

Bicarbonate anion catalyzed transformation of CO₂ to cyclic carbonates: A DFT corroborated study

정경선, Kuruppathparambil Roshan Roshith, 박대원†

부산대학교

(dwpark@pusan.ac.kr†)

The standalone catalytic potential of common organic bases such as imidazole, pyridine and dimethylaminopyridine (DMAP) for the solvent-free cycloaddition of CO₂ with epoxides yielding five-membered cyclic carbonates is reported here. Appreciable conversion of various epoxides with excellent selectivity towards the desired products was materialized in this metal/halide/hydrogen bond donors/solvent-free reaction. The presence of catalytic amounts of water was found significantly advantageous in this base catalyzed chemical fixation of CO₂ and the conversion almost got doubled or tripled under the same reaction conditions. A definitive mechanism for the activation of base catalysis was also proposed with the aid of ab initio calculations performed at the B3LYP/6-31G (d,p) level. Besides, a bicarbonate anion mediated catalytic cycle was also proposed utilizing computational calculations. The possible intermediates and transition states as well as the related energy constraints of the base alone and base-water catalyzed reactions were deduced and the activation energy obtained was found higher for the former (~30 kcal mol⁻¹) than for the latter (~12 kcal mol⁻¹), which rationalizes the experimental observation of the higher activity of the latter.