NEW MULTICOMPONENT CO_2 FIXATION REACTIONS BY USING PROPARGYLIC SUBSTRATES AND ALLYL HALIDES: FROM ALKYNE ACIDITY PREDICTION TO CATALYSIS

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The continued release of CO_2 through fossil fuel combustion has raised urgent concerns, prompting the need for innovative strategies for its capture and transformation. One promising strategy in sustainable chemistry is the direct utilization of CO_2 as a renewable carbon feedstock for the synthesis of value-added organic compounds.[1] However, its high thermodynamic stability and kinetic inertness pose significant challenges to its efficient chemical activation.

Among the most attractive transformations is the catalytic or mediated incorporation of CO_2 into propargylic substrates such as alcohols and amines to afford cyclic α-alkylidene carbonates or carbamates.[2] These structural motifs are prevalent in pharmaceuticals, polymers, chiral auxiliaries, and polar aprotic solvents. Moreover, combining CO_2 fixation with carbon–carbon bond-forming reactions enables streamlined access to structurally complex products that typically require multi-step synthetic sequences.[3]

In this presentation, we will discuss our recent progress in developing copper(I)-catalyzed or -mediated multicomponent carboxylative cross-coupling reactions involving propargylic amines or alcohols, allyl halides, and CO_2 to synthesize functionalized oxazolidinones and dioxolanones under mild conditions. Particular emphasis will be placed on the observed stereospecificity of the transformation, as well as the stereoelectronic influence of aryl substituents including both inductive and resonance on the reactivity of alkyne substrates. The proposed reaction mechanism, supported by both experimental and computational studies, will also be presented and critically evaluated.

In parallel, the acidity of terminal alkynes, critical for understanding reactivity in CO_2 activation was investigated. Through a comprehensive computational study, we assessed various acidity descriptors including proton transfer energies, hydrogen exchange barriers, and NMR parameters. Two strategies showed excellent agreement with experimental pK_a values: energy barriers for hydrogen exchange and acetylenic proton chemical shifts. These models were further applied to predict acidity in bioactive alkynes such as ethynylestradiol and ethynyluracil.

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