Ch 121a HW

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1 Introduction

There is a growing global economy with steep energy demands (ref article from MIT). While an energy sector that depends on renewable options is ideal, it is infeasible to completely phase out fossil fuels that emit carbon dioxide, a potent greenhouse gas. The technology of carbon capture offers a way to remove this carbon dioxide from the atmosphere. To advance it, we need to isolate compounds that can selectively bind CO_2 for sequestration and conversion to other products, such as HCOOH. While many studies (cite here) have selectively analyzed borane complexes for capture, they do not investigate conversion to HCOOH and other products. Additionally, while irreversible CO_2 binding is significant in the thermodynamic driving force behind selective CO_2 capture, an understanding of the mechanism of the reversible capture of CO_2 is needed. In this paper, we utilize NiBo for reversible CO_2 binding. In addition, we look to elucidate the first steps of conversion of CO_2 to HCOOH via the heterolytic activation of H_2, done via a Frustrated Lewis Pair (FLP) type mechanism previously investigated in phosphine-borane complexes (cite). Provided the simplistic approach of using Lewis Basic sites for capturing CO_2, the sp2-hybridized centers of the nitrogen present in the complex are also particularly intriguing for electrochemical reduction of CO_2 to longer alkyl chain products as well. Along with the possible electrochemical pathways that these NiBo compounds introduce (cite), the lack of expensive metallic catalysts involved in their capture of CO_2 means that NiBo and their derivatives remain a point of interest for CO_2 capture.

2   Methods

To assess the feasibility of these provided Nitrogen-Borane heterocycles for CO2 capture, we utilized Density Functional Theory (DFT) quantum mechanical calculations. We utilized the M06-2X-D3 hybrid functional *why did you use this one...if you don't know cite a paper that had a similar purpose where this one was used,* adjusted with dispersion correction. We also used the 6-311G++** basis set, with incorporated diffuse polarization functions. In using these methods, we ensure a high precision of calculations in final energy calculations and states, with all optimized structures adjusted to have no imaginary frequencies, and all Transition State structures the with one imaginary frequency.

3   Evaluation of Initial Structures

In verifying the usage of a Nitrogen-Borane heterocycle for CO2 capture, we must intuitively analyze the thermodynamic driving force of nucleophilic attack of the nitrogen on the electrophilic carbon center, and subsequent bonding by the oxygen to the boron, in a concerted manner. In transition state calculations, we may also assume that nucleophilic attack is the rate-determining step, provided the subsequent electrophilicity of the boron upon binding by the oxygen. Depending on the nature of the NiBo species, we may also investigate H2 activation via a Frustrated-Lewis pair type mechanism, which includes heterolytic cleavage of the H2 molecule following nucleophilic attack. To analyze the