances; (b) average $\mathrm{Cc}-\mathrm{Oc}$ distance of $\mathrm{CO}_{2}$; (c) $\mathrm{Cc}-\mathrm{C} 2-\mathrm{N} 3$ (black), $\mathrm{Cc}-\mathrm{C} 2-\mathrm{Q}$ (blue) and $\mathrm{Oc}-\mathrm{Cc}-\mathrm{Oc}$ (red) angles. Q is the mid-point of N 1 and N 3 of imidazolium cations. (d) Time evolution of the $\mathrm{C} 2-\mathrm{Cc}$ (green) and average $\mathrm{Cc}-\mathrm{Oc}$ (red) distances with the constraint on the $\mathrm{C} 2-\mathrm{Cc}$ distance removed after $\mathrm{EMI}^{+}$-to- $\mathrm{OAc}^{-}$proton transfer. The arrow marks the point of the constraint removal.

