Supporting Information

CO₂ capture in ionic liquid 1-alkyl-3-methylimidazolium acetate: A concerted mechanism without carbene

Fangyong Yan,¹ Nilesh R. Dhumal,¹ Hyung J. Kim^{1,2}*

- 1. Department of Chemistry, Carnegie Mellon University, Pittsburgh, PA, USA.
- 2. School of Computational Sciences, Korea Institute for Advanced Study, Seoul 02455,

Korea

* Permanent address: Carnegie Mellon University. Email: hjkim@cmu.edu

Table of Contents

- S1 Supplementary tables
- S2 Classical molecular dynamics simulations for IP and IP/CO₂ mixture.
- S3 CO_2 geometry and charge variations in the 12 IP + 6 CO_2 system.
- S4 Constrained ab inito simulation results for the $2 \text{ IP} + 40 \text{ CO}_2$ system.
- S5 Supplementary figures.

S1 Supplementary tables

IP and IP/CO ₂ mixture	Density (g/cm^3)
8 IP	1.080
8 IP + 1 CO ₂	1.115
8 IP + 2 CO ₂	1.100
8 IP + 16 CO ₂	1.133
12 IP + 6 CO ₂	1.019
$2 \text{ IP} + 40 \text{ CO}_2$	1.006

Table S1. IP and IP/CO₂ mixture densities^{a)}

^{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 *NVT* ensemble at 298 K, classical MD configurations whose densities are arbitrarily close to the average densities of the *NPT* ensemble are used as starting structures.

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

System	$E_a^{(b)}$	Activation free energy ^{b)}
$2 \text{ IP} + 40 \text{ CO}_2$	~ 12.5	~ 8-9

^{a)} Energy units: kcal/mol.

^{b)} Obtained by integrating the mean force (Fig. S5) from 2.4 Å to 3.9 Å

^{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 IP + 64 CO₂ mixture were annealed from 600 K to 298 K in steps of 50 K in the *NPT* ensemble at 1 bar, while the 256 IP + 512 CO₂ 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 CO₂ geometry and charge variations in the 12 IP + 6 CO₂ system.

For the C2-Cc distance between 2.7 Å to 4 Å, the average value of the Oc-Cc-Oc angle remains unchanged at 172° - 173° with the maximum value of 180° (Fig. S3). This indicates that CO₂ mainly retains a linear geometry away from the cation. Nonetheless, the minimum value of the Oc-Cc-Oc angle reaches 156° , revealing that there is significant bending of CO₂ in some cases. This is due to interactions of CO₂ with Oa of OAc⁻. As CO₂ approaches the C2 site of EMI⁺ more closely, its geometry becomes progressively more bent. The electron density migration to CO₂ and the resulting increase in C2-Cc interactions (cf. Fig. S2) are responsible for this geometry change. The Oc-Cc-Oc angle shows a rather abrupt change near the C2-Cc distance of 2.1 Å. This is caused by transfer of H2 from the C2 site of EMI⁺ to one of the Oa sites of OAc⁻.

S4 Constrained ab inito simulation results for the 2 IP + 40 CO₂ system.

As shown in Figs. S6 and S7, the 2:40 system composed of 2 IPs and 40 CO₂ molecules (corresponding to a dense CO₂ 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 C2 and Cc at 2.38 Å 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 C2 and Cc following proton transfer is on average not strong. Thus, when the constraint on the C2-Cc distance is removed after proton transfer, in some cases, CO₂ approaches the C2 site rapidly and forms a carboxylate compound but in other cases, CO₂ moves away and proton transfers back to the C2 site quickly. The energy cost for CO₂ approach within 2.4 Å of EMI⁺ was found to be ~12.5 kcal/mol (cf. Table S2 and Fig. S5).



Fig. S1 Classical MD results for radial distribution functions at 298 K. (a) Distributions of C2 (solid) and H2 (dashed) of EMI^+ around Oa of OAc^- . (b) Distributions of Cc, carbon atom of CO₂, around C2 (solid) of EMI^+ and Oa (dashed) of OAc^- . The results for the 256 IP + 64 CO₂ and 256 IP + 512 CO₂ mixture systems are shown in blue and red, respectively, while those of neat IL (256 IPs) are displayed in black.



Fig. S2 CO₂ charge variations with the C2-H2 distance (blue circles) and Oc-Cc-Oc angle (red squares) in the 12 IP + 6 CO₂ system at 298 K. The C2-Cc distance is fixed at 2.1 Å.



Fig. S3 Oc-Cc-Oc angle of CO_2 at different C2-Cc distances in the 12 IP + 6 CO_2 system. The maximum and minimum values of the fluctuating Oc-Cc-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 CO_2 -EMI⁺-OAc⁻ conformation with the C2-Cc distance fixed at 2.09 Å in the 12:6 mixture: (a) C2-H2 (blue) and H2-Oa (black) distances; (b) average Cc-Oc distance of CO_2 ; (c) Cc-C2-N3 (black), Cc-C2-Q (blue) and Oc-Cc-Oc (red) angles. Q is the mid-point of N1 and N3 of imidazolium cations. (d) Time evolution of the C2-Cc (green) and average Cc-Oc (red) distances with the constraint on the C2-Cc distance removed after EMI⁺-to-OAc⁻ proton transfer. The arrow marks the point of the constraint removal.



Fig. S5 Mean force between C2 of EMI^+ and Cc of CO_2 in the 2 IP + 40 CO_2 system.



Fig. S6 Time evolution of CO_2 -EMI⁺-OAc⁻ conformation with the C2-Cc distance fixed at 2.38 Å in the 2:40 mixture: (a) C2-H2 (blue) and H2-Oa (black) distances; (b) average Cc-Oc distance of CO_2 ; (c) Cc-C2-N3 (black), Cc-C2-Q (blue) and Oc-Cc-Oc (red) angles. Q is the mid-point of N1 and N3 of imidazolium cations. (d) Time evolution of the C2-Cc (green) and average Cc-Oc (red) distances with the constraint on the C2-Cc distance removed after EMI⁺-to-OAc⁻ proton transfer. The arrow marks the point of the constraint removal.



Fig. S7 Time evolution of CO_2 -EMI⁺-OAc⁻ conformation with the C2-Cc distance fixed at 2.50 Å in the 2:40 mixture: (a) C2-H2 (blue) and H2-Oa (black) distances; (b) average Cc-Oc distance of CO_2 ; (c) Cc-C2-N3 (black), Cc-C2-Q (blue) and Oc-Cc-Oc (red) angles. Q is the mid-point of N1 and N3 of imidazolium cations. (d) Time evolution of the C2-Cc (green) and average Cc-Oc (red) distances with the constraint on the C2-Cc distance removed after EMI⁺-to-OAc⁻ proton transfer. The arrow marks the point of the constraint removal.