10º SIMPÓSIO DE ESTRUTURA ELETRÔNICA & DINÂMICA MOLECULAR
SEEDMOL
4 a 8 novembro | 2024
Pirenópolis, Goiás

Hydrogenation of Unsaturated Compounds Mediated by Intramolecular Frustrated Lewis Pairs

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Keywords: Hydrogenation; Frustrated Lewis pairs; unsaturated compounds; aminoborane; Intramolecular.

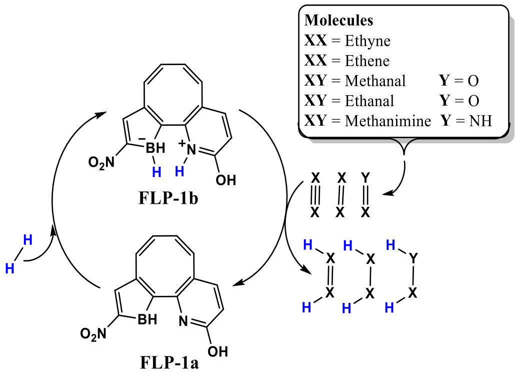
Abstract

This study explores the hydrogenation of unsaturated compounds using a substituted Frustrated Lewis Pair (FLP) system by means of Density Functional Theory. The results highlight the greater reactivity of simple imines and aldehydes compared to alkenes and alkynes, with lower reaction barriers, evidencing the potential of FLP in selective hydrogenation.

Introduction

The chemistry of Frustrated Lewis Pairs (FLPs), introduced by Stephen and collaborators,[1] originated from the observation of the reversible activation of the H_2 molecule in a metal-free system. Since then, the reactivity of FLPs has been extensively explored in the activation of small molecules and the hydrogenation of unsaturated organic compounds, including (imines, ketones, aldehydes, and CO_2).[2,3] FLPs are composed of a Lewis base (LB) and a Lewis acid (LA), both characterized by steric or structural hindrances that prevent the formation of a classical Lewis adduct.[4] These FLP systems can be classified as either intermolecular or intramolecular depending on the relative arrangement of their components (LB and LA).[5] The reactivity of FLPs is determined by a combination of factors such as the acidity and basicity of the Lewis centers, steric hindrance, and the functional groups attached to these centers.[6,7]

Hence, this study is focused on examining the activation of H_2 using the FLP-1a (Scheme 1) structure derived from cyclooctatetraene (COT)[8] by means of Density Functional Theory (DFT) calculations. The reactivity of this structure is evaluated along the catalytic hydrogenation of unsaturated compounds such as acetylene, ethylene, formaldehyde, acetaldehyde, and methanimine. A detailed discussion regarding the mechanism of this process provides a valuable theoretical framework that can guide the development of more efficient FLPs for hydrogenation applications.



Scheme 1. Hydrogenation reactions mediated by the FLP-1a vicinal aminoborane system considered in this study.

Methodology

The calculations were performed using the Gaussian 09 software (Revision D.01).[9] The M06-2X exchange-correlation functional[10] was employed along with def2-TZVP basis sets.[11] Structural optimizations aiming equilibrium geometries were conducted without the imposition of symmetry constraints. Thus, minimum points (reactants, intermediates, and products) and transition states (TSs) are found and validated through vibrational frequency calculations. Additionally, Intrinsic Reaction Coordinate (IRC) calculations were performed to ensure that the TSs obtained indeed correspond to each reaction. The equilibrium structures were then used for energy analysis. All calculations are done in gas phase and thermodynamic properties are determined at 1 atm and 298.15 K.

Results

The analysis of thermodynamic results for the reactants, intermediates, and TSs (Enthalpies and Gibbs energies for barriers and elementary steps) reveals important information about the reactivity of the molecules studied with respect to the hydrogenation process. Hence, all global reactions have negative reaction enthalpy variations, ΔH_r, indicating that they are exothermic. As seen in Fig. 1, the reaction Gibbs energy variations, $\Delta G_{r,}$ are also negative, suggesting that the global reactions are spontaneous. In terms of Gibbs energies of activation, $\Delta G^{\ddagger}$, the ethene and ethyne molecules present the highest reaction barriers, while methanimine and aldehydes (formaldehyde and acetaldehyde) have the lowest barriers. This suggests that FLP-1a will lead to faster hydrogenation reactions of imines and aldehydes compared to alkenes and alkynes.

Discussion

The dissociation reaction of the H_2 molecule in the presence of FLP-1a, forming the intermediate FLP-1b, exhibits a $\Delta G^{\ddagger}$ value of 7.36 kcal/mol and a reaction energy ΔG_r of -4.27 kcal/mol. These values suggest that the H_2 dissociation reaction is thermodynamically favorable and fast at room temperature. The formation of FLP-1b is a crucial step, as this compound acts as an intermediate in the subsequent hydrogenation reactions. The negative reaction enthalpy indicates that the process is exothermic, contributing to the stability of FLP-1b, which can then react with the unsaturated compounds.

Specifically, as show in Fig. 1, the methanimine hydrogenation reaction stands out with the lowest reaction barriers, with a $\Delta G^{\ddagger}$ value of only 4.36 kcal/mol. Thus, the hydrogenation of methanimine is predicted to be faster compared to the same process in other unsaturated compounds analyzed. In addition, the reaction energy ΔG_r for methanimine is also significantly negative, -21.13 kcal/mol, indicating that this reaction is highly exergonic, which corroborates its spontaneity. Although the hydrogenation of formaldehyde has a slightly higher Gibbs activation energy than that of methanimine, $\Delta G^{\ddagger}$ = 8.01 kcal/mol, it should still provide a quite fast hydrogenation process at room temperature. The ΔG_r value of -5.57 kcal/mol is again exergonic. Similar considerations hold with respect to the other aldehyde considered, acetaldehyde.

In contrast, the hydrogenation reactions of ethyne and ethene show significantly higher barriers, with $\Delta G^{\ddagger}$ results from 28.98 kcal/mol above. Thus, these reactions should be much slower at room temperature, which implies a less effective hydrogenation process of these molecules compared to aldehydes and methanimine using the FLP-1a catalyst.

Therefore, based on Gibbs energy results, the hydrogenation reactions of imines and aldehydes catalyzed by the FLP system investigated here are found to be the most favorable ones. This suggests that these compounds would be preferentially hydrogenated under the conditions studied, reflecting their greater reactivity compared to alkenes and alkynes. Hence, FLPs might be used in selective hydrogenation routes.

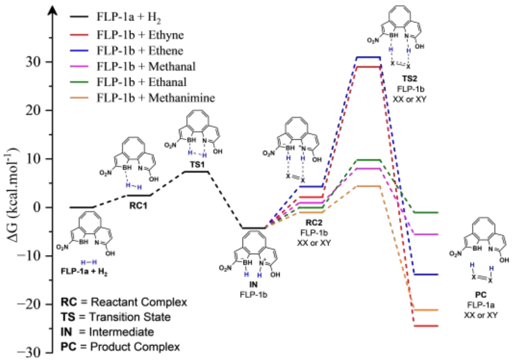


Figure 1. Reaction profiles for the hydrogenation reaction between FLP-1b species and unsaturated compounds (ethyne, ethene, formaldehyde, acetaldehyde and methanimine). Relative free energies computed at 298 K (ΔG).

These insights are highly relevant to the development of more efficient FLP systems to hydrogenation processes and can contribute to experimentalists by providing an alternative and less expensive approach to the development of new systems.

Conclusions

The results of this study show that the hydrogenation of methanimine and aldehydes (formaldehyde and acetaldehyde), mediated by the FLP-1a catalyst, provides quite small Gibbs energies of activation at room temperature, indicating a greater efficiency of these reactions compared to similar process using ethyne and ethene, for instance.

Thermodynamic and kinetic data show that methanimine is the most reactive of these unsaturated compounds as using the FLP-1a catalyst, with significantly lower $\Delta G^{\ddagger}$ values. Next, formaldehyde appears as the second most reactive unsaturated compound investigated here, followed closely by acetaldehyde.

Therefore, we can conclude that the theoretical investigation of FLPs in the hydrogenation of unsaturated compounds can provide a direction for the development of more efficient catalytic systems. Hence, the understanding of reaction barriers and relative reactivity of the different molecules contributes to advances in the design of new FLP-based catalysts.

Acknowledgements

The authors would like to thank the following institutions: IQSC-USP, UFF, CAPES (88887. 653938/2021-00), CNPq (306763/2021-4), and São Paulo Research Foundation (FAPESP – grant 2022/05138-0).

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