



Computational Investigation on Nitrogen Activation Process



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Introduction

The Haber-Bosch process has atmospheric Nitrogen and Hydrogen gas react over an iron catalyst at high temperatures (450°C-500°C) and high pressure to form Ammonia, NH_3 . The focus of this research is investigating some proposed molecular catalysts that other researchers have positive findings with, testing their calculations, and investigating similar structures based on other studies for better results.

Molecule systems were designed based on empirical data and current research findings on Frustrated Lewis Pair (FLP) catalysts. A molecule with opposing Lewis's acid and Lewis's base groups (FLP) has strong catalytic effect as it can interact with opposing electron environments on its substrate. Current Nitrogen synthesis apparatuses use heavy metal catalysts which are rare and expensive, FLP catalysts are metal-free and have been researched for other reactions for this reason as well.

Methods

The Gaussian16 computational chemistry software with B3LYP Functional Group and 6-311g basis set will be used to optimize transition states and find intrinsic reaction coordinates (IRC) of potential catalytic reactions to split Dinitrogen. A successful IRC calculation would indicate a broken dinitrogen triple bond as a product. That product would then be verified to have an imaginary vibrational frequency in the transition state.

Results

Previous studies on Nitrogen and Hydrogen activation have findings with FLP Borane Tetrafluoride BF_3 , and Cyclic Alkyl Amino Carbenes (CAACs) derivatives.

- Figure 1.) a Lewis acid and a Nitrile ($C \equiv N$) Lewis base. This molecule was optimized and found through a QST2 calculation. Nitrogen was not activated from this transition state
- Figure 2.) The Lewis base is Pyridine. The final state in the IRC is identical to the starting state so Nitrogen was not activated during this calculation.
- Figure 3.) The Lewis base is Pyrrole. The final state in the IRC is identical to the starting state so Nitrogen was not activated during this calculation.

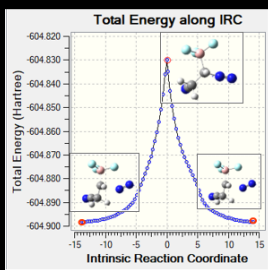


Figure 1.) $NCCH_2CH_1BF_3$ IRC Visualization

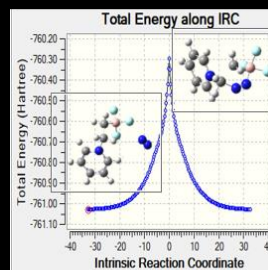


Figure 2.) $(C_5H_5N)CH_2CH_2BF_3$ IRC Visualization

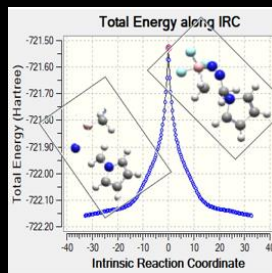


Figure 3.) $(C_4H_4N)CH_2CH_2BF_3$ IRC Visualization

Discussion

The examples are a few of various attempts of interesting proposals, however, the IRC graph does not show a reaction it only displays a transformation with no reaction taking place. Throughout various attempts and calculations, this paper has not found a significant catalyst. The following findings and molecules are not conducive to a conclusion but may provide steps and insight for future purposes. Further experimentation may have findings with heterocyclic nitrogen compounds like Pyridine and Pyrrole but should look to change the carbon spine, Lewis acid, or create a derivative of typical heterocyclic compounds that are CAACs. Further experimentation will attempt to find symmetrical structures that cleave the Nitrogen triple bond with inspiration of FLP.

References

Impact sensitivity and activation energy of pyrolysis for tetrazole compounds, Chen, Z.-X. and Xiao, H. (2000) Int. J. Quantum Chem., 79: 350-357. *Understanding reaction mechanisms of metal-free dinitrogen activation by Methylene boranes*, Jie Zeng, Jiaying Su, Feiying You, Jun Zhu, Chinese Chemical Letters, Volume 34, Issue 2, 2023, 107759, ISSN 1001-8417,