Investigation of the Role of Ammonium Ions in Deoxydehydration Reactions

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Contents

Abstract

A rising interest in the scientific community is the development of an effective catalyst for a reaction known as deoxydehydration (DODH), which converts vicinal diols, obtained from biomass, into olefins. This reaction is of high interest because it plays a role in the development of renewable chemical products that will be essential in the fight against climate change. Currently, there are wide-spread research efforts surrounding this reaction, specifically, developing a sustainable and effective catalyst. The most promising results come from the use of high oxidation state rhenium catalysts which have produced olefin yields of well over 80%. Ammonium-based rhenium catalysts have especially shown higher catalytic activity than their counterparts. The reason for this occurrence has yet to be determined. This work goes in-depth on attempting to determine why ammonium ions increase catalytic activity. There are four current theories on this phenomenon: 1) Ammonium ions help increase the solubility of the catalyst. 2) Ammonium ions provide a counterion necessary for catalytic activation. 3) Ammonium ions provide acidity to the reaction. 4) Ammonium acts as a reducing agent in the reduction of diol into an olefin. Several laboratory-scale reactions, with different components and methods, are designed and performed to give insight and potential conclusions on these theories. By observing diol conversions and decene yields for each experiment, the four scenarios can be distinguished. Results from these reactions will be discussed in further sections. However, there was no conclusive evidence to suggest that any of the four proposed hypothesis are correct. Although this is the case, the results still provide useful insight to an area that was previously under researched. Continuing to research DODH along with new hypotheses is essential as it can then lead to a commercially viable DODH catalyst which would enable replacing fossil feedstock-based processes with sustainable, biomass feedstock-based processes.

Introduction

Over the last several years there has been a rising concern over the use of non-renewable carbon sources for chemical production as they are major contributors to climate change. Most of the modern-day chemicals are produced from fossil resources, especially plastics [1]. Due to the energy needed for these processes, the feedstocks used, and the products produced, these chemical production facilities produced 184.1 million metric tons of CO_2 in 2020 [2]. Production cycles such as these are hurting the planet as CO_2 emissions are causing a global temperature rise. This temperature rise is causing stronger hurricanes, rising sea levels, more droughts and heat waves, etc., and it is only going to get worse if CO_2 emissions are not reduced [3]. However, it is not logical to stop using fossil resources for chemical production because 46% of manufacturing feedstocks used petroleum-based fossil resources in 2018 [4]. Not only is the use of fossil fuels in chemical production contributing to the overall climate crisis, but fossil fuels come from finite resources that eventually will run out. There are many different estimations for when the world will run out of fossil fuels, however, some estimate that as early as 2052 the world will see a significant shortage of these currently essential resources [5]. Due to these rising concerns, it is of utmost importance in the scientific community to work on ways of transforming chemical production into a renewable cycle.

A rising interest in the scientific community is the development of a sustainable catalyst for a reaction known as deoxydehydration (DODH), which converts vicinal diols into olefins with the use of a catalyst. This reaction is of such high interest due to the fact that DODH is a "renewable" reaction that can help in transforming chemical production into a more renewable cycle. The reaction is known to be renewable because the diol reactants can be produced from biomass. Biomass is simply an organic material, with traces of inorganic material, that comes

from plants that can be collected and further converted into chemicals such as the diols used in DODH. The biomass that is collected for chemical production is known as lignocellulosic biomass. Lignocellulosic biomass is non-edible and therefore, harvesting it does not take away from food supplies [6]. There are three main ways in which biomass is converted into fuels and chemicals: gasification, pyrolysis, and hydrolysis. The hydrolysis process is the way in which biomass is transformed into sugar monomer solutions, at low costs, that are then precursors for DODH reactions [6]. Although this paper will not discuss these three ways any further, it will be important in future research to understand the most effective way to create these DODH precursors to be used at an industrial scale. The use of biomass is why DODH is a prominent area of research. Being able to use a sustainable resource for reactants in chemical production instead of an oil reserve that will dry out in the near future allows for a more sustainable future.

Not only is it important for the diol to be sustainable but DODH uses a reductant in the reaction, so it is also important for this chemical to be sustainable. The reductant also forms a byproduct during this reaction, so it is also important that this byproduct is not toxic. There are many potential reductants that could be used for this reaction and this paper will not investigate every option. However, an example of a common reductant is triphenylphosphine (PPh_3). PPh_3 is known to be a renewable chemical and the byproduct that it produces is triphenylphosphine oxide. Triphenylphosphine oxide is a nontoxic chemical and has the potential to be collected and used in other processes. Triphenylphosphine oxide can be used as a solvent to activate crystallization of chemical compounds [7]. Although there are many other examples, this gives a glimpse of the renewable factor that needs to be considered when choosing the right reductant.

The DODH reaction does not produce useful chemicals directly, instead, it is used to produce valuable olefins known as platform molecules. These platform molecules can then be

used further in the production of valuable chemicals. Although this direction for chemical production sounds good in theory, there is still extensive knowledge to learn about the DODH reaction before it can be used on an industrial scale. Currently, there is ongoing research surrounding developing a sustainable and effective catalyst in hopes of one day industrializing the process. The most promising results have come from the use of metal complex catalysts that contain one of the following metals: vanadium, molybdenum, and rhenium. High oxidation state rhenium catalysts have produced the best results with product yields of well over 80%. Due to the high cost of rhenium, vanadium and molybdenum catalysts are of interest, however, they have not reached yields nearly as high as the rhenium catalysts. Since DODH research is relatively new there are still many questions that have yet to be answered. These questions include, what can be done to lower the cost of catalyst? Why are catalysts becoming less active after a few runs and how can that be fixed? And why does the presence of ammonium ions increase product yield? There has been some research to try to answer these questions, however, the mysteries surrounding ammonium ions are the main interest of this research.

When first looking at why ammonium ions may have effect an on DODH reactions, it is important to understand the reaction mechanism. The way in which counterions interact with the diol/intermediates during the reaction has been proposed by Shakeri et al. and can be seen in Figure 1. Figure 1 suggests that the counterion, seen as Z^+, is playing some role in reaction progression [8]. Principally, the cation is not expected to play a very important role in the reactions since the active species is the anionic complex of an active metal. However, data in the literature clearly show that catalysts containing the same anion, but different cations exhibit different activity. This will be discussed further in the literature review. Understanding this

mechanism further along with the reasons for differences in activities could provide important insight that may allow for the opportunity to tune the catalysts.
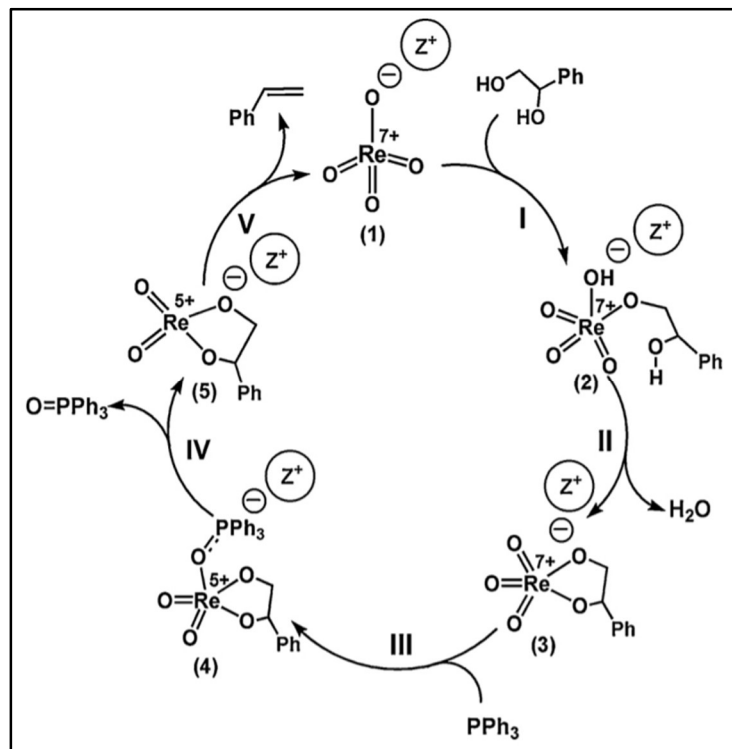
Figure 1: Proposed reaction mechanism for the DODH reaction of phenyl-1,2-ethanediol to styrene in the presence of $Z^+ReO_4^-$ and PPh_3 as the catalyst and the reductant, respectively [8]

Literature Review

Deoxydehydration Reaction Mechanism

Before diving into the heart of DODH research, it is important to understand what the reaction mechanism looks like. A broad overview of the reaction scheme can be seen in Figure 2. As shown, the production of olefins comes from removing the OH groups of the diol with the use

of a strong reductant. The reaction takes place in the presence of a high oxidation state (group V-VII) transition metal complex to promote faster reduction. The majority of DODH research focuses on finding the most effective catalysts and reductant combinations to have a high yield of olefins. A more in-depth look at the reaction mechanism can be seen in Figure 3. In theory, the reaction begins with the diol attaching to the metal catalyst and releasing water along with it. From there, the reductant is used to remove the double-bonded oxygen from the metal complex. Although these complexes are known to form, the order that these steps take place is still up for debate and another potential area of research. The reaction then goes through "olefin extrusion" thus completing the reaction and regenerating the catalyst [10]. Although researchers are confident in this general mechanism, the way that certain ions and other compounds affect the reaction is often unknown. These unknown effects will be discussed later in the paper.
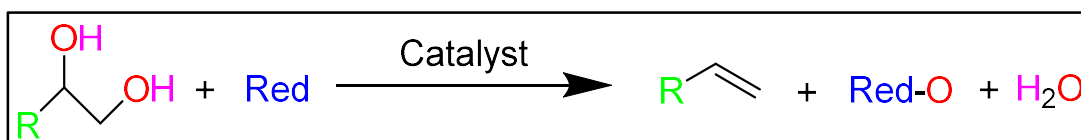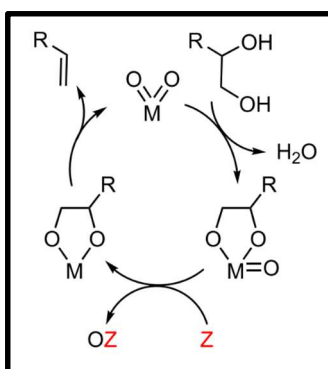

Figure 2: DODH Reaction Scheme

Figure 3: Reaction Mechanism for DODH [10]

Figure reprinted from "Deoxydehydration of vicinal diols by homogeneous catalysts: a mechanistic overview" by DeNike et al. [10]

Current Metal Catalysts Used in DODH

Looking for the perfect catalyst to use in DODH is an ongoing area of research with many different research groups using different metals, supports, etc. in attempts to find the most effective combination. There are many things to consider when deciding which catalyst to test. Such as using a heterogeneous or homogeneous catalyst, using a supported or unsupported catalyst, and many other factors. Not only are these considered, but it is also very important to choose a metal that will be catalytically active. Throughout the literature, there are three metals that are widely used and have shown the highest activity. Those three metals are vanadium, molybdenum, and rhenium. In the next few sections, this paper will discuss the combinations that have been used in the past and where the best results are being obtained relevant to the scope of this review.

Vanadium-Based Catalysts

The use of vanadium-based catalysts is of interest due to the fact that they are cheaper than most rhenium and molybdenum catalysts. In 2018 a research group from the University of Denmark used ammonium vanadate (NH_4VO_3) to reduce glycerol into allyl alcohol. At a reaction temperature of 275 °C and reaction time of 5 hours, they were able to obtain an allyl alcohol yield of 22% [11]. After proving the activity of this catalyst, they tested other vanadium-based catalysts such as $NaVO_3$ and V_2O_4, however, none of them produced yields that were as good or better than NH_4VO_3. The research group proposed that the ammonium vanadate may have had better solubility than the other catalysts, hence producing higher catalytic activity. They also tested other widely used catalysts such as methyltrioxorhenium (MTO). Once again, MTO did not show more

catalytic activity than the ammonium vanadate, as the MTO only produced 17% yields of allyl alcohol [11].

Another example of the use of vanadium catalyst comes from a dissertation by Sharkey from the University of Massachusetts in 2020. Sharkey did work with all three of the common metal catalysts and also used ammonium vanadate. As with the research group from Denmark, Sharkey saw the best yields from the ammonium vanadate compared to other vanadium complexes. However, the 14% alkene yield did not stand up to the yields produced from the rhenium catalysts which were as high as 87% [12].

Molybdenum-Based Catalysts

Similar to vanadium-based catalysts, molybdenum catalysts are of great interest because of the earth's abundance and relatively low cost of these Mo catalysts when compared to desired rhenium catalysts [13]. In 2019 a research group from the University of Arkansas wanted to observe whether these Mo catalysts could replace the expensive Re catalysts. Due to previous research showing that ammonium heptamolybdate was active in DODH but showed very low alkene yields at harsh conditions, this research group decided to use a "Mo-dioxo complex bearing a chelating pincer ligand" [13]. This new type of catalyst showed to be relatively active as it produced yields as high as 59%. At the time this was the highest yield seen from any molybdenum catalyst and was performed at much lower temperatures, around 150 °C, than past research [13]. This research is definitely a step in the right direction for a cheaper and effective DODH catalyst.

In 2020, a research group from Utrecht University made significant progress with higher yields from molybdenum-based catalysts. In this case, they used [Cp*MoO$_2$]$_2$O where the

Cp=1,2,3,4,5-pentamethylcyclopentadienyl to reduce aliphatic vicinal diols. With these

components, the reaction was able to reach alkene yields of up to 65% with an olefin selectivity

of 91% [14]. However, this reaction needed to take place at a relatively high temperature of

200 °C which is not ideal as this requires more energy if ever to be used at an industrial scale

[14]. So, although these results show higher yields than the research at the University of

Arkansas, the much higher reaction temperatures put a damper on the significance of the 65%

yield.

Once again looking at the dissertation presented by Sharkey, more molybdenum catalyst

tests can be found. Within the many experiments presented, the molybdenum complexes that

showed the most significant yields were anionic molybdenum salts with ammonium as the

cation. Specifically, $(NH_4)_2MoO_4$ produced the highest yield with a value of 52% and full

conversion of the reactant [12]. Other ammonium molybdate complexes showed similar yields as

seen in Table 1. An interesting idea to come out of this research is that these ammonium

complexes showed the best results, leading to the thought that ammonium ions may have an

effect on the activity of these catalysts [12]. This idea will be built upon further in this paper.

Table 1: Various Molybdenum Catalyst Results [12]

Catalyst	Time (h)	Diol Conversion (%)	Alkene Yield (%)	Selectivity (%)	Activity (mol alkene)(mol Metal)$^{-1}$h^{-1}
$(NH_4)_2MoO_4$	21	100	52	52	0.49
	5	74	32	42	1.21
$(NH_4)_2Mo_2O_7$	21	100	48	48	0.42
	5	62	25	41	0.79
$(NH_4)_6Mo_7O_{24}$	21	100	52	52	0.42
	5	54	21	38	0.83

Table reprinted from Sharkey dissertation "Development and Characterization of Robust and Cost-Effective Catalysts for Selective Biomass Upgrading to Fuels and Chemicals by Deoxydehydration." [12]

Rhenium-Based Catalysts

Rhenium-based catalysts have shown the most promising results of the three metals as rhenium has produced the highest yields in many different forms. Although these catalysts are rather expensive, for the time being, they have the largest potential for industrial use. In 2018, a research group from the University of Louisiana used methyltrioxorhenium (MTO) to produce alkene yields of 72% [15]. In 2020, a research group from Utrecht University used ReO_2^+ ligand-supported catalysts and saw alkene yields of well over 90% [16]. Also in 2020, Sharkey saw the most promising yields from rhenium catalysts as well. Supported rhenium oxide catalysts show the best results with yields of well over 80% [12]. These are just a few of the many works that discuss the great success of using rhenium catalysts in many forms.

Rhenium catalysts are not only the most active, but they also seem to be the most versatile as they have been explored through the world of nanoparticles. In 2019, a research group from the University of California prepared unsupported rhenium oxide nanoparticles to use as a heterogeneous catalyst for DODH. Using these nanoparticle catalysts produces very

good yields with the optimized yields being above 80% [17]. Another interesting example of the use of rhenium oxide nanoparticles comes from the same research group out of the University of California in 2020 when they explored these catalysts further. In this research, they were converting tartaric acid into γ-butyrolactone which they were able to do with similar yields of well over 80% [18]. It is also important to note that these nanoparticle catalysts have shown great recyclability which is very promising as this is a feature lacking in many other DODH catalysts.

Not only are rhenium-based catalysts being tested with nanoparticles, but they are also being shown to be effective on zeolites. In 2021, a research group from Aachen University used ammonium perrhenate supported on different zeolite types. Meiners et al. used H-β, H-ZSM-5, and H-Y zeolites, and they all were shown to be relatively active. The productivity of these catalysts was measured after only 0.5 hours and Meiners et al. saw excellent results with productivity reaching $0.24 \text{ mol}_{\text{1-hexene}} * g_{\text{Re}}^{-1} * h^{-1}$. These results outperformed any other supported rhenium catalysts in the literature. Once again, these zeolite catalysts were shown to have more recyclability compared to the metal-oxide supported rhenium catalysts in past research [19].

Problems Surrounding DODH Research

DODH is starting to show very promising results with the development of new catalysts such as zeolite-supported rhenium catalysts or rhenium oxide nanoparticles, however, there are still a lot of problems that remain in the research area.

High Catalyst Cost

One of the most pressing issues with the DODH reaction is the high cost of the catalyst, especially rhenium. With rhenium showing the most promise for effective DODH, it is important

to make sure using these catalysts will not be too expensive. When comparing the prices of the three common metals used, the price discrepancies can be seen easily. Rhenium has an average cost of $1,300 per kg, molybdenum has an average cost of $44.39 per kg, and vanadium has an average cost of around $30 per kg [20-22]. From this price comparison, it is very clear that using rhenium on an industrial scale would not be effective from an economic point of view. This is why so many research groups are attempting to find ways to make molybdenum catalysts more effective as they are significantly cheaper. Also, due to the high cost of rhenium, it is very important for the rhenium catalyst to have a high turnover number before deteriorating and needing to be replaced. This is because if the catalyst can last for several reactions, then maybe the high cost is a negative factor that can be overlooked. However, if the catalyst is significantly less active after one or two runs, then replacing the catalyst will cost a lot of money. If it is found that these molybdenum and vanadium catalysts will never be as effective as rhenium, it then becomes a question for a company that wants to industrialize this process whether the high cost of the catalyst is worth it to make these valuable products.

Leaching Causing a Decrease in Catalytic Activity

Another major problem in catalytic DODH research is that solid rhenium catalysts are known to have terrible recyclability and often significantly decrease in activity after only a few runs. The exact cause of this deactivation is unknown, however, it is hypothesized that it is most likely due to the fact that rhenium is dissolving into the solution. After dissolving, the rhenium is not moving back out of the solution, therefore, decreasing the rhenium concentration on the catalyst over a very short time. In 2019, Sharkey and Jentoft wanted to further understand this leaching issue and did some research on how much rhenium is leaching and how much

deactivation is occurring. Some of the significant results from this experiment can be seen in Figure 4. As seen, the catalysts that were very active in the initial runs lost a significant amount of activity after the first run. Then, looking at the graph on the right, we can see that this decrease in activity is directly related to how much rhenium is being leached into the solution [23]. This direct correlation proves that these rhenium catalysts are not sustainable and, along with the high cost, it is important to keep researching catalysts that exhibit less of this behavior, such as the nanoparticle or zeolite catalysts mentioned earlier in this paper.
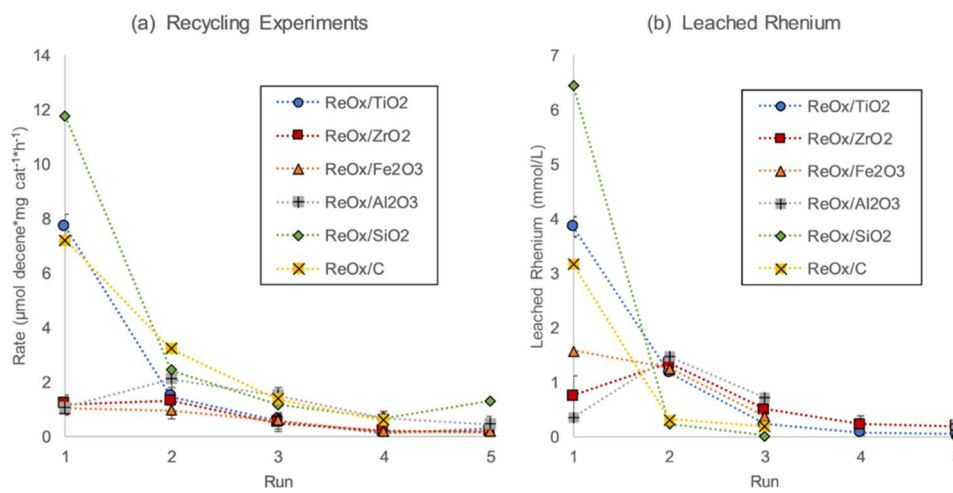

Figure 4: (a) Catalyst activity over multiple runs showing the deactivation over time (b) leached rhenium over time showing that deactivation relates to leaching [23]

Finding the Best Reductant

With many different research groups performing their own DODH reactions, there have been a plethora of external reductants used throughout the literature. A question surrounding this is what is the best reductant to use? It is important to choose a reductant that is commercially available and not harmful to the environment so that way it is not adding a lot of extra costs or considerations to the process. Some of the most common reductants used are triphenylphosphine, 1-propanol, 1-octanol, dimethyl-3-pentanol (DMP), etc. All of these reductants have shown significant alkene yields depending on diol choice and reaction condition, and so, there has not been a conclusion on which is best. Due to the vast amounts of possible reductants, in order for this process to one day be commercialized, it is important to find the most efficient and cost-effective reductant.

Questions Regarding the Use of Ammonium Ions

One problem that may be the most interesting of these issues is that there are a lot of questions surrounding the role of ammonium ions in DODH reactions. Many researchers often use commercially available oxidometallates that are typically sodium or ammonium salts. Due to this, it is easy to see any changes in catalytic activity between sodium and ammonium salts. In many DODH articles, an increase in catalytic activity in the presence of ammonium ions has been detected. Why this occurs is still puzzling to many researchers and there have been very few studies that have looked into this issue. This increase in activity has been seen with many different catalysts such as the ammonium vanadate providing the highest yields in the research discussed earlier in this paper. It has also been seen in research done at Purdue University where they saw ammonium perrhenate providing the highest yields compared to other rhenium

complexes [24]. Another researcher that saw this anomaly was Sharkey who saw that not only did the ammonium need to be in the catalyst compound but that adding ammonium chloride with methyltrioxorhenium also increased catalytic activity [12]. The reason for this increase in catalytic activity has yet to be specified. Sharkey was one of the few to do investigative work with these ammonium ion issues, however, despite significant efforts and extensive investigation, there were no conclusive results, and the question is still up for debate. Due to this, the next few sections will be dedicated to discussing potential answers to why these ammonium ions are increasing the effectiveness of these catalysts.

Potential Answers to the Ammonium Ion Question

Do Ammonium Ions Help Increase Homogeneous Catalyst Solubility?

The first thought on how these ammonium ions seem to increase olefin production is that maybe these ions are helping to promote the solubility of the catalyst when using soluble catalysts. There was not really anything found in the literature to explain this phenomenon and give any confirmation that this may be the answer. However, in Sharkey's work, he did look to analyze this and did see that dissolving the catalyst before the reaction promotes better activity. Not only did pre-dissolving the catalyst help, but Sharkey also pre-ground the catalyst which also resulted in increased catalytic activity [12]. This all leads to the idea that it is important for the catalyst to obtain good solubility in the reaction mixture, especially in the reactions performed in this research as it is homogenous catalysis.

Do Ammonium Ions Provide an Activating Counterion?

The idea that ammonium ions provide an activating counterion comes directly from the ideas presented by Shakeri et al. as discussed in the introduction. Shakeri et al. suggests that the counterion interacts specifically with the perrhenate complex in a way that encourages activation [8]. This would then suggest that other counterions such as sodium or potassium are not interacting with the catalyst. There is also a thought that counterions such as sodium and potassium can inhibit catalyst activation.

Do Ammonium Ions Provide an Activating Proton?

Another theory of why ammonium ions seem to promote DODH activity is the possibility that a proton source is required to activate the reaction. Whether this is to activate the catalyst or simply act as a catalyst on its own is still up for debate, however, there is some evidence that may provide some insight. The first researchers that suggested this theory was the research group from Purdue University that was mentioned earlier. They had seen that solid rhenium catalysts that contained ammonium counter ions produced much higher yields than those without [24]. They suggested that there is a "need for proton or an activating cation to be associated with the perrhenate anion to make it catalytically viable" [24]. Although they are suggesting a need for a proton for perrhenate catalysts, other catalysts should share this need for an activating proton source. Outside of using metal catalysts for DODH, a research group from the Taiyuan University of Technology used formic acid without the presence of a catalyst to effectively facilitate a DODH reaction [25]. These show an effect of using a Bronsted acid, and therefore, there is a possibility that the ammonium protons are acting as a promoter and helping the reaction proceed on its own.

Do Ammonium Ions Act as a Reductant?

The final theory is that the ammonium is acting as a weak reductant and participating in the reduction process. As discussed earlier and seen in Figure 1, DODH only occurs in the presence of a reductant. So, maybe ammonium is acting as the reductant in small amounts which is leading to more product creation. This may seem to be the easiest explanation; however, it also seems to be the most improbable. This is due to the fact that nowhere in the literature has ammonium been used as a reducing agent before and ammonium has never been known to exhibit these properties. Although ammonia is often used as a reductant, such as ammonia borane being used in the reduction of organic compounds, its counterpart ammonium has not seen the same successful use [26]. Not only is ammonium not actively known as a reductant, but Sharkey did also attempt to see how well ammonium performed at reducing diols, and the results were not promising. When using ammonium chloride as a reductant (and varying catalysts) the highest yield that was able to be obtained was only 9% [12]. Comparing this to using triphenylphosphine as a reductant, which produced yields over 80%, the ammonium was not a good reductant [12]. Although there have been no signs pointing to ammonium acting as a reductant, it is still a possibility that it is a very weak reductant and should not be discounted. Along with ammonium acting as a reducing agent, it has been theorized that the diol itself could serve as a reductant. Although this has not been proven, DODH without an external reductant has demonstrated the ability to produce alkenes [27]. This implies that it is not 100% true to say an external reductant is required for this reaction. Given all this, there are still several questions surrounding DODH reductants and ammonium ions should not be discounted.

Objective

Overall, the vast gap in knowledge surrounding the effects of ammonium ions in DODH reactions was the main motivation for the research performed in this paper. There are a lot of potential reasons that ammonium ions are increasing catalytic activity. This research dives into the ones discussed above in attempts to bring clarity to each of them in hopes to better understand DODH and the mechanism that surrounds it.

Approach and Rationale for Approach

Investigation of Catalyst Dissolution Kinetics with IR Spectroscopy

When looking at the first hypothesis in which it is suggested that ammonium ions help catalyst solubility, the easiest way to determine this would be to look at solubility kinetics. By using IR spectroscopy, graphs can be generated that show the amount of catalyst dissolved over time. This can be done for perrhenate catalysts with different counterion to see if the ammonium perrhenate clearly dissolves faster than others.

Determining a Solvent in Which Full Catalyst Dissolution is Obtained

An alternative method to determine whether ammonium ions help catalyst solubility is to have the catalyst fully dissolved before the reaction takes place. In order to do this, there first needs to be a solvent in which it is known that perrhenate catalyst can reach full dissolution. Therefore, tests were done to determine this solvent.

Analyzing the Effect of Ammonium Ions on Catalyst Solubility

Once a solvent has been found in which full catalyst dissolution can be obtained, a reaction can be performed to test the effects of catalyst solubility in a reaction. In this reaction,

the catalyst will be fully dissolved before the reaction takes place. The reason for this is that it now prevents solubility effects from being able to cause differences in catalyst activities. If the catalyst is fully dissolved before the reaction takes place, and the reason for differences in catalyst activities is due to solubility differences, then these new reaction results should see similar yields between all perrhenate catalysts.

Investigating the Counterion Effect of Ammonium Ions

As mentioned in previous sections, there is a hypothesis in which the catalyst counterion interacts with the catalyst to help its structural arrangement to allow it to perform better in reactions. To test this, crown ethers were utilized and added to all perrhenate reactions. Crown ethers are cyclic molecules that utilize internal oxygens to capture cations and prevent them from interacting/reacting with other molecules around it. So, crown ethers were added in attempts to encapsulate the counterion so it can no longer interact with anything [28].

Using Boric Acid to Analyze Acidic Effects on Catalyst Activation

As discussed, there is thought that the ammonium ions provide an acid that helps in catalytic activation. To test this, reactions were performed in which boric acid was added. The reason boric acid was used is because it has a similar acidity as ammonium ions. To be specific, the pKa of ammonium ions is 9.3 while the pKa of boric acid is 9.15 [29,30]. The boric acid was added in stoichiometric amounts to the amount of ammonium ions usually in solution when ammonium perrhenate is used.

Investigating the Effect of Ammonium Ions as Reductants

It is difficult to determine if ammonium ions act as a reductant as there are other things that can act as a reductant. As discussed, it has been seen that the solvent can act as a reductant along with the diol itself. In attempts to single out the ammonium ions acting as a reductant, ammonium chloride was used. Previous reactions have been performed in which only the diol and reductant were present, with no catalyst. These reactions have shown small conversions and yields. Due to this, this reaction was performed again but now in the presence of ammonium ions. Catalysts were not used in this reaction as it allows for the investigation of ammonium ions effects without the chance that the ammonium ions are once again interacting with the catalyst and helping it activate in that way.

Methods

Investigation of Catalyst Dissolution Kinetics with IR Spectroscopy

To first investigate catalyst solubility kinetics, a Mettler Toledo ReactIR probe was used to record IR spectra of dissolving catalysts. Three solutions with ammonium perrhenate catalyst in water were created. The solutions had increasing molarities of 0.01 M, 0.05 M, and 0.1 M. Ammonium molybdate and ammonium vanadate were tested in similar fashions at concentrations of 0.01 M and 0.05 M. After the water solvent tests, two solutions of decanediol in toluene were tested at diol concentrations of 0.2 M and 0.3 M. Results from these tests were insignificant and will be discussed more in the results section.

Determining a Solvent in Which Full Catalyst Dissolution is Obtained

A few different solvents were explored in attempts to find a solvent in which the desired catalysts reach full dissolution. To do this, 0.01 M solutions of both ammonium perrhenate and sodium perrhenate were created in the following solvents: toluene, 1-octanol, 2-propanol, and 1-propanol. Decanediol was added to all solutions at a concentration of 0.2 M. Solutions were stirred for an extended period of time in order to observe if full dissolution occurred. If full dissolution did not occur over a few hours, heat was often added to attempt to increase solubility.

Analyzing the Effect of Ammonium Ions on Catalyst Solubility

To do this, five-hour reactions were performed in which catalysts were fully dissolved before the reaction. First, a 25 ml stock solution was created with 1-propanol, 0.2 M decanediol, and 0.1 M hexadecane (internal standard). Then, 5 ml of stock solution was added to Ace reaction tubes. Ammonium perrhenate and sodium perrhenate were then added to respective reaction tubes at a concentration of 0.01 M. This allows for a 20:1 ratio of diol to catalyst. After the catalysts were fully dissolved, triphenylphosphine was added with a 0.23 M concentration. Reactions took place at 150 °C. All post-reaction solutions were analyzed using gas chromatography.

Investigating the Counterion Effect of Ammonium Ions

Once again, five-hour reactions were performed, however, crown ethers (18-crown-6) were added to every reaction. Crown ethers were added in slight excess to the catalyst. The three catalysts used were ammonium perrhenate, sodium perrhenate, and potassium perrhenate at a concentration of 0.01 M. Once again 1-propanol was used as the solvent, 0.2 M decanediol, 0.1

M hexadecane, and 0.23 M triphenylphosphine were added. Reaction temperature was controlled at 150 °C. All post-reaction solutions were analyzed using gas chromatography.

Using Boric Acid to Analyze Acidic Effects on Catalyst Activation

When attempting to understand the effect of an acid in DODH reactions were performed with sodium and potassium perrhenate at 0.01 M and boric acid had a concentration of 0.01 M. All other reaction conditions are the same as above.

Investigating the Effect of Ammonium Ions as Reductants

To analyze the effects of ammonium chloride in DODH three reactions were performed with various reductants. The first reaction contained both a triphenylphosphine reductant along with ammonium chloride. The second only had PPh_3. The third only had ammonium chloride. In all cases the ammonium chloride concentration used was 0.23 M. All other conditions are the same as previous reactions.

Results and Discussion

Investigation of Catalyst Dissolution Kinetics with IR Spectroscopy

After performing several tests in which the ammonium perrhenate concentration in water was increased all the way up to 0.1 M, the IR spectra graph did not show any peaks that represented dissolved catalyst. It was expected to see absorption bands at wavenumbers of around 800 cm^{-1}, 1400 cm^{-1}, and 3200 cm^{-1} as seen in Figure 5 [31]. No peaks were seen with the decanediol solutions as well, even when the diol concentration was increased to 0.3 M. Therefore, since the one thing that was desired to monitor over time could not be detected, it was

determined that using IR kinetics of dissolution would not be a good way to answer the solubility questions. Therefore, it was then desired to find a solvent in which the catalyst fully dissolves, to remove any complications from solubility during the reaction.
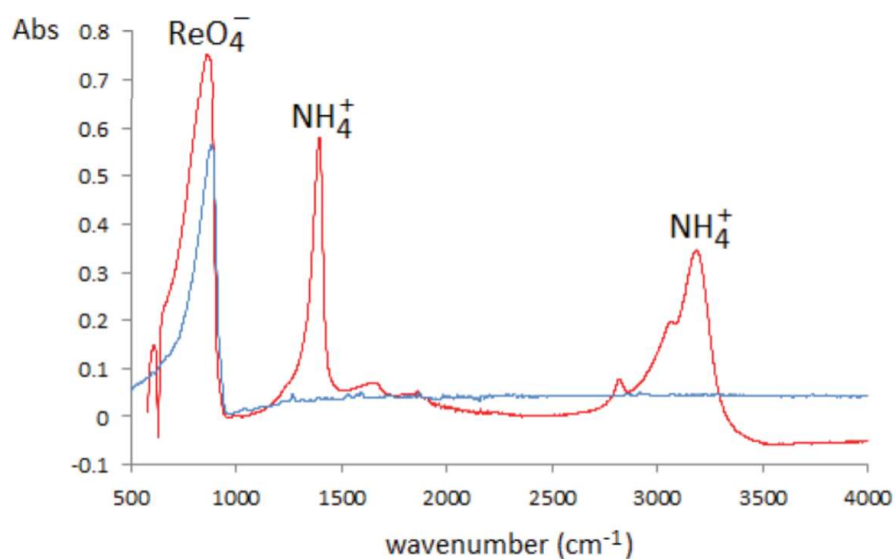

Figure 5: Ammonium perrhenate IR spectra represented by the red line [31]

Figure reprinted from "Production and Analysis of Recycled Ammonium Perrhenate from CMSX-4 Superalloys", Gonzalez-Rodriguez et al. [31]

Determining a Solvent in Which Full Catalyst Dissolution is Obtained

Table 2 provides a summary of all the different solvent, catalyst combinations tested and whether full catalyst dissolution was seen. It was decided that the best solvent to use would be 1-propanol as we see full dissolution of both catalysts. The reason why 2-propanol was not used is because secondary alcohols have been known to act as a reducing agent in the past and it is not desired to add more factors into the reaction. It is important to note that pre-dissolving the diol, before the catalyst, is required to get full dissolution at room temperature.

Table 2: Results of catalyst solubility tests

Catalyst	Solvent	Full Dissolution
Ammonium Perrhenate	Toluene	No
Sodium Perrhenate	Toluene	No
Ammonium Perrhenate	1-Octanol	No
Sodium Perrhenate	1-Octanol	No
Ammonium Perrhenate	2-Propanol	Yes
Sodium Perrhenate	2-Propanol	Yes
Ammonium Perrhenate	1-Propanol	Yes
Sodium Perrhenate	1-Propanol	Yes

Another small test was performed to investigate the difference in catalyst solubility in which ammonium perrhenate and sodium perrhenate were added to their own reaction tubes in the presence of 1-propanol and decanediol. The solutions were stirred continuously and monitored to see how long it too for each catalyst to dissolve. This would indicate whether ammonium-based catalysts do in fact dissolve faster than others. Although, from the results above, we know that solubility is not a major cause of activity differences, it still could be playing a small role. However, since the catalyst being fully dissolved is only determined visually, it is hard to see the exact moments when each catalyst is dissolved. So, the test showed that both catalysts seemed to be fully dissolved after about 30 minutes but no significant difference in solubility time was discovered.

Analyzing the Effect of Ammonium Ions on Catalyst Solubility

The results from this test can be found in Figure 6. To best understand these results, it is important to note what is being looked for. If both the catalysts were dissolved before the reaction took place, then catalyst solubility is no longer in question. So, if ammonium ions were only helping the solubility of the catalyst, then both catalysts should produce the same conversions and yields. There then should be no differences in catalysts. However, this is not the case. There is still a large difference in the conversions and yields with the ammonium perrhenate when compared to the sodium perrhenate. Therefore, it can be concluded that there must be another factor that is causing this vast difference in catalytic activity.
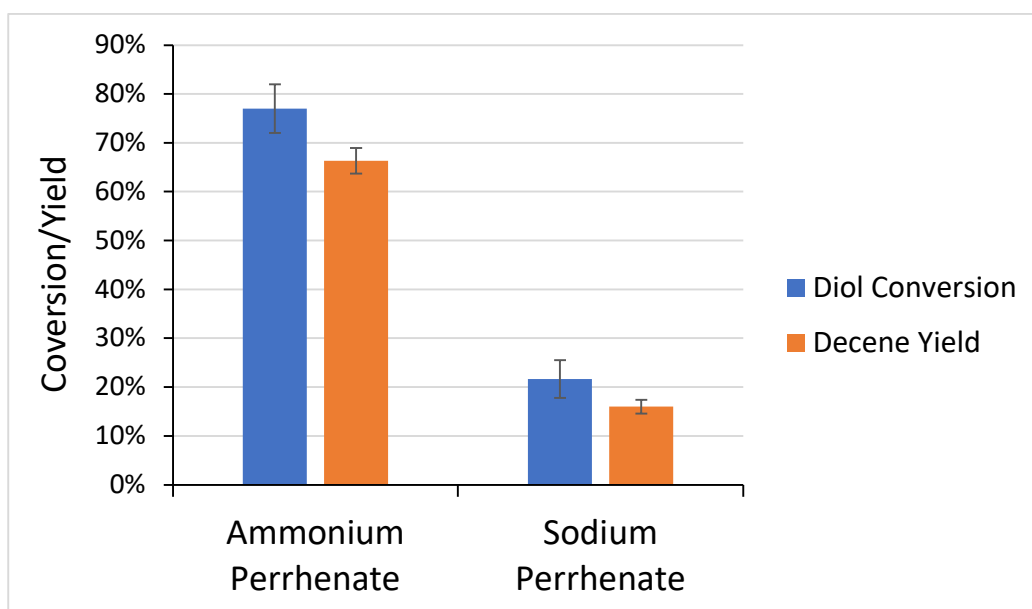

Figure 6: 5-hour reaction in which catalysts were fully dissolved before the reaction. 150 °C, 5 mL, 1-propanol solvent, 0.2 M decanediol, 0.23 M PPh_3, 0.1 M hexadecane, 0.01 M rhenium

Investigating the Counterion Effect of Ammonium Ions

The results from the reactions with crown ethers present can be seen in Figure 7. The conversions and yields continue to be consistent with what has been seen in the past. The ammonium perrhenate still produces much higher conversions and yields than the other catalysts.

This was not as expected for this reaction. Once again, it was expected that all the perrhenates would perform at a very similar level if the counterion is being encapsulated by the crown ethers. There was a thought that 18-crown-6 is the not the best for capturing ammonium ions, however, literature suggests that the 18-crown-6 ability to capture ammonium and sodium is very comparable. The log K for ammonium reacting with 18-crown-6 is 4.32 while the log K for sodium is 4.36. Both are for a methanol solvent [32]. So, it seems that in this case the crown ethers are not working effectively and there is the potential that more would need to be added. However, based on these test results, nothing significant can be concluded about the counterion interaction with the catalyst.
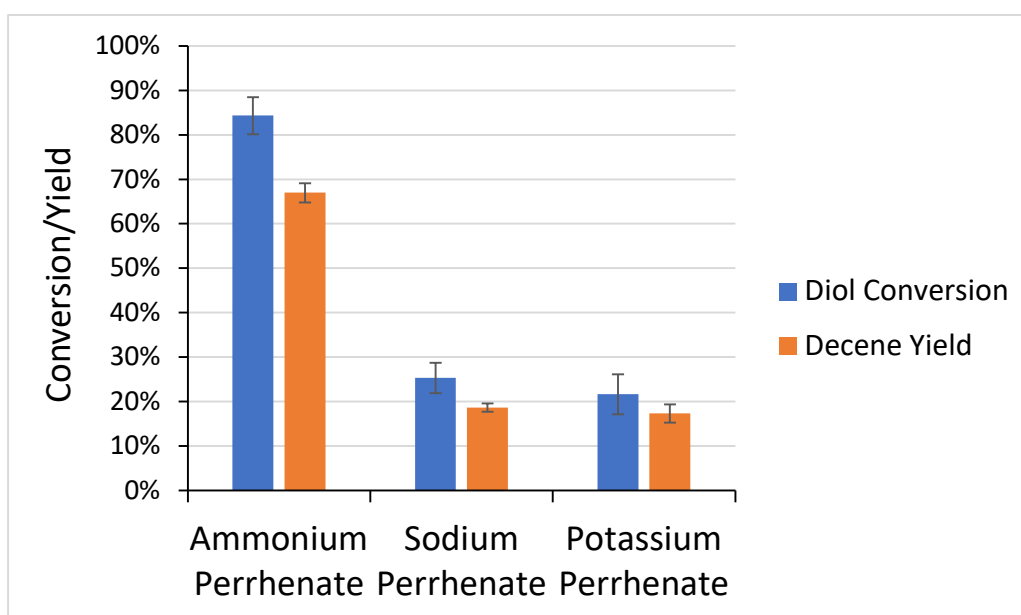

Figure 7: 5-hour reaction in which catalysts were fully dissolved before the reaction. Crown ethers were present to limit counterion interaction. 150 °C, 5 mL, 1-propanol solvent, 0.2 M decanediol, 0.23 M PPh_3, 0.1 M hexadecane, 0.01 M rhenium, 0.012 M 18-crown-6

Although these results were not as expected, they did help confirm that solubility is not a major factor. When crown ethers were used, the solubility of all catalysts improved. In fact,

potassium perrhenate would not dissolve at all in 1-propanol until crown ethers were present. As mentioned, catalyst solubility is only determined by visual inspection which means that in the previous tests, although it looked like all the catalyst was dissolved, some small amounts could have not been. However, since the crown ethers seemed to help solubility, these tests prove even further than solubility effects are not the major contributor to differences in activity as we still see ammonium perrhenate far outperforming the others.

As discussed in the literature review, there were also thoughts that some counterions may be prohibiting catalyst activation. This meaning that ammonium ions may not be increasing activation, but sodium and potassium may be prohibiting it. However, if the crown ethers were at least capturing the sodium and potassium ions, this would not be the case. If sodium and potassium ions were inhibiting the catalyst but are now encapsulated by crown ethers, then there should be an increase in conversion and yield. This was not the case as the conversions and yields are comparable to previous results within experimental uncertainty. So, it can also be concluded that sodium and potassium ions are not prohibiting catalyst activation.

Using Boric Acid to Analyze Acidic Effects on Catalyst Activation

The results from the tests in which boric acid was added to mimic the acidic effect of ammonium ions can be seen in Figure 8. The conversions and yields obtained from both sodium and potassium perrhenate are comparable with the results seen in previous test. There was no significant sign of catalyst activity increase with the presence of boric acid. Although it may be interesting to try different acids, in this case, it can be concluded that acid presence, with similar acidity to ammonium ions, does not seem to increase catalytic activity. It is important to note that reproduction experiments were not able to be conducted for this test. This should be done in the future to confirm these results and to be able to produce error bars.
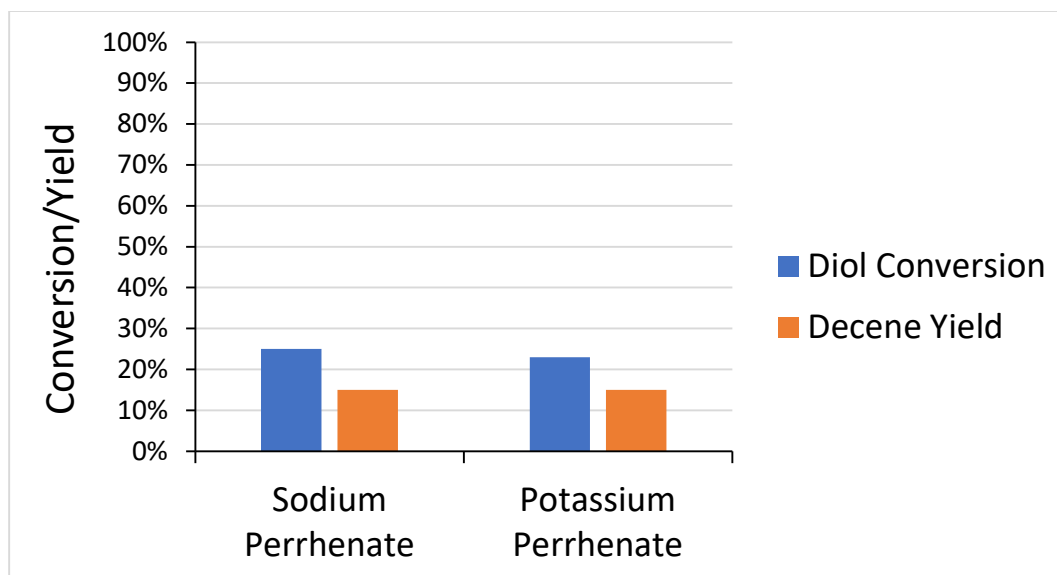
Figure 8: 5-hour reaction in which catalysts were fully dissolved before the reaction. Boric acid was added to mimic the acidity of ammonium ions. 150 °C, 5 mL, 1-propanol solvent, 0.2 M decanediol, 0.23 M PPh_3, 0.1 M hexadecane, 0.01 M rhenium, 0.01 M boric acid.

Investigating the Effect of Ammonium Ions as Reductants

The results from the three experiments done with ammonium salts can be seen in Figure 9. This data shows that there was no increase in conversions and yields with the addition of ammonium chloride. The reaction in which both PPh_3 and NH_4Cl were used has very comparable results to the reaction that uses PPh_3 only. The reaction in which only NH_4Cl is used shows a very small amount of yield. Once again, this could be due to slight reduction of the diol on itself or the solvent as well. Overall, there is no evidence from these results that ammonium ions act as a reducing agent, especially to the high level that would cause the large differences seen in the catalytic reactions. Once again, error bars are not present as reproduction experiments were not able to be performed.
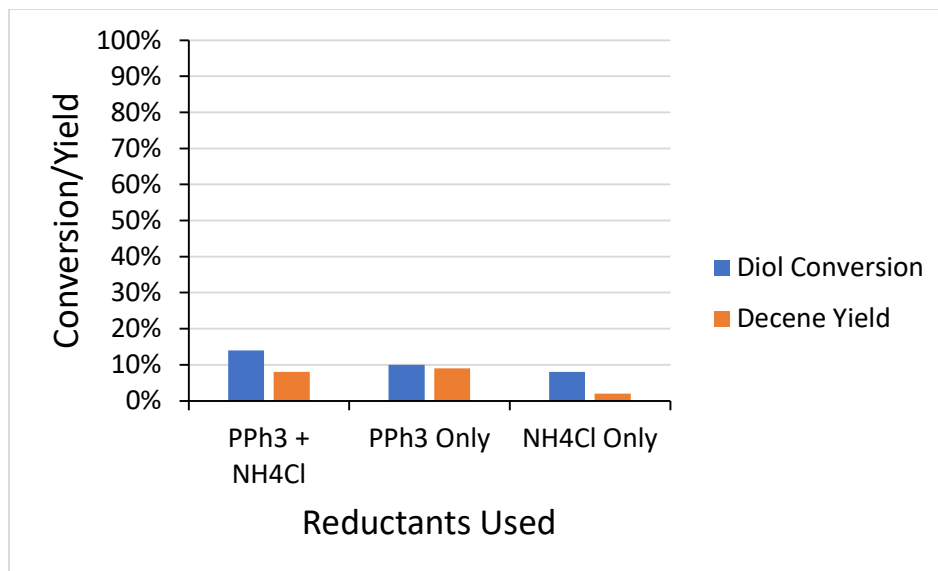
Figure 9: 5-hour reaction with the use of different reductants to analyze the effects of ammonium salts. 150 °C, 5 mL, 1-propanol solvent, 0.2 M decanediol, 0.1 M hexadecane

Conclusions

The overall goal of this paper was to investigate the reasons why ammonium ion presence in DODH reactions increases catalytic activities. As mentioned, there are several literature resources that present this occurrence, and a reason has yet to be determined. There were four hypotheses proposed in this paper and were all investigated with lab-scale experiments. After performing reactions in which the catalysts were fully dissolved before the reaction took place, catalysts that contained ammonium counter ions still showed significantly higher conversions and yields. This led to the conclusion that ammonium ions helping the solubility of the catalyst cannot be the major cause of these differences in activities. The use of crown ethers in the next reactions allowed for prohibiting counterion interaction with the catalysts. Results showed that counterion encapsulation was not the most effective as ammonium perrhenate was still significantly more effective than sodium and potassium perrhenate. From this, nothing could be concluded. Boric acid was then added to reactions in attempts to mimic the acidic affect of ammonium ions. Once again, sodium and potassium perrhenate reactions still showed low

conversions and yields and did not increase. This suggests that the acidity of ammonium ions is not causing ammonium perrhenate to out-perform other catalysts. Finally, ammonium chloride was used without the presence of catalyst to analyze if ammonium ions can act as reducing agents. Reactions that contained NH_4Cl did not have large increases in conversions and yields. Therefore, this evidence suggests that ammonium ions are not acting as a reductant. Although all of the results in this paper did not point to a specific answer of why ammonium ions increase catalytic activity, the data seems to disprove all these hypotheses which allows for other areas to be explore. This is a large stride in DODH research as ammonium ion investigation has not been the focus of a lot of studies.

Future Work

This research progressed through several different hypotheses for why ammonium ions are seen to increase catalytic activity. As discussed, none were conclusive. This leaves a lot of room open for new and exciting ideas to be researched and developed. For instance, there are ongoing tests to continue this work in which ammonium chloride is still being used but this time in the presence of catalyst. This may give insight to the ammonium ion interacting with the perrhenate complex if conversions and yields seems to go up in the sodium and potassium perrhenate reactions. This is just one thing currently being done; however, new hypotheses will need to be discovered and researched as well.

Also, there are several other tests that could be done to better understand what is going on. For example, finding a good way to determine all the components being reduced in the reaction would help understand the reaction and all the components that are helping in diol reduction. The reason why this is currently difficult to do is that the peaks obtained when running GC analysis are often clumped together, leaving speculation on what every peak

represents. Due to this, it is hard to capture any ammonium reduced products to see if ammonium ions are acting as a reducing agent. This is also something that could be explored. Along with this, relating back to the ammonium salt experiments, ammonium chloride does not dissolve well in 1-propanol. This is something that may not allow for the ammonium ions to be fully present when NH_4Cl is used. Finding a solvent in which catalysts and ammonium chloride readily dissolve may prove beneficial for more experiments of this type.

There are many areas to explore when attempting to understand the full DODH mechanism and how every component interacts during the reaction. Aside from ammonium ions, the literature suggests there is a plethora of other areas of exploration as well. There is still room for growth in finding less expensive alternatives, solid catalysts that do not leach, etc. DODH is a very promising way to help in the fight against climate change as it will allow for the production of chemicals from a biomass source, however, a lot of work still needs to be done before this reaction can be used in commercialized processes.

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Appendix

GC Calibrations

- <u>Retention Times</u>

Compound	Retention Time (min)
1,2-Decanediol	11.197
Triphenylphosphine	14.975
Hexadecane	11.987
1-Decene	7.06

- <u>Response Factors Used in Calculations (with respect to hexadecane)</u>
  - Response factors obtained from Dr. Sharkey's data [9]

Compound	Response Factor
1,2-Decanediol	0.4519
1-Decene	0.6552

GC Conditions

- For GC analysis flame ionization detection (FID) was used in which hydrogen gas was used for the air flame.

- The program used to run the GC that specified the temperature, flow rates, etc. was set up by Dr. Sharkey and was not altered for this project.

Sample Calculations

Diol Conversion

In order to calculate diol conversion, we first need beginning and final concentrations. The beginning concentration was calculated based on the creation of the stock solution and can be seen below.

$$Cd\_i = Md / (MWd * Vs)$$

Where Cd_i is the initial diol concentration, Md is the mass (grams) of diol added, MWd is the molecular weight (g/mol) of the diol and Vs is the volume of the stock solution (L).

Then, the final diol concentration was calculated using peak areas from the chromatogram and known response factors.

$$Cd\_f = (Ad * Ch) / (Ah * Rf)$$

Where Cd_f is the final diol concentration, Ad is the peak area for the diol, Ah is the peak area for hexadecane, Ch is the known hexadecane concentration, and Rf is the relative response factor for the diol and hexadecane.

The conversion was then calculated as follows.

$$\% \text{ Diol Conversion} = ((Cd\_i - Cd\_f) / Cd\_i) * 100$$

Decene Yield

In order to calculate decene yield, we first need to know the theoretical concentration of the decene with full conversion of the diol. Due to reaction stoichiometry, 1 mole of diol should produce 1 mole of decene.

$$Cdecene\_t = Cd\_i$$

Where $Cdecene\_t$ is the theoretical final concentration of decene and Cd_i is still the known

initial concentration of diol.

Then, the actual decene concentration is calculated from the chromatogram in a similar way the final diol concentration was calculated.

$$Cdecene\_a = (Adecene * Ch) / (Ah * Rf)$$

Where Cdecene_a is the actual decene concentration, Adecene is the peak area for decene, Ah is the peak area for hexadecane, Ch is the known hexadecane concentration, and Rf is a different response factor for decene and hexadecane.

The yield was then calculated as follows.

$$\% \text{ Decene Yield} = (Cdecene\_a / Cdecene\_t) * 100$$