Selective hydrogenation of C=O and C=N bonds in unsaturated compounds by means of Frustrated Lewis Pair systems

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Highlights

Activation of H_2 and selective hydrogenation of C=O and C=N bonds are achieved with Frustrated Lewis pair systems, suggesting new routes for the synthesis of value-added products.

Abstract

The activation of H_2 and the hydrogenation of multiple bonds mediated by Frustrated Lewis Pair (FLP) systems[1] based on 1,4-azaborine frameworks containing aminoborane centers were investigated through Density Functional Theory (DFT) calculations. Reactivity is assessed toward a series of unsaturated compounds, including formaldehyde, acetaldehyde, methanimine, butenone, furfural, and ethene. The calculations were performed with Gaussian 16[2] in the gas phase at room temperature and under standard conditions, by using the M06-2X functional[3] and the def2-TZVP basis set.[4] The analysis of the thermodynamic and kinetic profiles provides valuable theoretical insights into FLP-mediated hydrogenation mechanisms and the development of efficient catalytic pathways. After the initial H_2 activation steps, a concerted mechanism involving hydrogen transfer to the unsaturated moiety takes place: the protic hydrogen ($H^{\delta+}$) migrates to the nucleophilic (N) center, followed by the transfer of the hydridic hydrogen ($H^{\delta-}$) to the electrophilic (B) center. The electronic effect of NO_2 substitution was explored by replacing a hydrogen atom bound to the carbon adjacent to boron in the catalyst. This group increases the acidity and electronegativity of the boron center, thereby promoting H_2 polarization and lowering the activation barrier for activation, as evidenced by Gibbs energies. Thus, strategic electronic modifications of FLPs can enhance H_2 activation and improve hydrogenation-based technology efficiency. In more details, compared to the reference system (FLP-0), the introduction of a nitro substituent leads to a significant reduction of the activation barrier for H_2 activation, especially in the “b” position (FLP-1b), with a decrease of approximately (7–8 kcal·mol^{-1}). This effect arises from electronic stabilization of the transition state for H–H bond cleavage, rendering the reaction not only faster but also thermodynamically more favorable. Thus, for polar substrates containing C=O and C=N bonds, H_2 activation constitutes the rate-determining step, since the barriers for hydrogen transfer (16.9–21.9 kcal·mol^{-1}) are lower than those for H–H cleavage (27.7 kcal·mol^{-1}). In contrast, for typical C=C substrates, the hydrogen transfer step exhibits a much higher barrier (42.7 kcal·mol^{-1}), turning the reaction unfeasible under the conditions investigated here. These results reveal an intrinsic selectivity pattern, favoring the hydrogenation of polar bonds over nonpolar ones. Therefore, positional modifications with electron-withdrawing substituents near the acidic FLP center can be exploited as a rational catalytic strategy, simultaneously tuning kinetic and thermodynamic aspects and ultimately providing control over reactivity and selectivity. These findings highlight the potential of FLPs in metal-free hydrogenation processes.[5]

References

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