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Greenhouse Gas to Environmentally Friendly Compound: Mechanistic Study of Carbon Dioxide

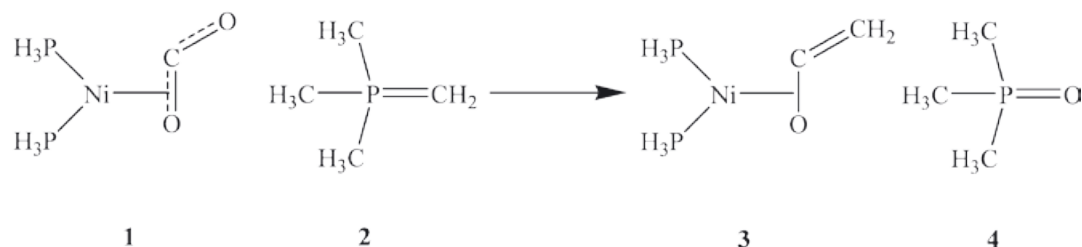
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The mechanism for a Wittig-type reaction of a coordinated carbon dioxide nickel complex with an ylide to yield a nickel ketene complex and phosphine is studied using theoretical chemistry (Scheme 1). Two model systems are also examined: one in which the hydrocarbon substituents are replaced by hydrogens and a second that does not include the metal center. Preliminary data from the mechanistic studies of the carbon dioxide complex and the non-metal reveal that the intermediates in these two reactions are more stable than the products and indicate that these reactions will stop at the intermediates rather than proceeding to completion. However, analysis of the non-metal model system using various levels of theory suggests that these results may vary depending upon the level selected.

Scheme 1



Theoretical chemistry's utility in chemical analyses is a relatively recent development that has come with advances in computing capabilities. Solving quantum mechanical equations that describe the system of interest can provide information on systems that may be inaccessible to other techniques due to instability under ordinary laboratory conditions, such as transition states and intermediates in reaction mechanisms. Understanding mechanisms in which carbon dioxide (a greenhouse gas which is thought to contribute to global warming) is a reactant can aid in designing efficient reactions that utilize this material to produce useful and environmentally friendly compounds. This paper provides a very brief overview of theoretical chemistry and the motivations for studying carbon dioxide as well as examining the mechanism of a reaction involving carbon dioxide and two model systems.

Theoretical Chemistry

The goal of this investigation was to gain knowledge of reactions between carbon dioxide and a nickel complex by elucidating the mechanism of reaction (series of elementary steps the reaction goes through on its way from reactants

to products). Although experimental data can be used to propose mechanisms, the intermediates are not always sufficiently stable in the laboratory to be isolated and then investigated experimentally. Theoretical chemistry, however, is a technique that can alleviate this problem and even be used to obtain information not available experimentally. In this sort of project, the tools of theoretical chemistry can be used to address questions such as: What is the mechanism of reaction from reactants to products? What are the most important intermediates in the reaction? Which is the rate limiting step? Are the important intermediates and rate limiting steps similar for different metals? How do these factors vary as functions of the metal complexes used?

Crash Course in Theoretical Chemistry

Many of us are familiar with Newton's Laws that are equations describing what happens to everyday objects in the world. When an apple falls from a tree, the force acting on the apple at a particular moment is equal to the object's mass multiplied by the second derivative of its position, or acceleration:

FORCE = MASS X ACCELERATION

In a similar way, there are quantum mechanical equations that describe the world at the molecular level. These equations take into account the atoms (with their electrons, protons and neutrons) that make up molecules and in turn provide information on molecules (which are composed of many atoms), such as their energies and spectroscopic characteristics. The larger and more complicated the molecule, the more complex the set of equations is. Unfortunately, only equations for very simple molecules (such as the hydrogen atom) can be solved exactly, so we must use approximations for the larger molecules. The number and type of approximations leads to different levels of theory, and the various levels of theory are more accurate (meaning that the results from the calculations agree with experimental observations) for different sorts of information. If one is investigating hydrogen bonding, for example, one level of theory might be chosen while another level would be selected for optimizing the geometry. The higher the level of theory used (or the fewer approximations made) the more accurate the equations are; although, obtaining this increased accuracy requires greater computing resources to solve the equations. Thus, theoretical chemistry is a balancing act between the accuracy needed and the time and resources required to obtain that accuracy. In the work reported here, we have been primarily concerned with calculating the energies of optimized geometries for the compounds in the step-wise change from

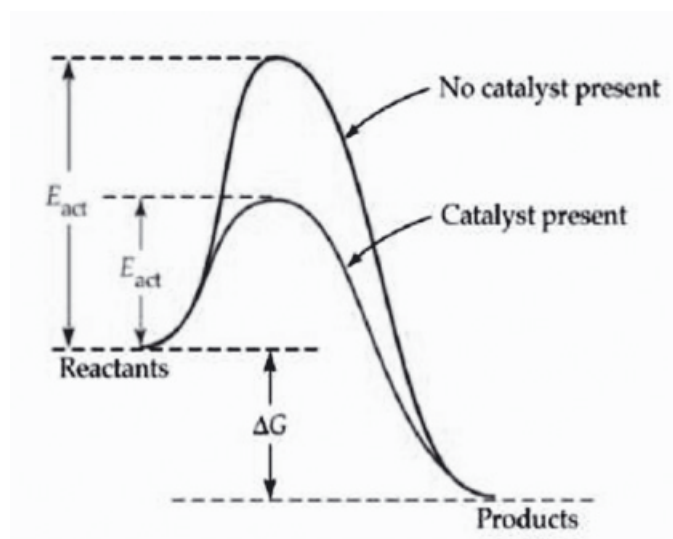
reactants to products for a Wittig-type reaction between carbon dioxide and an ylide.

Why study carbon dioxide?

Carbon dioxide (CO₂) is a greenhouse gas that is thought to contribute to global warming at the Earth's surface. Many of the efforts to curb the emission of greenhouse gases are policy oriented, such as the Montreal and Kyoto Treaties, or are aimed at reducing emissions. Implementing these sorts of efforts depends on initiatives coming from governments and industries and can be costly in both arenas as well as in enforcement. For industry, costs lie in retrofitting industrial machinery in existing factories, and governmental regulation is dependent upon individual countries regulating emissions. Failing to curb global warming could have immense environmental costs and possibly even irreversible damage. An additional approach to the policy strategy is to develop a methodology to contain greenhouse gases and then convert them into environmentally-friendly compounds that can be used in other production processes. However, attaining this goal is not without obstacles.

Carbon dioxide is a stable compound, which means that it is not particularly reactive on its own. One way to coax stable molecules into reacting is to put energy into the reaction to drive it towards the products. However, doing this could result in the production of more carbon dioxide depending upon the source of the energy. Because a main motivation

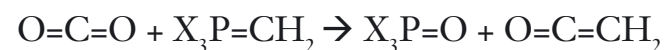
FIGURE 1. ACTIVATION ENERGY (E_{act}) FOR REACTIONS WITH AND WITHOUT A CATALYST¹



for this project is to curb the production of carbon dioxide into the atmosphere, we must be wary of reactions' energy costs. One approach is to use a catalyst to lower the activation energy (E_{act} , energy required for a reaction to occur) for the reaction (Figure 1). Utilizing a catalyst is the method we have selected to investigate for the reaction of a carbon dioxide coordinated nickel complex **1** with an ylide **2** in a Wittig-type reaction to yield nickel ketene **3** and phosphine **4** (Scheme 1).

Reaction Involving Carbon Dioxide: The Wittig Reaction

The Wittig reaction is an important method in synthetic chemistry for forming carbon-carbon bonds. In this reaction, a hydrocarbon with a carbonyl (carbon dioxide for the purpose of this analysis) reacts with an ylide to form phosphine and an alkene, respectively:



where X is usually a methyl (CH_3) or phenyl (C_6H_5) group. Due to its utility, the Wittig reaction has been extensively investigated using both theoretical and experimental techniques. For example, Lu et al. have investigated mechanisms for Wittig reactions and shown that simplifying the substituents on the ylide

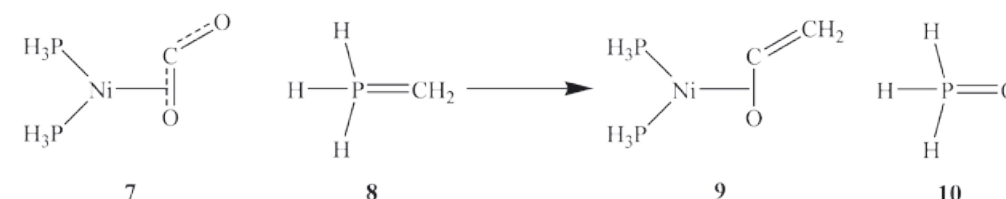
with hydrogens reasonably predicts the energy barrier for the rate determining step and that replacing the phenyl groups (C_6H_5) with methyl groups (CH_3) is reliable for examining the entire reaction.² Additionally, Wittig-type reactions have been investigated in which the carbonyl is in a carbon dioxide nickel

complex.³ The metal complex stabilizes the ketene product which can then be directly converted into other molecules such as alcohols, aldehydes, acetones and acids.⁴ Work by Yamataka and Nagase examined how variations in ylides (that is the $\text{X}_3\text{P}=\text{CH}_2$ part) have the propensity to influence the reaction's products.⁵

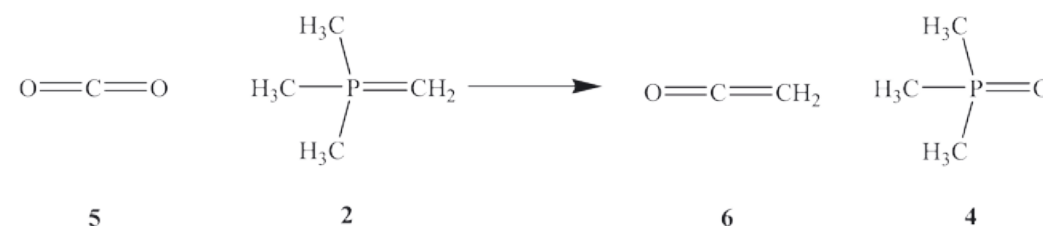
For our investigation, we examined a coordinated carbon dioxide nickel

complex based on Wright et al's work⁴ with simplifications in the ylide substituents³ (Scheme 1). The presence of nickel (a transition metal with many electrons) in the reaction made the equations more complex to accurately describe the system and subsequently increased the computing time required; therefore, we conducted initial calculations on two model systems: hydrogen-only (Scheme 2) and non-metal (Scheme 3) versions of the system.

Scheme 2



Scheme 3



Model Systems: Hydrogen-only and Non-metal

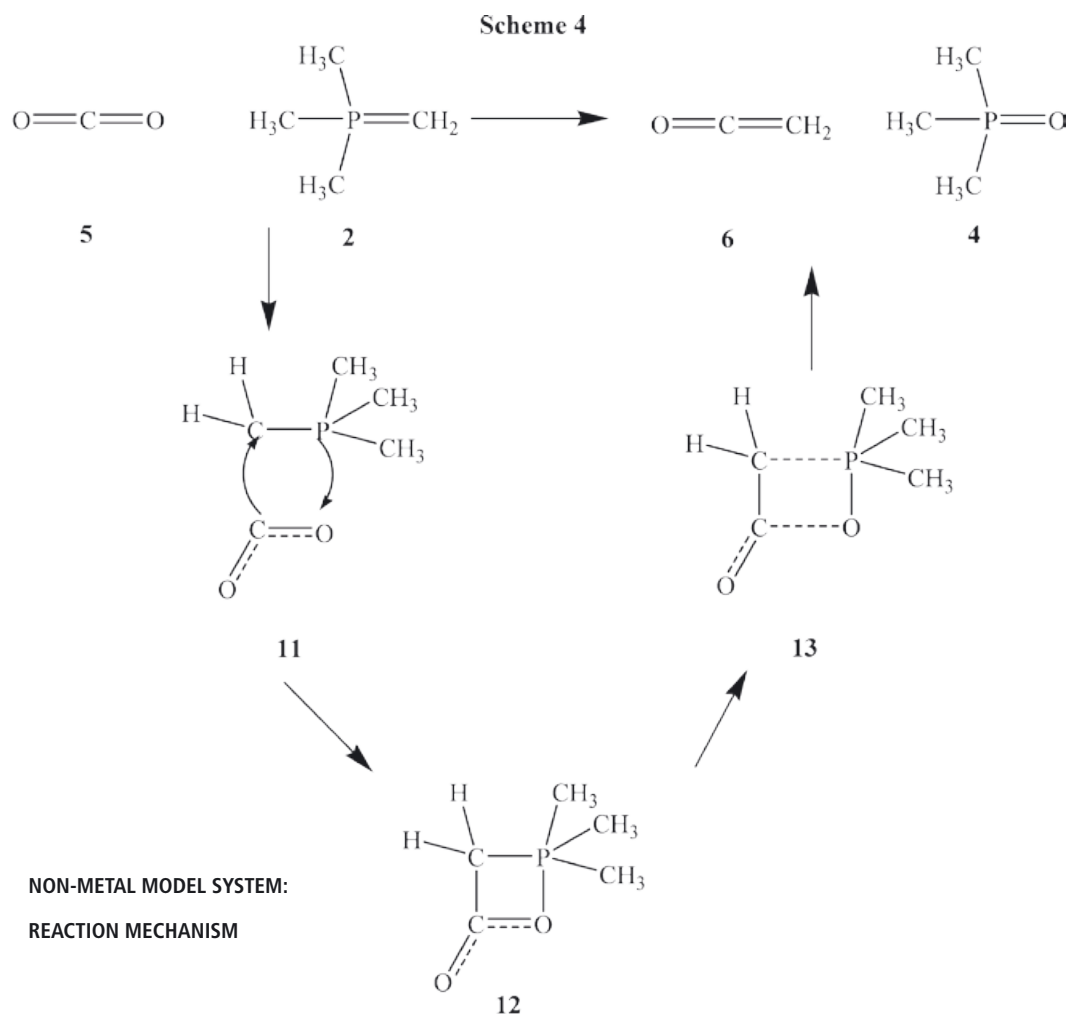
Prior to calculating the mechanism of the nickel catalyst (**1**) with ylide **2**, we examined two model systems with approximations of the catalytic

system. Information from these shorter calculations can subsequently be used in the design of the full catalyst mechanism (Scheme 1). The first model system utilized hydrogen atoms in place of methyl groups (methyl = CH_3 , Scheme 2) while the second model system differed only in that it did not include the metallic center or additional groups that are not directly

involved in the reaction (Scheme 3). Although the mechanisms were examined for the full catalyst reaction (Scheme 1) and the non-metallic version (Scheme 3), the energy of reaction (ΔE_{rxn}) was calculated for all three systems. While all the systems are exothermic (meaning that the products are lower in energy and therefore preferred to the reactants), the two systems that include the metal center (the hydrogen-only and full catalyst, Schemes 2 and 3 respectively) are more exothermic than the non-metal system (Scheme 3) (Table 1). This finding indicates that the

nickel center has a stabilizing effect on the reaction. Of the three systems, the full catalyst is significantly more stable (more negative value for the energy of reaction) than the hydrogen-only and non-metal systems (-27.2 kcal / mol vs. -18.9 and -12.5 kcal / mol, respectively).

Model systems can be employed to enhance our understanding of the contribution made by the different components of a system (such as the effect of the metal center) as well as to serve as simplified versions of the system of interest which enable calculations to be performed more



quickly. The former feature was exploited in the previous analysis of reaction energies for the full catalyst (Scheme 1), hydrogen-only and non-metal versions (Scheme 2 and 3, respectively). The latter attribute of model systems that enable speedy calculations enabled the non-metal mechanism to be calculated quickly (Schemes 3 and 4) and many times using various levels of theory.

The non-metal reaction mechanism proceeds through two transition states and one intermediate in the transformation of carbon dioxide (5) and ylide 2 to alkene 6 and trimethylphosphine oxide (4). A molecule is in a transition state when it is in the process of changing from one molecule to another. An intermediate is a molecule which is relatively stable but not a product or reactant. Intermediates quite frequently can be found in a mechanism immediately before or after transition states.

In a mechanism for the non-metal system (Scheme 4), the first step is that the two reactants (5 and 2) approach each other and form a loose complex in which the two molecules are loosely associated. The subsequent transfer of electron density between atoms in each of the reactants (5 and 2) during transition state 11 forms bonds leading to cyclic intermediate 12. The carbon atom in carbon dioxide (5) transfers electron density to the methylene (CH_2) carbon in ylide 2 and phosphorus in ylide 2 transfers electron density to one of the oxygens in carbon dioxide (5). The C-O and C-P bonds of intermediate 12 then lengthen in transition state 13 until finally separating to form the two new molecules 6 and 4. Once the molecules are completely separate, the alkene 6 and trimethylphosphine oxide (4) products are formed.

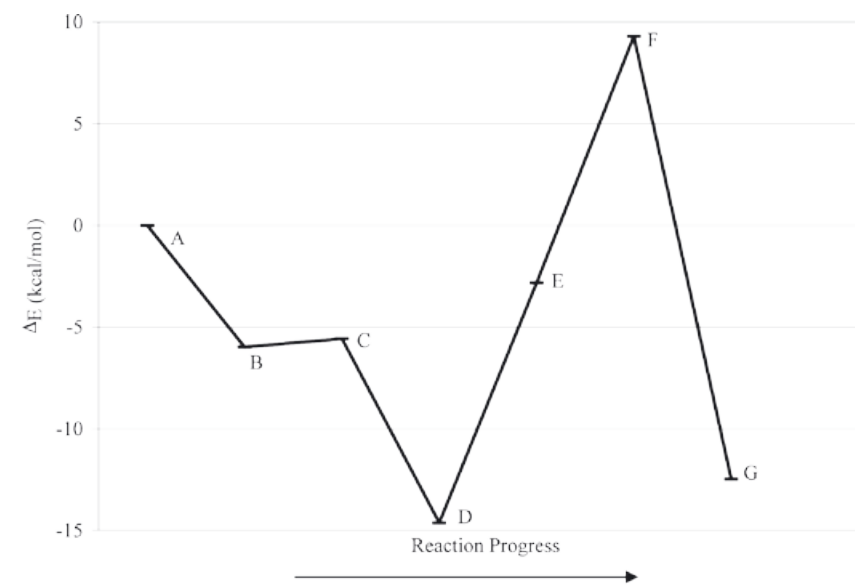
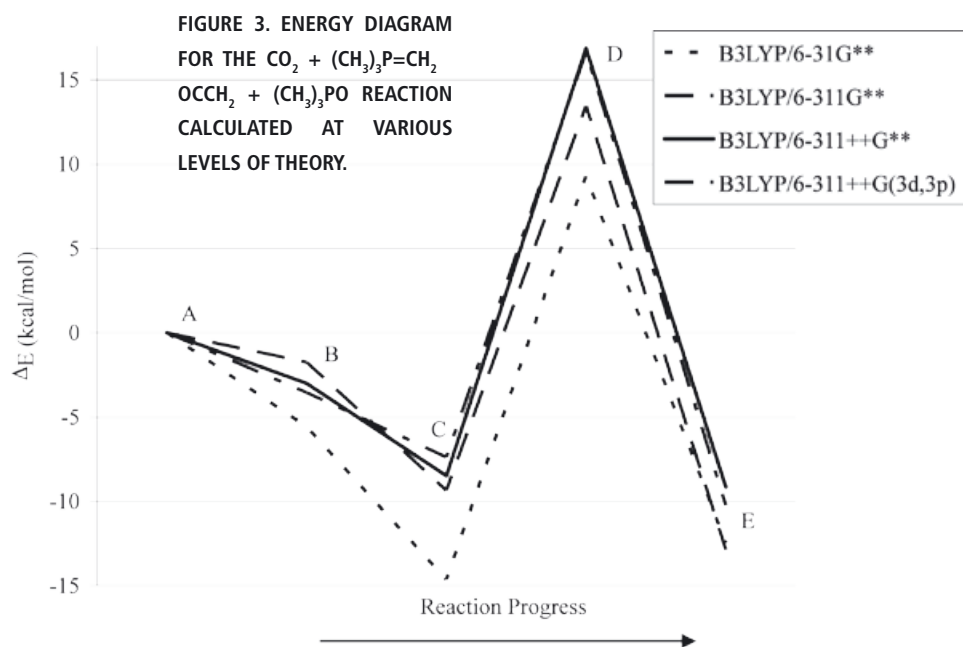


FIGURE 2. ENERGY DIAGRAM FOR THE $\text{CO}_2 + (\text{CH}_3)_3\text{P}=\text{CH}_2 \rightarrow \text{OCCH}_2 + (\text{CH}_3)_3\text{PO}$ REACTION.

A plot of the changes in energy as a function of reaction progress illustrates the energy of molecules as the reaction proceeds (Figure 2). In this type of representation, the minima are intermediates (Figure 2, B and D) and maxima are transition states (Figure 2, C and F). For this reaction, the plot indicates that the non-metal reaction is unlikely to proceed to completion as intermediate **12** (Figure 2, D) is 25 kcal / mol more stable than the following transition state **13** (Figure 2, F), which means that intermediate **12** would require an energy input of 25 kcal/mol to overcome the energy barrier. Additionally, the products **6** and **4** (Figure 2, G) are less stable than intermediate **12**, and would not be a driving force for the reaction to overcome the energy barrier at transition state **13** because the compounds would be less stable as the products **6** and **4** (Figure 2, G) than as the intermediate **12** (Figure 2, D). Therefore, the reaction would likely stop at intermediate **12** (Figure 2, D).

Non-metal Model System: Levels of Theory

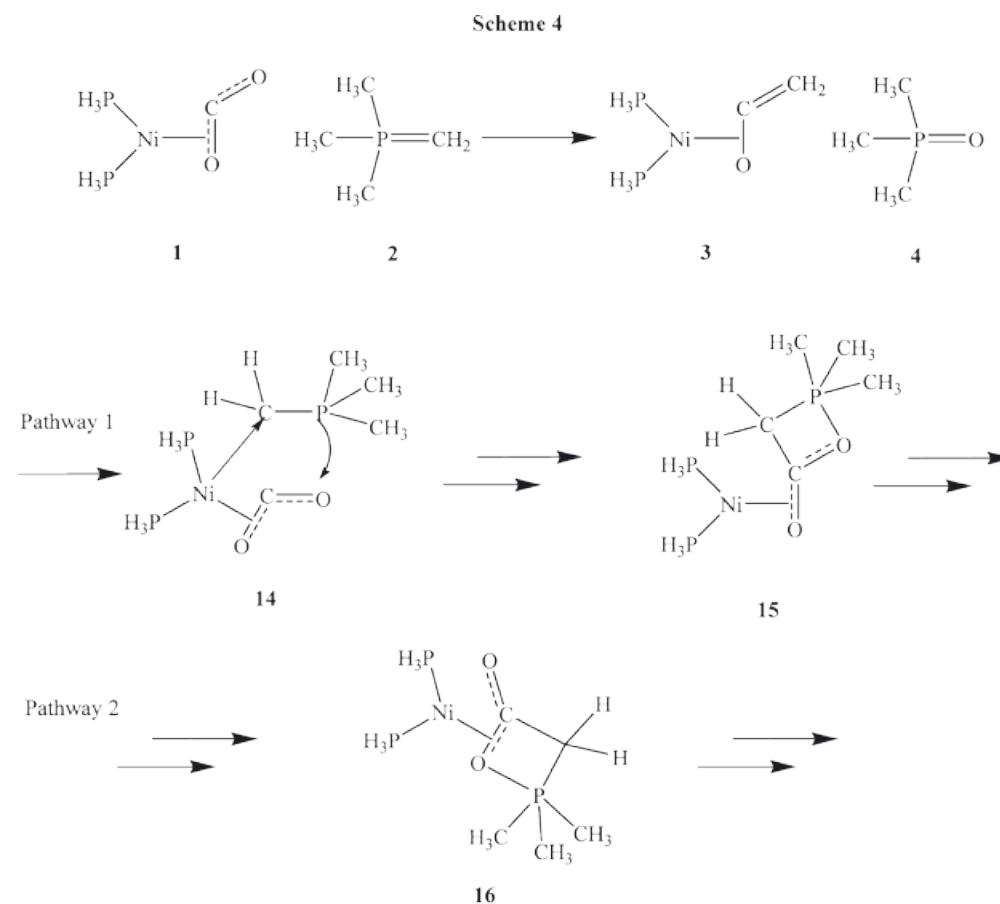
In addition to investigating the mechanism of reaction using the non-metal model system, this model also provides the opportunity to investigate the effect of different levels of theory on the reaction progress as the time required for calculations is not an inhibiting factor. The levels of theory increase from B3LYP/6-31G** to B3LYP/6-311G** to B3LYP/6-311++G** and finally to B3LYP/6-311++G(3d,3p). The energy diagram illustrates that the changes in energy (ΔE) for the different levels of theory are roughly the same and all of the same order of magnitude (Figure 3); however, at the transition state the values differ by roughly 6 kcal / mol (Figure 3, D) and the relative energies of the intermediate (Figure 3, C) and products (Figure 3, E) are not in agreement with the lowest level of theory which was used



to calculate the energies in Figure 2. In Figure 2 (B3LYP/6-31G** in Figure 3), the intermediate is lower in energy than the reactants; whereas using the other, higher levels of theory, the energy of the intermediate is either higher or almost equal to that of the reactants (Figure 3). The differences in energy between the transition state at D and intermediate at C (Figure 3) are approximately the same (25 kcal / mol) for the lowest and highest levels of theory (B3LYP/6-31G** and B3LYP/6-311++G(3d,3p), respectively).

Full Catalyst: Reaction Mechanism

The mechanism for the catalyst complete with the nickel center is being investigated using similar methodology as that for the non-metal model system, and this section presents the preliminary findings. This system has two potential routes through which it can proceed: Forming the heterocycle with the carbon and oxygen that are 1) farthest from the nickel center (Scheme 4, Pathway 1) or 2) directly



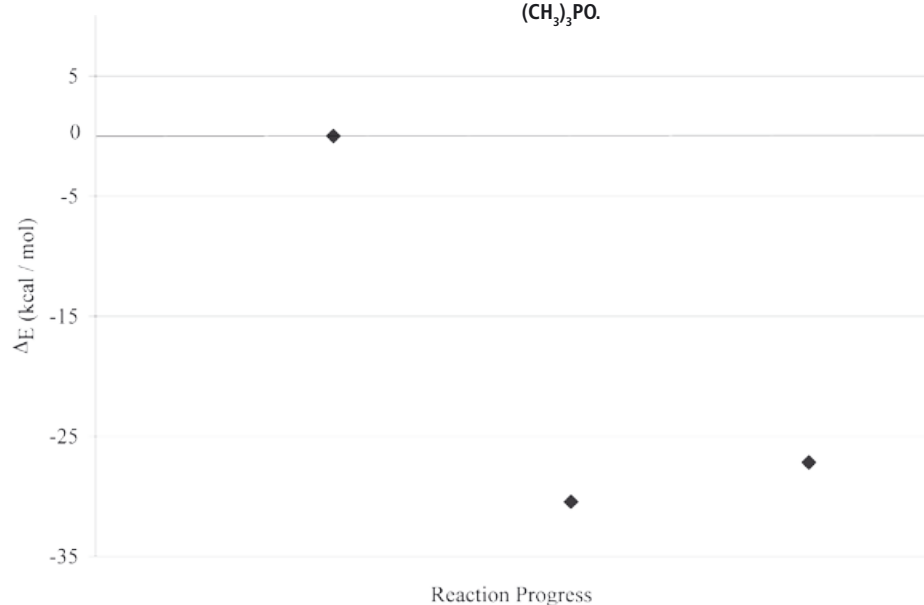
attached to the nickel atom (Scheme 4, Pathway 2). To date, our efforts have been only on Pathway 1 (Scheme 4).

In Scheme 4, Pathway 1, the ring forms along the carbon-oxygen bond that is not directly attached to the nickel atom. Although the complete mechanism has not yet been determined, initial calculations indicate that the mechanism begins with the formation of a bond between nickel in the catalyst **1** and the methylene (CH_2 group) carbon atom in the ylide **2** (Scheme 4, Pathway 1). The formation of the phosphorus-oxygen bond between the catalyst **1** and ylide **2** completes the formation of loose complex **14**. A potential intermediate **15** has been identified which may follow these bond forming steps; the transition states, however, to reach this compound and to go from intermediate

15 to the products **3** and **4** have not yet been identified (Scheme 4, Pathway 1). If the mechanism does indeed proceed through intermediate **15**, there is a trend similar to that observed in the non-metal model system (Scheme 3, Figure 3) with respect to the relative energies of the intermediate and products.

In calculations of the full catalyst for Pathway 1 (Scheme 4), the energy of intermediate **15** is lower than that of the products **3** and **4** by approximately 3 kcal/mol. This difference with the lower energy molecule intermediate **15** makes it highly improbable that the reaction will proceed to completion, just as with the non-metal model system, because systems seek conformations with the lowest energy.

FIGURE 4. ENERGY DIAGRAM FOR REACTANTS **1** AND **2**, INTERMEDIATE **15** AND PRODUCTS **3** AND **4** IN THE REACTION $(\text{PH}_3)_2\text{Ni}(\text{CO}_2) + (\text{CH}_3)_3\text{PCH}_2 \rightarrow (\text{PH}_3)_2\text{Ni}(\text{COCH}_2) + (\text{CH}_3)_3\text{PO}$.



Conclusions and Future Work

Over recent years computing technology has advanced to the point where it is now possible to solve quantum mechanical equations that include sufficient approximations. This advancement in technology has made theoretical chemistry a useful tool to investigate molecules and systems that are unstable under laboratory conditions and thus inaccessible to experimental methods. In this project, we employed theoretical chemistry to investigate the mechanism of reaction between carbon dioxide attached to a nickel atom (the catalyst) and an ylide. Additionally, we examined two model systems: one in which hydrogen atoms are used in place of methyl groups and a second that does not include the nickel center. Comparison of the energies of reaction for the three systems indicates that the molecules with nickel are more stable than those without. Utilizing the non-metal model system we were also able to examine the effect of the level of theory on the molecules' energies that were calculated. Finally, mechanistic studies of the full catalyst and non-metal model system suggest that in both cases the reaction will stop at the respective intermediates rather than proceed to completion as the intermediates are lower in energy than the products. The preliminary data reported in this paper should further be augmented by completing the mechanistic study of the full catalyst and subsequently by

combining these data with others to inform the design of what will, hopefully, be a reaction to turn carbon dioxide from a greenhouse gas into an environmentally friendly and useful compound.

System	ΔE_{rxn} (kcal/mol)
Hydrogen-only Scheme 2	-18.9
Non-metal Scheme 3	-12.5
Full Catalyst Scheme 1	-27.2

TABLE 1. ENERGIES OF REACTION FOR THE HYDROGEN-ONLY, NON-METAL AND FULL CATALYST SYSTEMS INVESTIGATED.

Citations

- 1 Chemistry 1105 Lecture 17. "Chapter 7: Reaction Rates" [Internet, WWW]. ADDRESS: <http://www.chem.neu.edu/Courses/1105Tom/05Lecture17.html> [Accessed: 28 March 2005].
- 2 Lu, W. C.; Wong, N. B.; Zhang, R. Q. *Theor. Chem. Acc.* **2002**, *107*, 206.
- 3 Wright, C. A.; Thorn, M.; McGill, J. W.; Sutterer, A.; Hinze, S. M.; Prince, R. B.; Gong, J. K. *J. Am. Chem. Soc.* **1996**, *118*, 10305.
- 4 Geoffroy, G. L.; Bassner, S. L. *Adv. Organomet. Chem.* **1988**, *28*, 1. Wolczanski, P. T.; Bercaw, J. E. *Acc. Chem. Res.* **1980**, *13*, 121. Blyholder, G.; Emmet, P. H. *J. Phys. Chem.* **1960**, *64*, 470. Muetterties, E. L. *J. Chem. Rev.* **1979**, *79*, 479.
- 5 Yamataka, H.; Nagase, S. *J. Am. Chem. Soc.* **1998**, *120*, 7530.

Endnotes

- 1 Chemistry 1105 Lecture 17. "Chapter 7: Reaction Rates" [Internet, WWW]. ADDRESS: <http://www.chem.neu.edu/Courses/1105Tom/05Lecture17.html> [Accessed: 28 March 2005].
- 2 Lu, W. C.; Wong, N. B.; Zhang, R. Q. *Theor. Chem. Acc.* **2002**, *107*, 206.
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- 4 Sample publications: Geoffroy, G. L.; Bassner, S. L. *Adv. Organomet. Chem.* **1988**, *28*, 1. Wolczanski, P. T.; Bercaw, J. *E. Acc. Chem. Res.* **1980**, *13*, 121. Blyholder, G.; Emmet, P. H. *J. Phys. Chem.* **1960**, *64*, 470. Muetterties, E. L. *J. Chem. Rev.* **1979**, *79*, 479.
- 5 Yamataka, H.; Nagase, S. *J. Am. Chem. Soc.* **1998**, *120*, 7530.

The Kodaly Method: Standardizing Hungarian Music Education

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The name Zoltan Kodaly is synonymous with solfege, singing, composition, ethnomusicology, and music education. He, single handedly, changed the music education program in Hungary and made it what it is today. His method, or philosophy, rather, has been used as one of the main music education models worldwide. His concepts have changed music education for the better. This paper hopes to explain what the Kodaly method is and how it works, while giving a background on the beginnings of Kodaly's work as an ethnomusicologist, composer, and educator. It also offers a glimpse of the differences between a Hungarian elementary music classroom and a Mississippi music classroom.

1. Introduction

My Fulbright project began when my theory professor approached me about studying abroad at the Zoltan Kodaly Pedagogical Institute of Music about three years ago. I was the director of a community children's choir, and she thought I could really benefit from the school. I was familiar with the Kodaly method after a brief study in my elementary