Hydrogenation of carbon dioxide with [CuI(dtbpf)]-like organocatalysts: A theoretical and computational insight

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Highlights

Computational approaches show the importance of the DBU base in the catalytic process for the activation of the H_2 bond.

Abstract

Despite advances in recycling, reuse, and conversion processes of CO_2 into high-value-added chemicals, significant challenges remain because the CO_2 molecule, under normal temperature and pressure conditions, is kinetically inert and thermodynamically stable. Therefore, the use of catalytic procedures, such as the application of organometallic complexes, offers more favorable energetic pathways and is useful for increasing its chemical reactivity. In this context, this work proposes a catalytic route for the hydrogenation reaction of CO_2 using the previously obtained organometallic complex [CuI(dtbpf)][1]. Computational modeling at the B3LYP-D3(BJ)/def2-SVP level of theory was performed to elucidate and characterize all stationary points present on the potential energy surface, enhancing the understanding of the kinetic and thermodynamic aspects of the process. The free energy profile in Figure 1(b) indicates that Step 1 and Step 2, which correspond to the activation of the H_2 bond, are the rate-determining steps in the catalytic cycle. Specifically, the starting complex $[Cu(dtbpf)]^+$ (1) forms the hydrogenated intermediate $[CuH_2(dtbpf)]^+$ (2), which subsequently leads to the activated species [CuH(dtbpf)] (4) through an energetically feasible process. Furthermore, supporting the mechanism proposed by the DFT calculations, complexes (4) and (6) were experimentally identified using spectroscopic methods.

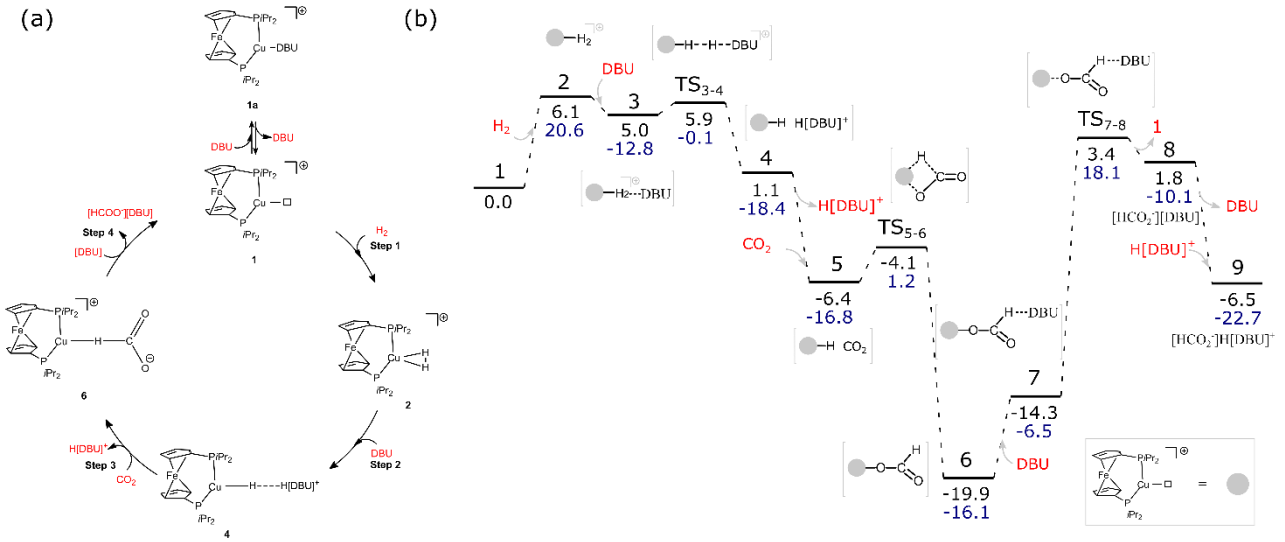

Figure 1. (a) Proposed mechanism for CO2 hydrogenation catalyzed by the $[Cu(dtbpf)]^+$ complex and (b) Free energy profile. Relative energies: ΔG (in black) and ΔH (in blue) at 298.15 K and 1 atm.

[1] Chaudhary K. *et al. Dalton. Trans.*, **49**, 2994 (2020).

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