

A concerted mechanism without carbene formation for N-heterocyclic carbenes chemistry: case study of EMIM-AC capture CO₂

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Ionic liquids consisting for imidazolium-based cations and acetate anions, such as 1-ethyl-3-methylimidazolium acetate (EMIM-OAc), are known to interact with CO₂ and form carboxylate compounds. N-heterocyclic carbene (NHC) is widely believed to be responsible by directly reacting with CO₂. However, the detection of NHC in the imidazolium acetate ILs has been elusive. In this poster, we present ab initio molecular dynamics simulation results for potential of mean force (PMF) between CO₂ and cation in EMIM-OAc. Our results reveal that the CO₂-C2 interaction weakens the C2-H2 bond which is already weakened by hydrogen-bonded interaction between cation and anion (C2=acidic carbon of EMIM; H2=hydrogen bonded to C2). This facilitates proton transfer from cation to anion while capturing CO₂ simultaneously. It is found that rehybridization of C2 orbitals from sp³ to sp² plays a critical role. Our results suggest that the reaction proceeds in a concerted fashion without forming carbene. In this context, CO₂ capture by EMIM is more “S_N2-like” than “S_N1-like”. Broader implication of the mechanism we propose is briefly discussed.