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Role of the Iridium-Nitrogen Interaction in Catalytic Transfer Hydrogenation

Morgan Noble
Department of Chemistry
The University of North Carolina Asheville
One University Heights
Asheville, North Carolina 28804 USA

Faculty Advisor: Dr. George Heard

Abstract

Transfer hydrogenation is the process of adding H_2 to a molecule from a non H_2 source. This process is more resourceful than direct hydrogenation because the non H_2 sources are more readily available and inexpensive compared to H_2 sources. Many different metal catalysts attached to ligands have been used to determine which is best for the reaction as well as the most effective way to get to the end product. An iridium catalyst will be used along with a non H_2 source to determine which hydrogen atom from the source goes where on the molecule, as well as discovering if the mechanism is going to be stepwise or concerted. This will be done using computational methods. After completing multiple trials of different orientations of the formic acid being added to the iridium-nitrogen sulfonamide, it was discovered that the mechanism is going to be stepwise.

1. Introduction

Transfer hydrogenation, referring to the addition of hydrogen to a molecule from a non-H_2 hydrogen source, is a convenient and powerful method to access various hydrogenated compounds. It is an attractive alternative to direct hydrogenation, and it has recently become the center of research in hydrogenation science.[1] This method is easier and more efficient than others because the H_2 donors are more readily available, inexpensive and safer to handle, the method itself does not have any intricate experimental setups, and any catalysts involved are normally available and not sensitive.[2] Transfer hydrogenation of unsaturated compounds is an important catalytic reduction reaction for preparing the corresponding saturated products without the use of explosive hydrogen gas or moisture-sensitive hydride reagents.[2] The use of a hydrogen donor has some advantages over the use of molecular hydrogen since it avoids risks and the constraints associated with hydrogen gas, as well as the necessity for pressure vessels and other equipment.[3] Many of these transfer hydrogenations involve ligand–metal bifunctional catalysis (metal–ligand cooperation); that is, the complexes contain electronically coupled hydride and acidic hydrogen atoms as a result of heterolytic dihydrogen cleavage that may be transferred to polar unsaturated substrates in an outer-sphere fashion or may be transferred via hydride migration.[4]

Previous research has proven that this transfer hydrogenation process can be done using an iron catalyst.[2] A number of transition metal complexes act as highly active and robust catalysts that are also highly enantioselective. The development of metal catalysts containing tridentate and tetradentate ligands, has led to advancements in the field. Recently, Fe catalysts with tridentate and tetradentate ligands were applied to transfer hydrogenation to develop an environmentally friendly process.[2] Further research has been done to prove that ruthenium, rhodium, and iridium complexes can be used as well as an iron catalyst. This is where our interest comes into play; looking into iridium cations with formic acid being the non-H_2 donor. Formic acid plays an essential role in this mechanism. Unlike other acids, formic acid has a convenient hydrogen atom readily able to be detached and added to another molecule. Going from iron to iridium is safe choice based on the fact that they are both transition metals and are likely to conduct this mechanism in a similar manner. As well, iridium has a high solubility of its cations in a neutral solution. Using the iridium as the catalyst will be more beneficial compared to using the other metal complexes because iridium

compounds are soluble in solvents that can be used as hydrogen sources, like water. Which means that this hydrogenation reaction can happen outside of a "glove box" meaning air is not going to have an effect on it, as well as not needing a highly basic medium. Knowing that air is not a potential factor is beneficial to the reaction because this is a more efficient way to run it.

Figure 1 and 2 above show the different orientations of the possibilities that are going to be analyzed.

The two images above show the possibilities that are going to be analyzed using the computational methods. The hydrogen from the nitrogen going to the oxygen, and the hydrogen from the iridium going to the carbon, and then vice versa. It is thought that the more likely orientation to work is image 2, because of there being less strain on the sulfonamide when it is entering into the molecule.

To be determined is how the iridium-nitrogen interaction with a non-H_2 source happens and if this mechanism is going to be a one or two step mechanism. We will also be looking at the two molecules of the end products in different orientations, to discover which one carries more energy concluding which one is more favorable.

2. Experimental Section

Computational chemistry was used to calculate reaction energies as well as to examine visual orientations of the molecules. The method that was used was Density Functional Theory (DFT).[5] Density functional theory uses a single determinant wave function to describe electrons in a molecule. DFT then generates a density from the square of a wave function and then calculates the energy of a molecule based on that density.[5] The DFT method and m06 were used to compare theories as well as predict other effects that could possibly happen during the reaction. The m06 method is especially useful in calculating the energies of transition state geometries. These methods were mainly used in determining if the mechanism was going to be stepwise or concerted.

Further calculations were ran using the QST3 method. This method requests another method during the process called The Synchronous Transit-Guided Quasi-Newton (STQN) Method.[5] The STQN method uses a linear synchronous transit or quadratic synchronous transit approach to get closer to the quadratic region around the transition state and then uses a quasi-Newton or eigenvector-following algorithm to complete the optimization.[5] This method will converge efficiently to the actual transition structure using an empirical estimate of the Hessian and suitable starting structures.[5] STQN does not require a presumption for the transition structure, it instead requires that the starting and final products are the input.[5]

GaussView[5] was used to visualize the geometries for the optimized ground state, transition state, and end state structures for energy calculations.

3. Results and Discussion

After running multiple computational tests with attempting to attach the formic acid straight to the iridium sulfonamide, the calculations came back as showing that this was going to be a stepwise mechanism. When the final visual orientation of the molecule being ran as a concerted mechanism was completed, the hydrogens from the formic acid were not added to the iridium-nitrogen sulfonamide. The two pictures below show the end results when calculations were ran as the concerted mechanism. The dark blue sphere represents the nitrogen atom, while the lighter blue sphere represents the iridium atom. Black arrows are depicted to show where the formic acid is located in comparison to the sulfonamide. White arrows are depicted to show the hydrogens that were supposed to be transferred to the iridium and nitrogen atoms.

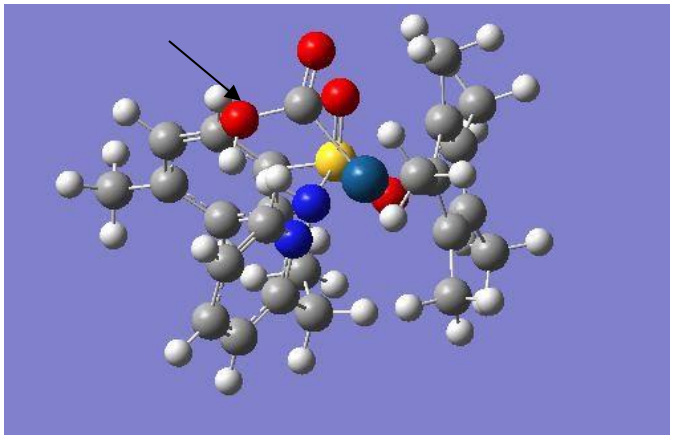

Figure 3 above shows how the molecule completed the reaction when the hydrogen from the oxygen atom on the formic acid was positioned close to the nitrogen atom on the sulfonamide.

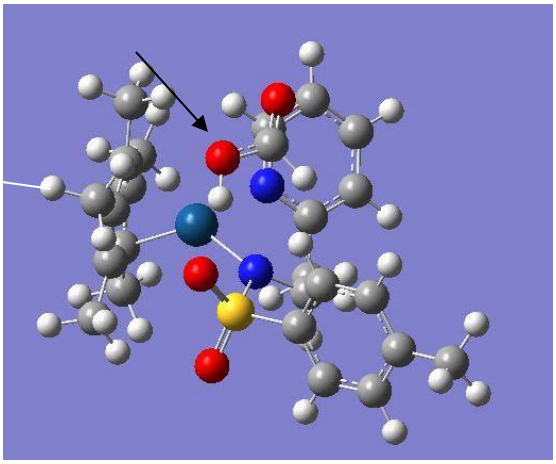

Figure 4 above shows how the molecule completed the reaction when the hydrogen from the oxygen atom on the formic acid was positioned close to the iridium atom on the sulfonamide.

In both orientations of the hydrogen from each molecule being flipped, neither were able to successfully attach to the iridium-nitrogen sulfonamide. As you can see in figure 3, only one hydrogen atom is pointed out with the white arrow, this is because the other hydrogen came off of the formic acid and attached to another molecule somewhere in the sulfonamide. In figure 4 neither hydrogen atoms, from the formic acid, were able to successfully detach and connect to the sulfonamide. With this information, it can be concluded that this transfer hydrogenation process is going to be stepwise.

With this conclusion, QST3 methods were ran on the molecule to determine how the stepwise reaction was going to be completed.

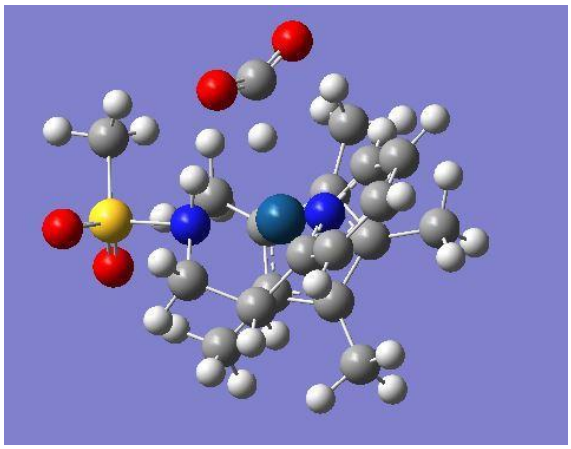

Figure 5 above shows the orientation of a QST3 that was ran with the hydrogen from the oxygen connecting to the nitrogen, and the hydrogen from the carbon atom in route to connecting to the iridium.

Figure 5 is promising to look at because it does show how the mechanism is going to play out being stepwise. From this figure 5 we can conclude that the hydrogen from the oxygen is going to leave the formic acid and connect to the sulfonamide first. Coinciding with the proposed hypothesis of the mechanism being stepwise rather than concerted.

3. Conclusion

With multiple tests being ran to see if the mechanism was going to be stepwise or concerted, it was determined to be stepwise based on the incomplete transfer of hydrogens during the concerted computational calculations. The mechanism also favors the hydrogen from the oxygen pairing with the nitrogen and the hydrogen from the carbon being paired with the iridium. Running more QST3's is going to be beneficial in fully concluding that this mechanism can work and how it is going to be completed.

4. References

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