

Mechanisms of CO₂ activation and catalytic reduction

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The use of CO₂ as a C1 chemical feedstock for the fine chemical industry is interesting both economically and ecologically, as it is non-toxic, abundant and cheap. Nevertheless, transformations of CO₂ into value-added products is hampered by its high thermodynamic stability and its inertness toward reduction. In order to design new catalysts able to overcome this kinetic challenge, a profound understanding of the reaction mechanisms at play in CO₂ reduction is needed. Using novel N/Si⁺frustrated Lewis pairs (FLPs), the influence of CO₂ adducts and different hydroborane reducing agents on the reaction mechanism in the catalytic hydroboration of CO₂ were investigated, both by DFT calculations and experiments.

In a second step, the reaction mechanism of a novel reaction for the creation of C–C bonds from CO₂ and aromatic silanes for the formation of esters and polyesters was analyzed by DFT calculations. It was shown that CO₂ plays a double role in this transformation, acting both as a catalyst and C₁-building block. The fine understanding of this transformation led to the development of a novel approach for the synthesis of sulfones and sulfonamides. Starting from SO₂ and aromatic silanes/silylated amines, these products were obtained in a single step under metal-free conditions. Noteworthy, sulfones and sulfonamides are common motifs in organic chemistry and found in a variety of highly important drugs. Finally, we could extend this concept to aromatic halides as coupling partners, and were thus able to show for the first time that a sulfonylative Hiyama reaction is a possible approach to the synthesis of aromatic sulfones.