DISSERTATION

CONVERSION OF LIPID BIOMASS TO LIQUID HYDROCARBONS VIA PERICYCLIC

DECARBOXYLATIONS OF α,β- AND β,γ- UNSATURATED FATTY ACIDS USING

POLYCYCLIC AROMATIC HYDROCARBON (PAH) SOLVENT SYSTEMS

Submitted by

Michelle Romanishan

Department of Chemistry

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Colorado State University

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Doctoral Committee:

    Advisor: Debbie C. Crans

    Charles S. Henry
    George Barisas
    Alan Van Orden
    Kenneth Reardon

ABSTRACT

CONVERSION OF LIPID BIOMASS TO LIQUID HYDROCARBONS VIA PERICYCLIC

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POLYCYCLIC AROMATIC HYDROCARBON (PAH) SOLVENT SYSTEMS

Development of a new process for converting lipid biomass, containing α,β- and β,γ-unsaturated fatty acids, to liquid hydrocarbon fuels (LHF) of varying carbon number is described in this dissertation. The theme for LHF production at present revolves around utilizing a catalytic system that requires high temperatures and pressures as well as multiple processing steps. The cost attributed to these types of processes has been a hindrance in moving the economy towards a cost-effective renewable fuel. Investigating possible catalyst-free processing techniques has led to the discovery of a lower energy reaction that utilizes specific unsaturated fatty acids into a cheap, high boiling point solvent system that has the ability to produce pure alkenes as LHF when heated to reflux temperature of the fatty acid.

This sustainable process has been proven to decarboxylate α,β- and β,γ-unsaturated fatty acids via a pericyclic rearrangement. Using a high boiling, polycyclic aromatic hydrocarbon (PAH) solvent, such as phenanthrene or pyrene, pure alkene products in high yields have been obtained from heating α,β- or β,γ-unsaturated fatty acids to a temperature no higher than reflux of the acid. The successful process development and subsequent conversion of lipid-like biomass will be discussed at length and confirmed by ^{1}H NMR and GC/MS.

DEDICATION

This dissertation is dedicated to my parents, Wayne and Olive Romanishan, my

neurosurgeon, Dr. Kevin Judy, and last but not least, Zander.

This dissertation would not have been possible without the support and guidance of many

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CHAPTER 1

INTRODUCTION TO PERICYCLIC DECARBOXYLATIONS FOR THE LOW ENERGY

PROCESSING OF FATTY ACIDS

1.1 INTRODUCTION

In a world of decreasing petroleum resources and increasing pollution from greenhouse gases, the field of renewable energy has advanced with an urgency to provide fuel from renewable sources to an ever-increasing public demand. Research groups have primarily focused on fuel production using techniques such as pyrolysis, catalytic deoxygenation, and esterification, however these process techniques require expensive catalysts as well as high temperatures and pressures to efficiently produce liquid hydrocarbon fuel.[1-8] Due to the fact that these processes have large energy requirements and multiple stages throughout production, these renewable fuels are still too costly to be economically feasible. In order to bring renewably derived fuels efficiently and cost effectively into the economy, a lower energy processing technique is needed.

The principal theme of this dissertation is to utilize the pericyclic decarboxylation of β,γ- and α,β-unsaturated fatty acids for the production of liquid hydrocarbons that are comparable to current transportation fuels using polycyclic aromatic hydrocarbons (PAH) as the solvent system. This process yields pure, liquid hydrocarbons in a single step without the need for catalysts or high temperatures and pressures. A complete process is proposed in Figure 1 and demonstrates how utilizing an appropriate starting material can dramatically decrease the energy required to convert renewable resources into hydrocarbon fuels.
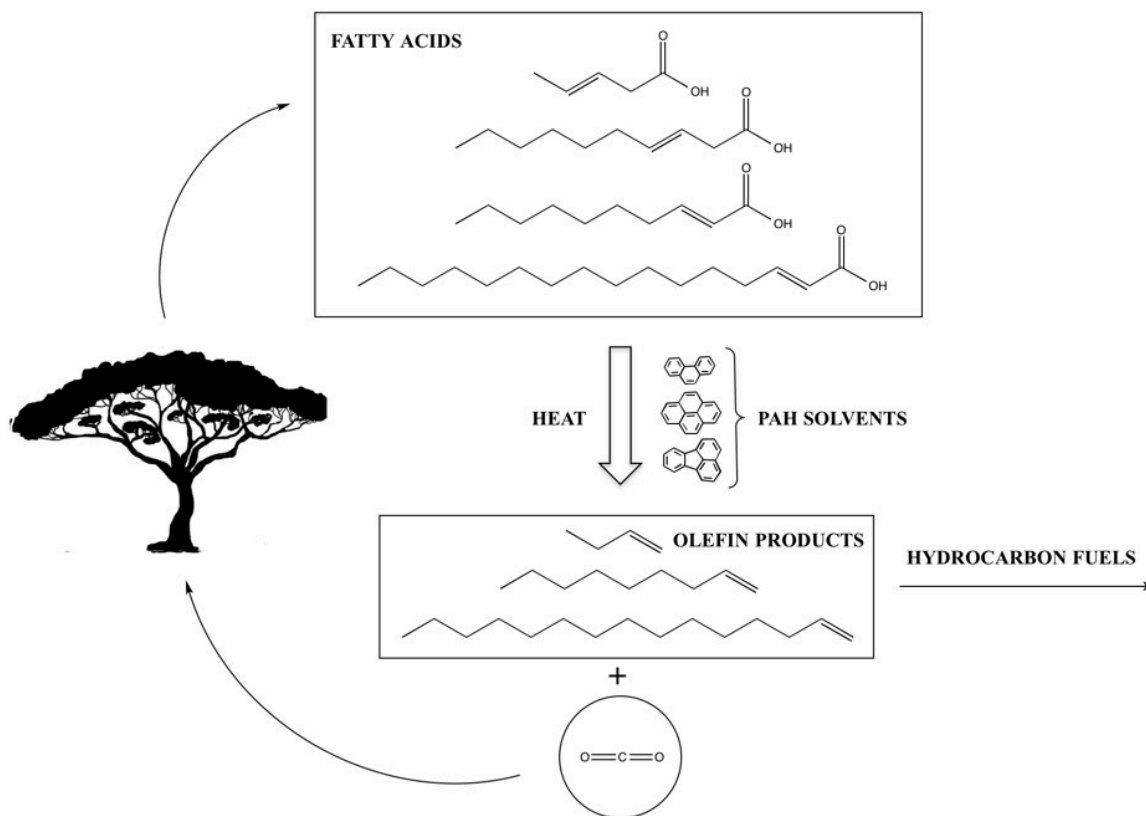
Figure 1.1 Fatty acids from plants, specifically the acacia tree, contain a large concentration of 3-decenoic acid and similar fatty acids. These naturally occurring β,γ- and α,β-unsaturated fatty acids can then proceed to a liquid hydrocarbon product through a single step, non catalytic, pericyclic decarboxylation using PAH solvent systems**.**

1.2 PERICYCLIC DECARBOXYLATIONS

Pericyclic reactions are well known in organic chemistry for being low energy processes that will proceed through a sigmatropic rearrangement, which allows for a concerted movement of electrons to rearrange, create or remove bonds. The Claissen and Cope Rearrangements are governed by this concerted movement; specifically by an allowed, 1,5 sigmatropic rearrangement, and result in a rearrangement of the position of unsaturation within the molecule.[9-11] The Diels Alder reactions are another example of reactions that proceed with a concerted electron density via a cyclic addition to produce a larger molecule from two smaller

ones.[9-11] Pericyclic decarboxylations, although not as well known as the previously named reactions, also follows the allowed, 1,5 sigmatropic rearrangement upon heating and results in the termination of CO_2 to produce an alkene, as can be seen in Figure 1.2. This low energy
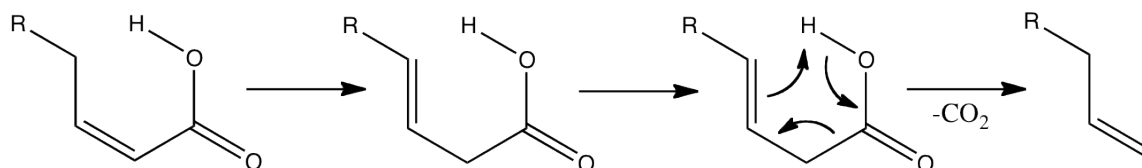
Figure 1. 2 Upon heating, the α,β- unsaturated fatty acids will isomerize to β,γ- unsaturated fatty acids in order to proceed through the thermodynamically favored pericyclic decarboxylation producing CO_2 and a terminal alkene. This terminal alkene is volatile and separates from the parent acid, which allows for the direct collection of liquid hydrocarbon product in a single step.

rearrangement is the motivation behind pursuing β,γ- and α,β- unsaturated fatty acids as potential starting materials for the production of renewable fuels.

Pericyclic decarboxylations have the potential to lower the energy requirements for processing liquid hydrocarbons from renewable resources. By utilizing a cyclic transition state, specific fatty acids can be decarboxylated to a pure olefin product in a single step and without the use of catalyst. D.B. Bigley and coworkers established this reaction with small chain β,γ-unsaturated carboxylic acids in 1964 and showed that by using a polycyclic aromatic hydrocarbon (PAH) solvent system these short chain acids could be decarboxylated without the use of catalyst.[12] Due to the isomerization of the α,β-unsaturated fatty acids to β,γ-unsaturated fatty acids upon heating, these acids are also readily decarboxylated to pure alkene product in a single step.[13,14]

There is a substantially small amount of literature in the field of pericyclic decarboxylations and this can be attributed to the motivation for using sigmatropic rearrangements, which has been highly driven towards building new, larger molecules instead of breaking carbon-carbon bonds. Although pericyclic decarboxylations are rare and have not been

investigated thoroughly in the last century, the low energy requirements needed to produce a pure, alkene product cannot be ignored and will be investigated, using long chain β,γ- and α,β-unsaturated fatty acids as a potential method for renewable fuel production.

1.3 POLYCYCLIC AROMATIC HYDROCARBONS (PAHs)

Polycyclic Aromatic Hydrocarbons (PAHs) are a combination of fused aromatic rings creating a larger, aromatic molecule that is highly stable with high boiling points and low volatilities. Although a large number of these PAHs have been found to be toxic to humans, the PAH solvents studied in this dissertation were not carcinogenic, mutagenic, or teratogens. A significant benefit to using PAHs as solvents, besides the high stability at temperatures above 300 °C, was to take advantage of the lipophilic properties which will fully solubilize the fatty acid oils and allow for complete decarboxylation. Specifically, phenanthrene (PHEN), pyrene (PYR) and mixed solvent system of PHEN:PYR, and fluoranthene (FA) were investigated as PAHs for the pericyclic decarboxylation of β,γ- and α,β- unsaturated fatty acids.

As a solvent, PHEN is only beneficial for short chain fatty acids that have boiling points below 300 °C. This is a problem for the decarboxylation of longer chain unsaturated acids, as most have boiling points that are higher than 300 °C. Therefore, solvent systems such as PYR, FA and various mixtures of PHEN:PYR were investigated to incorporate these long chain fatty acids as potential starting materials for this process without issues of contamination from the corresponding solvent. As long as the reflux temperatures of the fatty acid and the solvent are substantially separated, the reaction will proceed without contaminating the product with unwanted solvent.

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1.4 CONCLUSIONS

The search for a renewable fuel that will support the current infrastructure is a pressing issue. Although there have been significant advances in utilizing corn and other lignocellulosic biomass as renewable sources for fuel production, these processes have been limited economically due to high energy requirements needed to produce the final product. Instead of using common feedstocks and investigating ways to overcome the large energy barrier, this dissertation will describe a starting material, commonly found in the phosphatidyl glycerol of many plants and green algae[15-17], that undergoes a low energy transition upon heating to produce a liquid alkene that can be utilized as fuels.

Five (5) different fatty acids in various polycyclic aromatic hydrocarbon (PAH) solvent systems will be described in detail in the following chapters:

2) Pericyclic Decarboxylation of β,γ- Unsaturated Fatty Acids Using Polycyclic Aromatic Hydrocarbon Solvents: 3-pentenoic acid and 3-decenoic acid

3) Fatty Acids in Nature: Utilizing α,β- to β,γ- Isomerization to Incorporate a Wider Range of Feedstocks for Production of Liquid Hydrocarbons

4) Conjugated and Mixed Unsaturated Fatty Acids Undergo Pericyclic Decarboxylation using Polycyclic Aromatic Hydrocarbon Solvents: 2,4-hexadienoic acid, 3-pentenoic acid and 3-decanoic acid, as well as 2- and 3-decenoic acid

In Chapter 2, the confirmation of pericyclic decarboxylation is demonstrated with the short chain β,γ-unsaturated fatty acid, 3-pentenoic acid and 3-decenoic acid. The fatty acids are heated to reflux in a high boiling point, polycyclic aromatic hydrocarbon (PAH) solvent systems

consisting of either phenanthrene (PHEN), pyrene (PYR), fluoranthene (FA), or mixed ratios of PHEN and PYR (1:1, 1:2, and 2:1 ratios). The short chain fatty acid 3-pentenoic acid was reacted with each PAH above in solvent to substrate ratios of 10:1, 5:1, and 2.5:1 to determine the optimal ratio for olefin production. Reaction mixtures and products were monitored via ^{1}H NMR to confirm the stability of the solvent and the depletion of the reactant over time as well as the formation of a pure, liquid hydrocarbon product. GC/MS was used to analyze the headspace of the liquid product and the reaction mixture to determine product formation and the stability of the PAH solvent over time, respectively. The successful decarboxylation of 3-pentenoic acid to produce 1-butene will be described as well as a longer chain fatty acid, 3-decenoic acid, which was also successfully decarboxylated in the solvents mentioned above. The product, 1-nonene, is a more useful chain length for hydrocarbon fuel, and by utilizing the unsaturation in the β,γ-position, the heat capacity required for conversion to an oxygen-free product is significantly lower than it's saturated counterparts. Figure 1 above shows the general scheme for a renewable source of fatty acids undergoing the subsequent pericyclic decarboxylations to yield CO_2 and a pure liquid hydrocarbon product, capable of competing with current transportation fuels.

In Chapter 3, the issue of low availability of β,γ-unsaturated fatty acids found in renewable feedstocks is addressed. Investigation of the chemistry associated with the low energy pericyclic rearrangement in PAH solvents shows that β,γ-unsaturated fatty acids will readily lose CO_2 to produce a pure olefin. However, it is pertinent to know if the isomerization of the thermodynamically stable α,β-unsaturated fatty acids, readily found in nature, will occur to form the β,γ-unsaturated fatty acid before decarboxylation. This isomerization is essential for the subsequent pericyclic decarboxylation to occur and produce the corresponding hydrocarbon product. The decarboxylation product of 2-decenoic acid was compared to the product from 3-

decenoic acid to confirm the formation of the liquid hydrocarbon product, 1-nonene, for both substrates. Upon the successful decarboxylation of 2-decenoic acid, the decarboxylation of longer chain α,β- unsaturated acids was studied; specifically 2-hexadecenoic acid, readily found in the annual plant *Arabidopsis thaliana*. The major products produced from the complete decarboxylation of both α,β- unsaturated fatty acids were analyzed via ^{1}H NMR and determined to be purely hydrocarbons when using 2:1 PHEN:PYR. However, the products for the α,β- unsaturated fatty acids had a large concentration of smaller chain alkenes and alkanes, revealed via GC/MS, which were not present when decarboxylating β,γ- unsaturated acids. Possible sources of these breakdown products are also addressed in this chapter. ^{1}H NMR and GC/MS were used to confirm hydrocarbon product formation throughout the reaction as well as the stability of the solvent systems over time.

In Chapter 4, the PAH solvent systems described in Chapter 2 were applied to the conjugated fatty acid, 2,4-hexadienoic acid, to demonstrate the PAH solvent system's diversity to readily decarboxylate various fatty acids found in nature without the use of catalysts or high temperature and pressures. The mixed reactants of varying chain length, 3-pentenoic acid and 3-decenoic acid, and bond position, 3- and 2-decenoic acid, were also investigated and the products confirmed by ^{1}H NMR or GC/MS.

A brief summary of the work presented within this dissertation is described in Chapter 5. All publication quality results obtained during the author's graduate studies are described herein, however research that does not pertain to the theme of the dissertation or requires further work to be publishable can be found in the appendices described below:

- Appendix 1: The reflux of β,γ-unsaturated fatty acids in green solvents such as the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate, no solvent (neat) or thermodynamically stable graphite. ^{1}H NMR and GC/MS are used to confirm products, in reactions in which products formed.

- Appendix 2: Research fellowship performed during the summer 2012 at the National Institute for Advanced Industrial Science and Technology in Tsukuba, Japan is described. A synopsis of the author's 9-week fellowship in which heterogeneous, metal-oxide catalysts were synthesized and used in the catalytic conversion of bioethanol to chemicals such as propylene and acetone, currently produced from petroleum feedstocks. The author's participation in the Isao Nakamura laboratory, under the supervision of Tadahiro Fujitani, has advanced the laboratory's database of catalysts by synthesizing and characterizing twenty-one mixed metal-oxide catalysts, in ratios varying from 1-5%. The catalytic conversion of bioethanol to raw materials such as propylene and acetone was studied and quantified using GC/MS. Furthermore, an alternative mechanism than what is currently understood for the catalytic conversion of bioethanol to acetone was discovered. This alternate mechanism is still under investigation in the Nakamura group.

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CHAPTER 2

PERICYCLIC DECARBOXYLATION OF β,γ- UNSATURATED FATTY ACIDS USING

POLYCYCLIC AROMATIC HYDROCARBON SOLVENTS: 3-PENTENOIC ACID AND 3-

DECENOIC ACID

2.1 OVERVIEW

This work is a proof of concept in the pericyclic decarboxylation of short and long chain

β,γ- unsaturated fatty acids, 3-pentenoic acid (lit.[1] bp 192-194 °C) and 3-decenoic acid (lit.[1] bp

278.5 °C). Decarboxylation is facilitated by solvent systems of refluxing polycyclic aromatic

hydrocarbons (PAH), phenanthrene (PHEN, lit.[1] bp 332 °C), pyrene (PYR, lit.[1] bp 404 °C) and

fluoranthene (FA, lit.[1] bp 375 °C) in solvent to substrate ratios of 10:1, 5:1, and ~2.5:1. The

integrity of the solvent system was evaluated using ^{1}H NMR. Products were investigated using

^{1}H NMR to determine purity and observe the complete removal of CO_2 for each reaction system.

The efficiency of the solvent system was evaluated based on the purity and product yields of 1-

butene from 3-pentenoic acid after 24 h in each solvent. PAH solvent systems have boiling

points that will not interfere with the decarboxylation of longer chain fatty acids and is proven by

the successful pericyclic decarboxylation of 3-decenoic acid to 1-nonene, a more useful chain

length for the application of the liquid hydrocarbon as a renewable fuel. To the best of the

author's knowledge, this is the first report of a long chain, β,γ-unsaturated fatty acid undergoing

decarboxylation in PAH systems with confirmation provided by ^{1}H NMR and GC/MS.

Depending on which PAH solvent system was used, a 60-76% product yield was obtained of

which 84 % was found to be 1-nonene via GC/MS.

Although the decarboxylation of fatty acids is exothermic, the activation energy is high

and therefore difficult to carry out in typical organic solvents. However, by utilizing fatty acids

with unsaturation in the β,γ-position and high energy density PAH solvents, the activation energy required is lowered significantly from it's saturated counterparts by the stabilization of cyclic intermediates.

2.2 INTRODUCTION

Fuels from renewable feedstocks have remained expensive or impractical for the general population. The problem partially lies in the starting material chosen and ease of which it is converted into a high-energy hydrocarbon fuel. Lipids are readily found in nature in the form of carboxylic acids, which can undergo an exothermic decarboxylation to provide a pure hydrocarbon product. Although the reaction is exothermic, the activation energy required is typically high and therefore difficult to carry out. However, unsaturation or the presence of a carbonyl on the β carbon lowers this activation energy by stabilizing the reaction intermediate through resonance or by the formation of a more stable, cyclic intermediate, similar to the rearrangement observed in the acid catalysis of β-keto esters.[2-4] Using fatty acids with unsaturation in the β- position will allow for the exploitation of the inherently lower energy, sigmatropic rearrangement occurring upon heating. Therefore, β,γ-unsaturated fatty acids are an ideal renewable feedstock for the production of liquid hydrocarbons via decarboxylation in a single, non-catalytic step. Further demonstration of this can be seen in Figure 2.1.[2-6] Upon heating the fatty acid, the intermolecular rearrangement begins and is stabilized by a cyclic
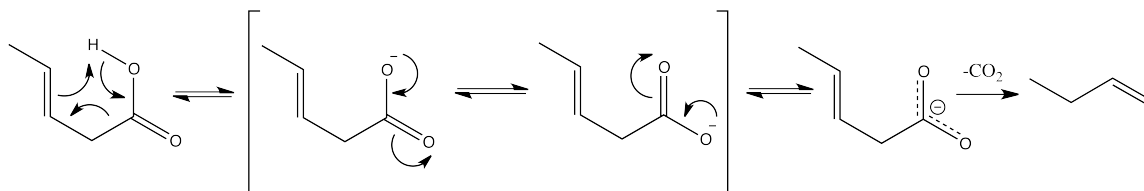
Figure 2.1 The pericyclic decarboxylation of β,γ- unsaturated fatty acids followed through the resonance stabilization of the conjugate base, composite resonance structure is also shown, to proceed via removal of CO_2 and form a pure, terminal alkene product. Specific reaction shown is for 3-pentenoic acid producing 1-butene.

intermediate that is in equilibrium with the resonance stabilized carboxylate anion. Due to the electron withdrawing nature of the carboxylate anion, the removal of CO_2 is highly favored.

As a fundamental organic chemistry process, pericyclic decarboxylations are well known among chemists, yet a thorough understanding of their potential has not been realized; evidenced by the sparse volume of publications in peer-reviewed journals. Current research trends are primarily concerned with the formation of carbon-carbon bonds, through pericyclic addition reactions such as Diels Alder, rather than their decomposition.[7-9] In 1964, Bigley and coworkers first investigated the rate of decarboxylation in multiple short chain, β,γ-unsaturated carboxylic acids via pericyclic decarboxylation.[6,10] Upon heating the substrate in phenanthrene (PHEN), decarboxylation was 70-90 % complete within 8 h and allowed for separation of the volatile olefin and it's parent acid in one step.[6] By condensing the volatile product, there is no need for further separation techniques, as the volatile olefin leaves the reaction flask immediately while the thermally stable PAH solvent, PHEN, remains unchanged in the reaction flask. Given this significant result, along with the high boiling points of the PAH solvents, it can be hypothesized that pericyclic decarboxylation using longer chain β,γ-unsaturated fatty acids will successfully produce liquid alkenes. As described in literature, the longer the carbon chain of the fatty acids, the larger the reflux temperature required to fully decarboxylate the molecule.[4] However, the energy barrier is overcome by the high stability of the PAH solvents at temperatures much higher than the temperature required to reflux the acid, which is not the case for typical organic solvents.

Pericyclic decarboxylations using PAHs, instead of catalysts, can readily overcome the activation energy barrier and is nearly spontaneous for short chain carboxylic acids such as 3-pentenoic acid upon heating.[6] This solvent system is therefore hypothesized to have the potential for decreasing the energy requirement to convert longer chain, β,γ-unsaturated fatty acids to pure

hydrocarbons. The use of short chain β,γ-unsaturated fatty acids has received some recent attention in literature. The breakdown of levulinic acid derivatives, such as γ-velerolactone, has been discussed and confirms the conversion of an intermediate, short chain β,γ-unsaturated fatty acid to liquid alkenes for transportation fuels.[11-14] Dumesic and coworkers have recently studied a breakdown pathway that utilize 3-pentenoic acid as a valuable intermediate to produce butenes through use of a SiO_2/Al_2O_3 catalyst at high temperatures and pressures.[11,12] The Gosselink group has also studied the conversion of levulinic acid derivatives to butenes via a similar value chain based in 3-pentenoic acid.[13,14] These groups have demonstrated unique pathways for the conversion of one of the most abundant lipid biomasses found in nature. More importantly, they established alkenes, as well as the oligimerized or hydrogenated form of the alkene, as a liquid hydrocarbon capable of competing with current transportation fuels.[12,14]

The purpose of this article is to introduce the process and ease in which short chain and subsequently longer chain β,γ- unsaturated fatty acids readily decarboxylate in polycyclic aromatic hydrocarbons (PAHs) to produce a liquid hydrocarbon comparable to current liquid hydrocarbon fuels. Although the fatty acids studied in this chapter have boiling points well within the limits of PHEN, β,γ- unsaturated fatty acids larger than C_{13} do not. The incorporation of bulkier PAHs such as PYR as well as mixtures of PHEN:PYR will allow the system to handle temperatures of up to 385 °C, which is sufficient for the fatty acids studied within this chapter. FA is also described but since it has a 5-membered ring surrounded by three (3), 6-membered aromatic rings, the stability of the solvent was compromised over time, even though it permitted the initial heating of up to 375 °C. FA, being one of the more carcinogenic and unstable PAHs over time, was therefore disregarded as a potential PAH solvent for pericyclic decarboxylations of β,γ-unsaturated fatty acids.

2.3 RESULTS AND DISCUSSION

The pericyclic decarboxylation of 3-pentenoic acid was performed in PAH solvents, specifically PHEN, PYR, and mixed solvent systems of PHEN:PYR. The reaction parameters can be found in Table 2.1. The substrate, 3-pentenoic acid, was previously studied in the PAH solvent PHEN[6] and was the only literature comparison available for the conversion of β,γ-unsaturated fatty acids to pure alkenes in a single, non-catalyzed step. The model substrate, 3-pentenoic acid, was refluxed in PHEN for 8 hours to confirm Bigley's results before pursuing pericyclic decarboxylations in other PAH solvent systems more suited for larger fatty acids.

Table 2.1 Reflux temperature and the duration, in hours, of 3-pentenoic acid in various PAH solvents and at multiple ratios. *Reaction was modeled after Bigley[6] to confirm alkene formation using PAH solvent systems.

Solvent	Ratio Sol:Sub (g)	Temp (°C)	Time (h)
PHEN*	10.0:1.0	220	8
PHEN	10.0:2.0	221	8,12,24
PYR	10.0:1.0	247	8, 12, 24
PYR	5.0:1.0	228	8, 16, 24
1:1 PHEN:PYR	10.1:1.0	256	8, 16, 24
1:1 PHEN:PYR	2.9:1.0	254	8, 12, 24
2:1 PHEN:PYR	5.0:1.0	204	8, 24
1:2 PHEN:PYR	10.1:1.0	212	8
1:2 PHEN:PYR	5.0:1.0	220	8

Alkene formation of 1-butene was confirmed using ^{1}H NMR for this proof of concept reaction and is plotted in Figure 2.2a. The signals within the spectrum are indicative of 1-butene and identified as δ/ppm(400 MHz, CDCl$_3$); 0.91 (3 H, m, CH$_3$), 1.52 (2 H, s, CH$_2$), 2.02 (2 H, m, CH$_2$), 4.87 (1 H, d, -CH), 4.90 (1H, d, -CH), and 5.85 (1 H, m, -CH). The successful pericyclic decarboxylation of 3-pentenoic acid confirmed Bigley's result and allowed for the investigation of β,γ-unsaturated fatty acids in other high boiling point PAH solvents such as 2:1 PHEN:PYR and PYR, Figure 2.2b and 2.2c respectively. Presence of the vinyl protons within the spectrum,
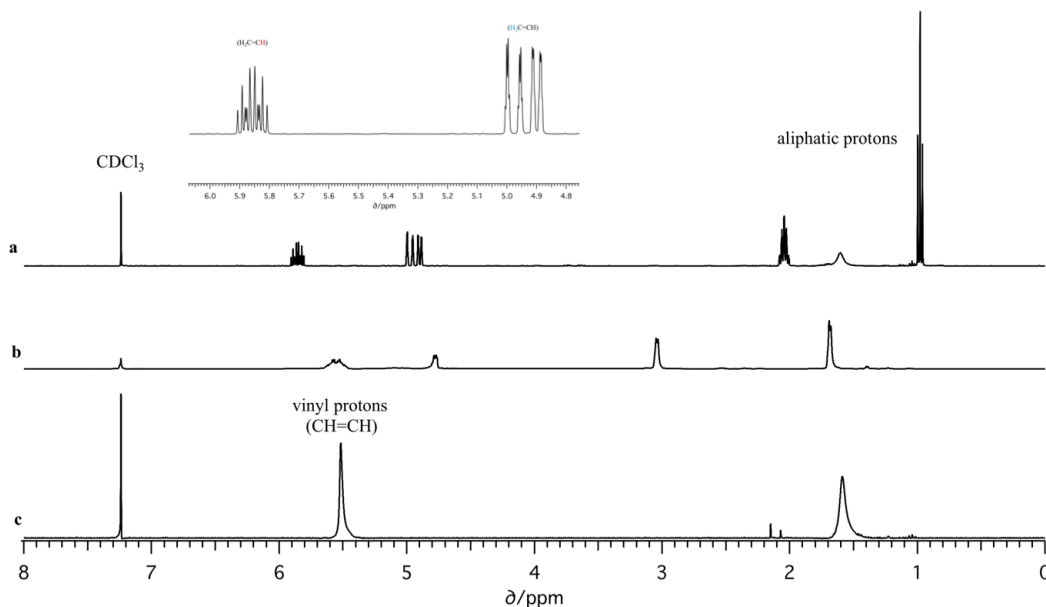
Figure 2.2 ^{1}H NMR spectra of the liquid hydrocarbon products after refluxing 3-pentenoic acid for 24 h in (a) PHEN, (b) 2:1 PHEN:PYR and (c) PYR, all at a solvent:substrate ratio of 5:1.

4.5-6.0 ppm, confirms alkene formation. However, the broad signal at 5.5 ppm in Figure 2.2c implies a mixed product formed instead of pure 1-butene. Proton signals from the vinyl protons of terminal alkenes have very indicative splitting patterns, shown in the inset on in Figure 2.2a. When this splitting pattern is not observed, but signals are still present within the vinyl region, alkene products have formed but are 2° or 3° alkenes.

To identify the mixed products formed, a 5:1 ratio of PYR:3-pentenoic acid was refluxed and the headspace of the product analyzed after 24 hours using GC/MS. The GC trace of the products is provided in Figure 2.3. It can be seen that butene was formed, although 2-methylpropene has approximately the same retention time as isobutene and therefore both alkenes make up the 41.2 % relative intensity. The conjugated alkene, 2,4-hexadiene, was also formed although in less than 1 %. The presence of a 2° and conjugated alkene confirm the results
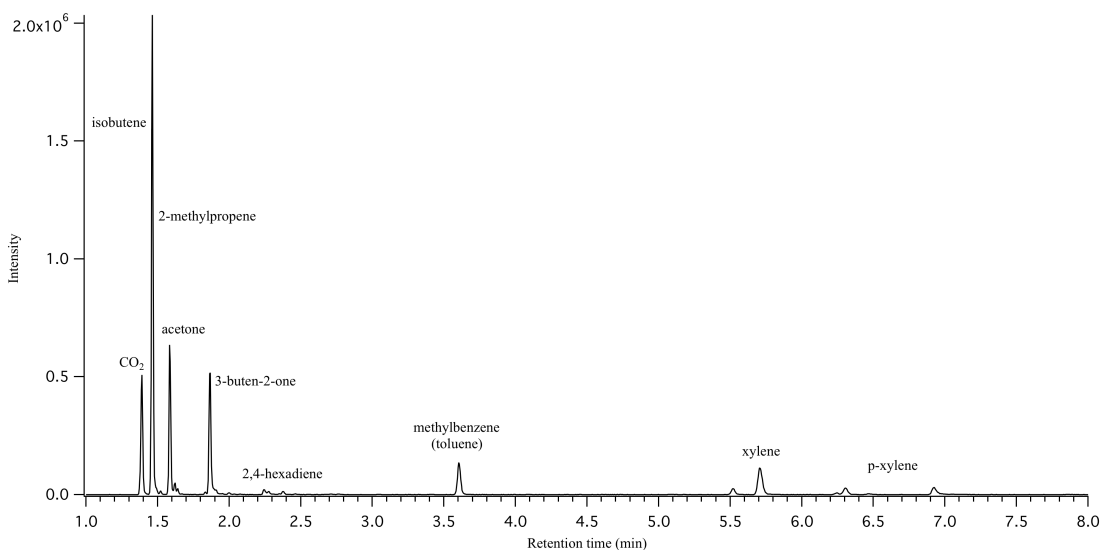
Figure 2.3 Gas chromatogram of the products formed after refluxing 3-pentenoic acid in PYR for 24 h. Products are labeled on the plot and confirmed via mass spectroscopy.

from the ^{1}H NMR that mixed alkenes were produced. This allows for the conclusion that alkenes will form in each solvent but the purity may suffer. The presence of acetone and CO_2 resulted from contamination when refilling the dry ice bath. The product also contains a ketone, 3-buten-2-one, in less that 0.5 % relative intensity and can be explained by thermal decomposition of 3-pentenoic acid instead of pericyclic decarboxylation. This product will require further separation techniques in order for PYR to produce purely hydrocarbon products. The product formed using the solvent 2:1 PHEN:PYR was not analyzed via GC/MS as resources were limited. However, as the ^{1}H NMR, Figure 2.2b, shows a separation of vinyl peaks, it can be reported that this solvent allows for the formation of terminal alkenes more so than mixtures of alkenes.

There is a significant portion of substituted benzene peaks within the GC/MS in Figure 2.3, totaling about 15.5 % of the total products. It is important to note that these aromatic signals were not observed in any of the ^{1}H NMR collected for the decarboxylation products of 3-pentenoic acid in PAH solvents. The main difference between product identification with these two techniques is the physical state of the sample used, i.e. ^{1}H NMR uses liquid samples and

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GC/MS analyzes the headspace formed above the liquid. Since these reactions are closed systems, any volatile breakdown of the aromatic solvent will be recovered in the product flask but may not be dissolved into the liquid product. This can be better explained comparing the ^{1}H NMR and GC/MS for the reaction mixtures.

Typical spectra collected at the start of reflux and throughout the reaction of 3-pentenoic acid in PAH solvents are shown in Figure 2.4, specifically for the 2:1 PHEN:PYR solvent. The reaction mixture at the time in which the solvent has melted and the solution has begun reflux (0 h) was sampled and is seen in Figure 2.4a. As can be seen, the signal for the PAH solvent, 7.5-9.0 ppm, and the aliphatic substrate, 0.8-2.5 ppm, are strong and are spatial resolved.
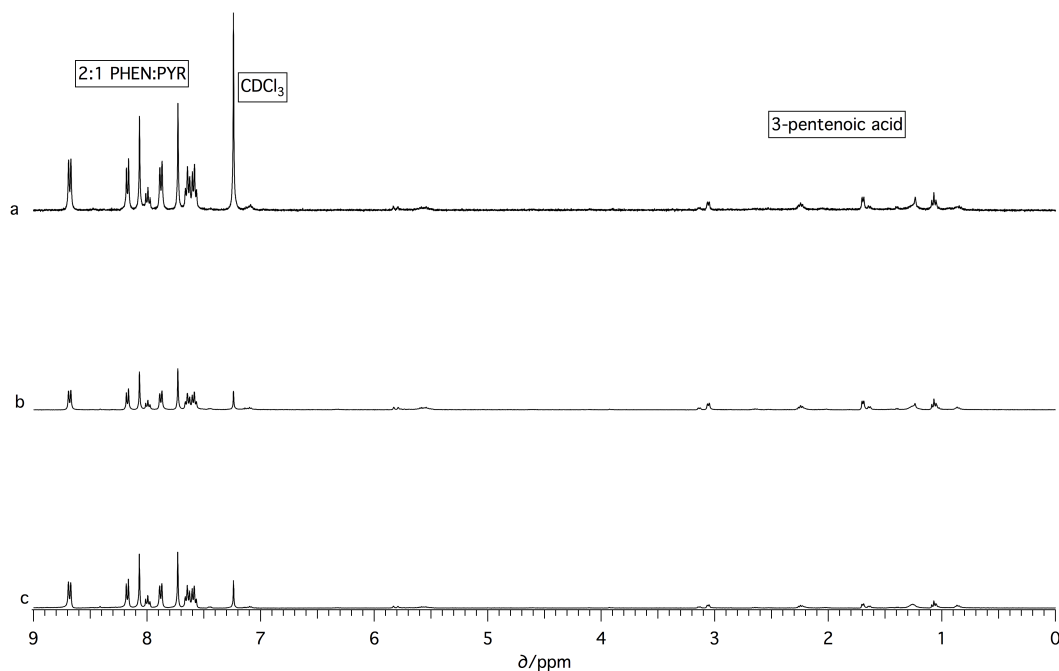
Figure 2.4 ^{1}H NMR spectra of reaction mixture containing 3-pentenoic acid in 2:1 PHEN:PYR at (a) 0 h, (b) 8 h, (c) 24 h. It can be seen that the aromatic region, 7.5-9.0 ppm- labeled as 2:1 PHEN:PYR, resists decomposition throughout heating without interfering with the product as the substrate, 3-pentenoic acid, depletes over time. This reaction spectrum is indicative for all reaction parameters described in Table 2.1.

As the reaction proceeds, the aliphatic region depletes and the aromatic region of the PAH solvent shows little to no decomposition after heating for 8 h and 24 h, Figure 2.2b and 2.2c respectively. This confirms that 3-pentenoic acid is removed from the system while the

PAH remains thermally stable and resists decomposition. However, the GC/MS for the product formed when PYR is part of the solvent system shows a large number of benzene side products. Upon analyzing the headspace of the reaction mixture after 24 hours using GC/MS, provided in Figure 2.5, the hypothesis that the contaminate was volatile and not dissolved in the liquid product was confirmed by the presence of all benzene side products that were unexplained in Figure 2.2. The ^{1}H NMR spectra collected for each solvent mixture over time mimicked Figure
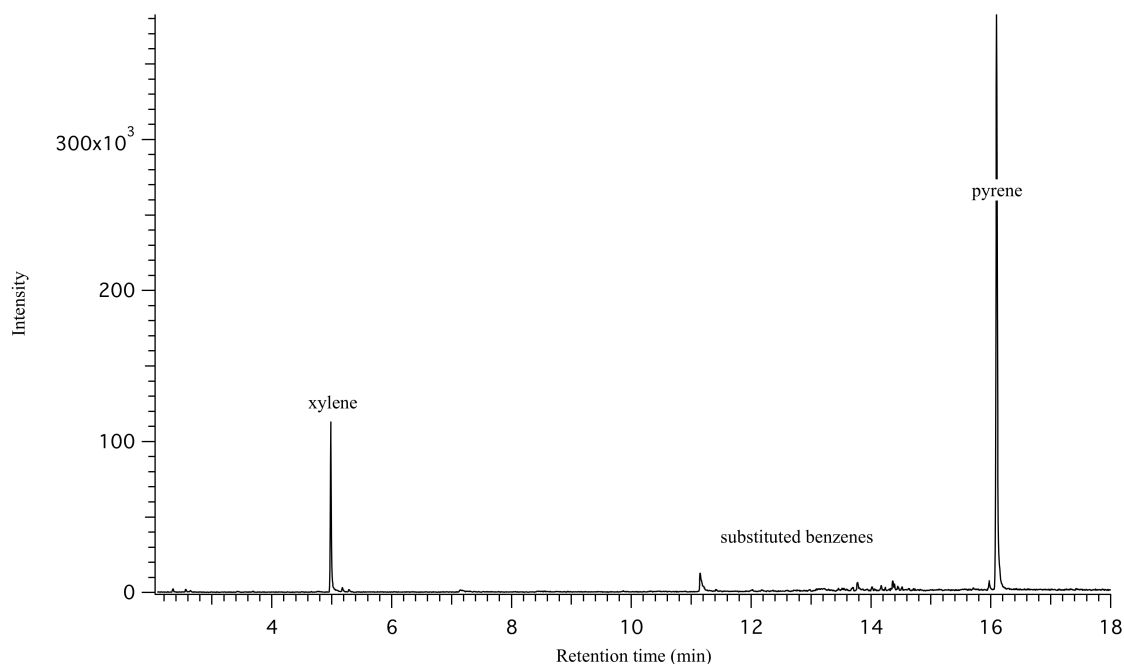
Figure 2.5 GC/MS of the solvent mixture, 3-pentenoic acid in PYR, after refluxing the solution for 24 h. Retention times and mass spectroscopy were used to determine the species present as volatile breakdown compounds from pyrene.

.4 and confirms the stability of all the PAH mixtures studied with 3-pentenoic acid as the signature peaks, ranging from 7.5-9.0 ppm, for the aromatic mixture remains unchanged over time for all reactions in Table 2.1. To be sure none of the breakdown products were present in2 the starting material, a sample was analyzed using ^{1}H NMR and is provided in Figure 2.6. The
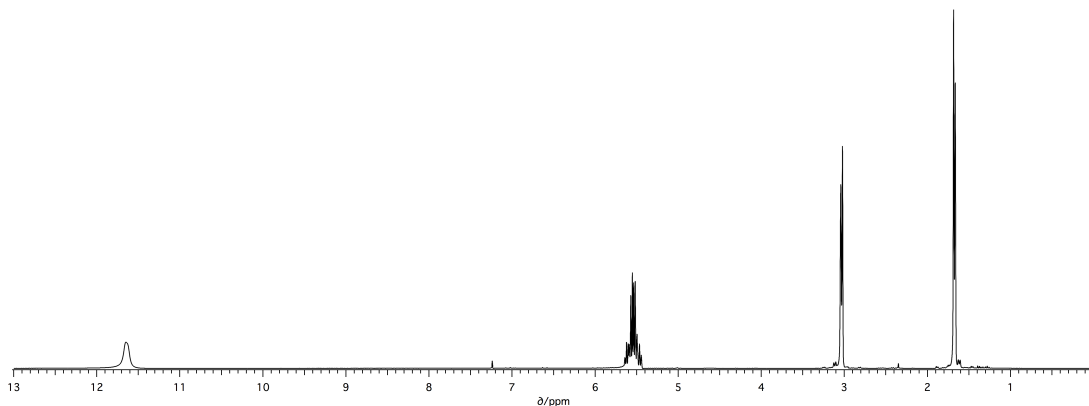
Figure 2.6 ^{1}H NMR spectrum of 3-pentenoic acid recorded at δ(400 MHz, CDCl$_3$); 1.705 (3 H, s, CH$_3$), 3.063 (2 H, s, CH$_2$), 5.583 (2 H, m, CH=CH), and 11.680 (1 H, s, OH) confirms the purity of the starting material.

strong signals and splitting pattern within the spectra confirms literature values[15] and the presence of pure 3-pentenoic acid.

The long chain, β,γ- unsaturated fatty acid, 3-decenoic acid, was studied in the PAH solvent systems described previously. This fatty acid was chosen based upon its 80 °C increase in boiling point compared to 3-pentenoic acid, its commercial availability, and its ultimate potential to produce a liquid hydrocarbon fuel that more closely resembles those used in transportation fuels. This substrate also allows for a further investigation of solvent stability and thermal capacities of the PAHs studied without fear of compromising product purity or contamination from aromatics as the boiling points are significantly resolved. Alkene products were obtained upon the reflux of 3-decenoic acid in various PAHs and ratios, as depicted in Table 2.2, but is shown specifically for the PAH solvent 2:1 PHEN:PYR in Figure 2.7. Since the 5:1 sol:sub ratio produced the highest yields in each solvent, the product yield for each reaction is shown for only these reactions. The % yield is calculated using the actual mass obtained compared to the theoretical mass, assuming a 100 % conversion to 1-nonene. The highest % yield, 76%, in PHEN was observed after 24 h at a 5:1 g sol:sub ratio. Each reaction and resulting

Table 2.2 The solvent and substrate parameters for the reaction of 3-decenoic acid in vrious PAHs. Product yields (% Yield) were calculated for 5:1 solvent:substrate ratios as it produced the highest yield without compromising reaction time or product purity. *97 % *trans*-3-decenoic acid used instead of 92 %.

Solvent	Ratio Sol:Sub (g)	Temp (°C)	Time (h)	% Yield (24 h)
PHEN*	10.0:1.0	280	8,12,24,36	
PHEN	10.1:1.0	289	8, 16, 24	
PHEN	5.0:1.0	287	8, 16, 24	76
PYR	10.0:1.0	284	8, 12, 24	
PYR	5.0:1.0	288	8, 16, 24	54
1:1 PHEN:PYR	10.0:1.0	286	8, 16, 24	
1:1 PHEN:PYR	5.0:1.0	282	8, 16, 24	
2:1 PHEN:PYR	5.0:1.0	278	24	63
2:1 PHEN:PYR	3.0:1.3	279	24	

product was analyzed via ^{1}H NMR confirming the formation of an alkene product and the stability of the solvent systems. Phenanthrene was found to be the optimal solvent for the conversion of 3-decenoic acid to pure 1-nonene in studies where purity and yield combined were the primary focus. However, 2:1 PHEN:PYR produced a larger product yield than PYR or other mixed ratios of the solvents and have been predicted to be the best solvent for future reactions with higher boiling point fatty acids.

Products observed from the decarboxylation in pyrene show an alkene product but with a much lower yield after 24 h. Mixed *cis* and *trans* isomers were used when pure *trans* 3-decenoic acid (98 %) was commercially unavailable. The appearance of the characteristic alkene peaks of 1-nonene was observed by ^{1}H NMR (Figure 2.7) and was positively identified as 1-nonene via GC/MS (Figure 2.8) after 24 hours of reflux in 2:1 PHEN:PYR. As can be seen in Figure 2.8, of the 63 % product yield obtained after 24 hours of reflux in 2:1 PHEN:PYR, 84 % of the product was found to be 1-nonene.

The GC spectrum in Figure 2.8 shows a GC trace for the conversion products of 3-decenoic acid after 24 h in the mixed 2:1 PHEN:PYR solvent. Retention times for the liquid
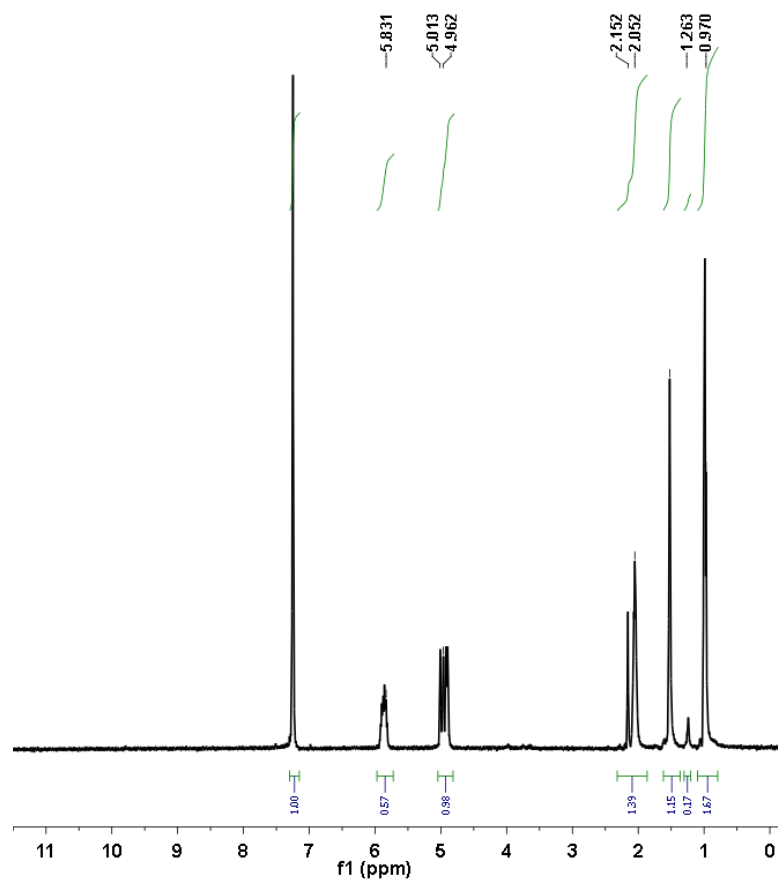
Figure 2.7 ¹H NMR spectra of the decarboxylated product, 1-nonene, after refluxing 3-decenoic acid in PHEN for 24 h. The aliphatic peaks, 0.9-2.2 ppm, as well as the spatially resolved signals in the vinyl region, 4.5-6.0 ppm, confirm the product 1-nonene.
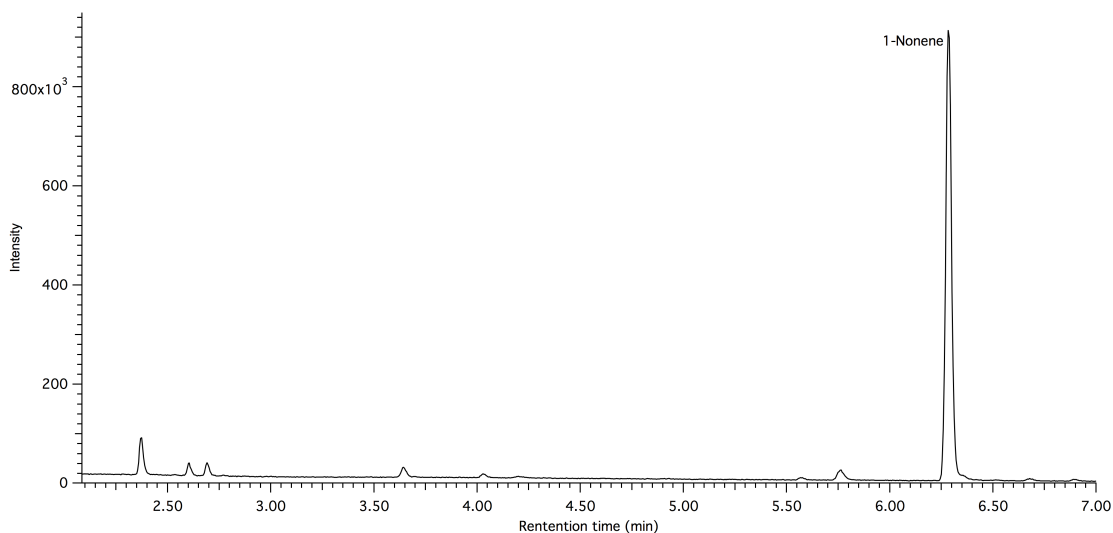
Figure 2.8 GC/MS spectrum of products formed after 3-decenoic acid (1.0 g, 5.9 mmol) was decarboxylated in 2:1 PHEN:PYR (5.0 g, 18.7:8.2 mmol) for 24 h. Major product identified by Mass Spectroscopy (min, relative %): 1-nonene (6.29, 83.97 %).

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hydrocarbon product were used to identify products that were confirmed by the NIST Mass Spectral Database provided by Wiley. Sampling the volatile headspace of the product and analyzing it with GC/MS in conjunction with ^{1}H NMR analysis has confidently allowed for the identification of decarboxylated products. The minor products have been identified in min, relative % as 1,3-dimethylbenzene (5.76, 2.27 %), methylbenzene (3.64, 1.64 %), 2-methylazetidine (2.69, 1.69 %), 2-ethylpiperidine (2.60, 1.62 %) and benzene (2.37, 5.21).[15] Most of these minimal products could only be identified with a 23 % ID quality and those below this certainty were not listed as products for this reaction. Since the 2:1 PHEN:PYR solvent is used as is, with no recrystallization, any benzene found in the product can been attributed to the breakdown of the solvent before the reaction begins. However, to the best of the authors knowledge, this is the first confirmed and reported alkene product formed from the pericyclic decarboxylation of a long chain β,γ- unsaturated acid.

In Figure 2.9a, the chemical shifts of the product formed after refluxing 3- decenoic acid in PYR for 24 h are shown and are reported as δ(400 MHz; CDCl3) 0.89 (3 H, s, Me), 1.28 (8 H, m, CH$_2$), 1.48 (2 H, m, CH$_2$), 2.03 (2 H, m, CH$_2$), and 5.48-5.62 (3 H, m, CH). The single peak in the vinyl region of the spectra, 5.48-5.62 ppm, is lacking splitting characteristics that will allow for the complete identification of the alkene product however it is clear that a mixed product is present by the observed broadening of the signal. Figure 2.9b and 2.9c show the reaction mixture at the onset of reflux and after 24 h, respectively. It can be seen that there is minimal depletion of the aromatic solvent region, ~7.5-9 ppm, with significant depletion of aliphatic protons, ~0.5-2 ppm, due to the pericyclic decarboxylation of 3-decenoic acid to its volatile alkene product after 24 h. It can also be seen that the depletion of the aliphatic substrate is not complete as there is still substrate present in the solvent, however the aromatic solvent
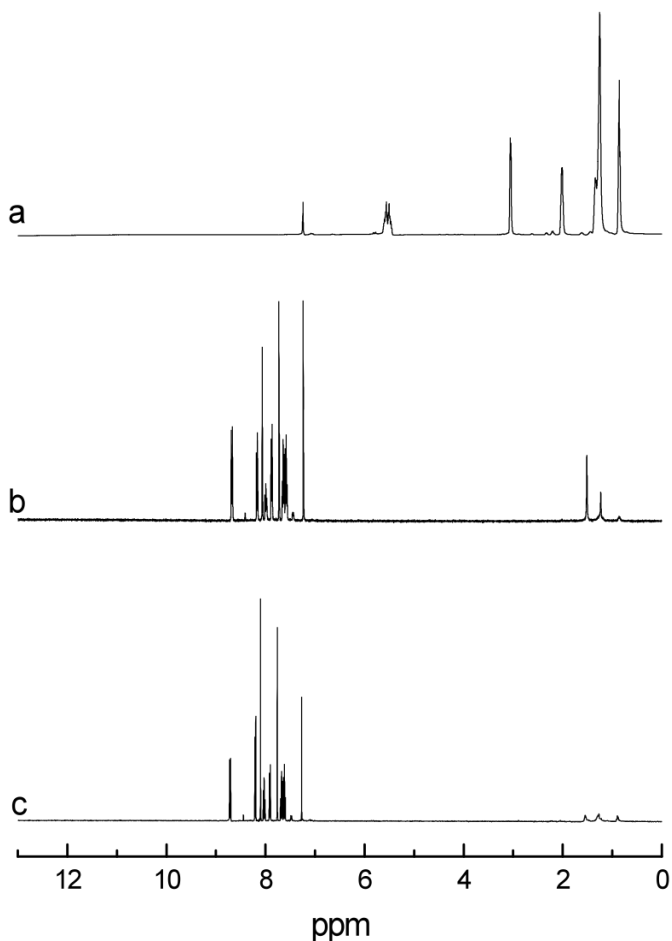
Figure 2.9 (a) [^1]H NMR of pure product, 1-nonene, in CDCl$_3$ produced from the decarboxylation of 3-decenoic acid after 24 h in PYR (b) [^1]H NMR of solvent and substrate, 3-decenoic acid, at the onset of reflux (0 h), and (c) solvent and substrate after 24 h.

remains stable after 24 h of reflux in PYR. This explains the 54 % yield calculated for the reaction at 24 h and the inability to obtain a pure, alkene product in PYR.

2.4 CONCLUSIONS

In conclusion, the potential of this process to be applied in the production of pure liquid hydrocarbons is significant. Being able to solubilize a fatty acid of chain lengths comparable to current hydrocarbon fuels and produce an 84 % pure, liquid, hydrocarbon product in a single, catalyst-free process has the ability for decreasing energy costs associated with the conversion of lipids and fatty acids to liquid hydrocarbon fuels. Confirmation of the pericyclic decarboxylation

of 3-pentenoic acid in PHEN provided the necessary information to improve this process to include long chain fatty acids. This is made possible by the efficient, higher boiling point PAH solvents that have proved to provide the energy density required to decarboxylate β,γ-unsaturated fatty acids without the need for expensive catalysts or extreme temperatures and pressures. The long chain fatty acid, 3-decenoic acid, was successfully decarboxylated in the solvents studied with the model system of 3-pentenoic acid. This result is significant in the fact that this is the first report of long chain fatty acids undergoing decarboxylation without the use of catalysts as well as providing a process for converting these acids that more readily resemble current liquid hydrocarbons used as transportation fuels. Utilizing ^{1}H NMR in conjunction with GC/MS has allowed for the complete understanding of the products formed in the PAH solvent systems.

The straight chain fatty acid, 3-decenoic acid, as well as the methyl substituted (Z)-3-methyl-3-decenoic acid are readily found in the flowers of the *Acacia farnesiana*, also known as *cassie*, tree.[16,17] Varying species of perennial acacia trees/shrubs containing large concentrations of 3-decenoic acid and its moieties can be found around the world, including 10 of the 50 states within North America. The β,γ- unsaturated fatty acids have also been reported in various microorganisms, as seen in an Annual Review of Microbiology.[18] The presence of these acids in nature, and their ease of extraction, coupled with the utilization of pericyclic rearrangements allow for a minimal energy conversion to a liquid hydrocarbon fuel.

Since the presence of β,γ- unsaturated fatty acids are limited to a few select strains of plants, as genetic modification of algae to produce these lipids and fatty acids has not been obtained in current literature, the utilization of a larger range of feedstocks is necessary. Since α,β- unsaturated fatty acids are more thermodynamically stable than the β,γ- form, there should be a larger number of renewable feedstocks containing the fatty acid that can be utilized. The

decarboxylation of the α,β- unsaturated fatty acids will be investigated and compared to the pericyclic decarboxylation of β,γ- acids in Chapter 3.

2.5 MATERIALS AND METHODS

Solvents phenanthrene (99%) and pyrene (98%) were obtained from Sigma Aldrich. Substrate 3-pentenoic acid (95%) was obtained from TCI and 3-decenoic acid (trans (>80%) and trans rich (>90%)) were obtained from Fluka and either Alfa Aesar or TCI, respectively. All reagents were used without further purification.

Experimental solvents examined were phenanthrene (PHEN), pyrene (PYR), 2:1 PHEN:PYR, 1:1 PHEN:PYR, or 1:2 PHEN:PYR which were all used in various gram ratios with substrates, 3-pentenoic acid or 3-decenoic acid. Reactions will be described in terms of a solvent:substrate ratio, abbreviated sol:sub. Various ratios as well as differing combinations of solvent and substrate were heated to reflux in a 25-mL, 3-neck pear shaped flask in a sand bath. Temperature of the reaction was monitored directly in solution. Product was collected in a receiving flask immersed in an acetone/dry ice bath held at -78 °C. Aliquots of product and reaction mixture were taken at least every 8 and 24 h. The CO_2 formed was collected in a sodium bicarbonate trap while the pure olefin condensed in the receiving flask. Multiple solvents were tested to determine the solvent of choice for higher boiling point systems using 3-pentenoic acid as the model fatty acid, Table 1.

The products were dissolved in $CDCl_3$ and each sample was analyzed using ^{1}H NMR on a Varian 400 MHz spectrometer using Varian programmed pulse sequences. Products were analyzed for composition and impurities. Aliquots of the reaction mixture were also dissolved in $CDCl_3$ and analyzed using a Varian 400 MHz NMR spectrometer. [1]H was used to monitor the

stability of the solvent over time as well as the disappearance of starting material as the reaction proceeded.

GC/MS analysis was used to accurately determine the percent yield of alkene product as well as any side products that may have formed. The headspace of the volatile product was collected via a 1 μL syringe and was subjected to an inlet temperature of 225 °C and a flow rate of 50.9 mL/min along a Zebron capillary GC column with an inner diameter of 0.25 mm at 30 m long. The sample was then heated to 180 °C at a rate of 5 °C/min after injection and the GC trace was collected. The retention time of the products were analyzed via MS and confirmed thru the digital database, Palisades Mass Spectroscopy Library, with at least 90 % confidence.

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CHAPTER 3

FATTY ACIDS IN NATURE: UTILIZING α,β- TO β,γ- ISOMERIZATION TO

INCORPORATE A WIDER RANGE OF FEEDSTOCKS FOR HYDROCARBON FUEL

PRODUCTION

3.1 OVERVIEW

In Chapter 3, the issue of low availability of β,γ- unsaturated fatty acids in renewable feedstocks is addressed. Investigation of the chemistry associated with the low energy pericyclic rearrangement in PAH solvents shows that β,γ- unsaturated fatty acids will readily lose CO_2 to produce a pure olefin. However, it is pertinent to know if the isomerization of the thermodynamically stable α,β- unsaturated fatty acids, readily found in nature, to the β,γ- unsaturated fatty acid occurs before decarboxylation. This isomerization is essential for the subsequent pericyclic decarboxylation to occur and produce the corresponding hydrocarbon product. The decarboxylation of 2-decenoic acid was compared to the product from 3-decenoic acid to confirm the formation of the liquid hydrocarbon product, 1-nonene, for both substrates. Upon the successful decarboxylation of 2-decenoic acid, the decarboxylation of longer chain α,β- unsaturated acids was studied; specifically 2-hexadecenoic acid, readily found in the annual plant *Arabidopsis thaliana*. The major products produced from the complete decarboxylation of both α,β- unsaturated fatty acids were analyzed via ^{1}H NMR and determined to be pure alkenes. However, the products for the α,β- unsaturated fatty acids had a large concentration of smaller chain alkenes and alkanes, revealed via GC/MS, which were not present when decarboxylating β,γ- unsaturated acids. Possible sources of these breakdown products are also addressed in this chapter. ^{1}H NMR and GC/MS were used to confirm hydrocarbon product formation throughout the reaction as well as the stability of the solvent systems over time.

3.2 INTRODUCTION

The pericyclic decarboxylation discussed in Chapter 2 confirms the successful decarboxylation of long chain β,γ- unsaturated fatty acids. However, many of these naturally occurring fatty acids are found in the thermodynamically stable α,β- form rather than the β,γ- unsaturated fatty acid. Since current petroleum fuels have carbon numbers of 8 and higher, investigating naturally occurring fatty acids of this chain length and larger is imperative. Upon researching the pericyclic reaction for β,γ- unsaturated fatty acid, it was obvious that PAHs that are thermodynamically stable at high temperatures contain the high energy density needed to provide a solvent system for longer chain β,γ- unsaturated fatty acids, without the use of catalysts. However, the isomerization inherently requires more energy than the pericyclic decarboxylation alone. It has been proven by Dodson and coworkers in 1950 that the α,β- to β,γ- isomerization will occur upon heating as the pericyclic rearrangement that subsequently occurs and facilitates decarboxylation is more favorable than being in its thermodynamically stable α,β- form, as seen in Figure 3.1.[1-3]
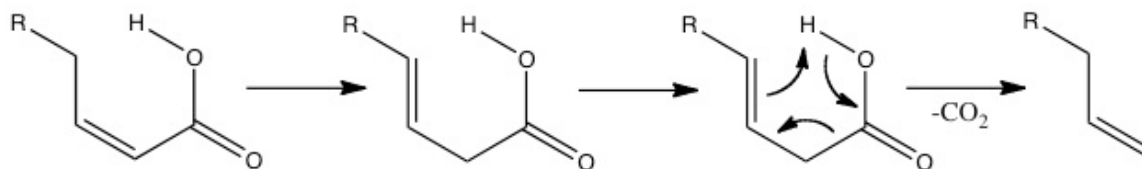
Figure 3.1 Applying heat to a PAH solvent system containing α,β- unsaturated fatty acids will allow the acid to isomerize to the β,γ- position in order to proceed through the thermodynamically favored, pericyclic rearrangement to produce a pure liquid hydrocarbon product. This mechanism has been successfully applied to 2-decenoic and 2-hexadecenoic acid.

This knowledge has allowed for an increase in the naturally occurring feedstocks available for this process, provided the PAH solvent has a large enough energy density to produce the hydrocarbon product without increased temperature or use of catalysts.

As described in Chapter 2, the stability of higher boiling point, PAH solvents like 2:1 PHEN:PYR, PYR, or FA over time was successfully investigated for temperatures up to 300 °C.

The decarboxylation of 2-hexadecenoic acid (lit.[4] bp 373.7 °C) will require a substantially higher amount of energy than 2-decenoic acid but should still be within the thermal capabilities of each solvent listed above and will be experimentally determined. The pericyclic decarboxylation of 2-decenoic acid and 2-hexadecenoic acid were best analyzed with GC/MS as ^{1}H NMR could not provide information on breakdown products, if any, due to the difference between various long chain alkene hydrocarbons not varying enough to confidently integrate signals and identify the product.[5] However, ^{1}H NMR was used to monitor the solvent stability as well as the formation of an oxygen-free, hydrocarbon product after 8 and 24 h for each reaction.

The phosphatidylglycerol of plant chloroplasts found in the *Arabidopsis thaliana* plant contains a large concentration of 2- and 3- hexadecenoic acid in the form of the fatty acyl, 3-*trans*-hexadecenoyl.[6-8] The carboxylate anion can be extracted and utilized as a feedstock within the PAH solvent system. However, the isomerization as well as the decarboxylation of an α,β- or β,γ- unsaturated fatty acid this large has not been previously investigated. Given the successful decarboxylation of 3-decenoic acid in Chapter 2, the corresponding α,β- unsaturated fatty acid, 2-decenoic acid, can be investigated and compared to previous results to confirm the isomerization and pericyclic decarboxylation to produce liquid hydrocarbons. The calculated heat capacity required for 2-decenoic acid is only 10 kJ/K higher than 3-decenoic acid.[9] Meaning, the amount of heat required for isomerization before decarboxylation is not increased significantly enough to hinder the reaction.

Herein, the experimental determination of the products formed from the isomerization and decarboxylation of long chain, α,β- unsaturated fatty acids in PAHs will be reported. This is, to the best of the authors knowledge, the first time α,β- unsaturated fatty acids have been converted to liquid hydrocarbons via a minimal energy PAH solvent system. It is important to

note that although 375 °C @ 760 mm Hg is a high temperature for some areas of science, in the petroleum industry the average temperature of the pyrolytic conversions can be anywhere from 500-750 °C, with the use of a catalyst.[10-14] Compared to these processes, the energy required for this pericyclic process is much lower and possibly a more efficient process.

3.3 RESULTS AND DISCUSSION

The reaction parameters for 2-decenoic acid and 2-hexadecenoic acid can be found in Table 3.1. Each solution mixture was heated to reflux and the resulting olefin was collected in a flask held at -78 °C. Even though PHEN cannot be used in the decarboxylation of 2-hexadecenoic acid, the solvent system was studied with 2-decenoic acid to compare the results obtained to those of 3-decenoic acid.

Table 3.1 Solvent reaction parameters for the α,β- unsaturated fatty acids 2-decenoic acid and 2-hexadecenoic acid in various solvents. Temperature was recorded when reflux was obtained and constant. Solvent solution and product were analyzed via ^{1}H NMR at the times listed; product analysis using GC/MS was only performed after reaction completion.

Substrate	Solvent	Ratio Sol:Sub (g)	Temp (°C)	Time (h)
2-decenoic acid	PHEN	5.1:1.0	282	8, 12, 24
2-decenoic acid	PYR	5.0:1.0	283	8, 12, 24, 36
2-decenoic acid	2:1 PHEN:PYR	10.0:1.7	280	8, 12, 24, 48
2-hexadecenoic acid	PYR	10.0:1.3	374	8, 20, 30
2-hexadecenoic acid	2:1 PHEN:PYR	4.9:1.0	368	8, 12, 16, 24
2-hexadecenoic acid	FA	5.0:1.0	370	8, 12, 16, 24

PHEN, PYR, and 2:1 PHEN:PYR solvents were used in a 5:1 ratio with 2-decenoic acid. The ^{1}HNMR spectrum for 2-decenoic acid, obtained from TCI, was collected in CDCl$_3$ and shown in Figure 3.2. As can be seen from the figure, the starting material has a spectrum that is comparable to literature values[18], however there are a small number of unidentifiable signals and broadening of peaks. As this is only a 92 % pure, commercial sample of 2-decenoic acid, fatty
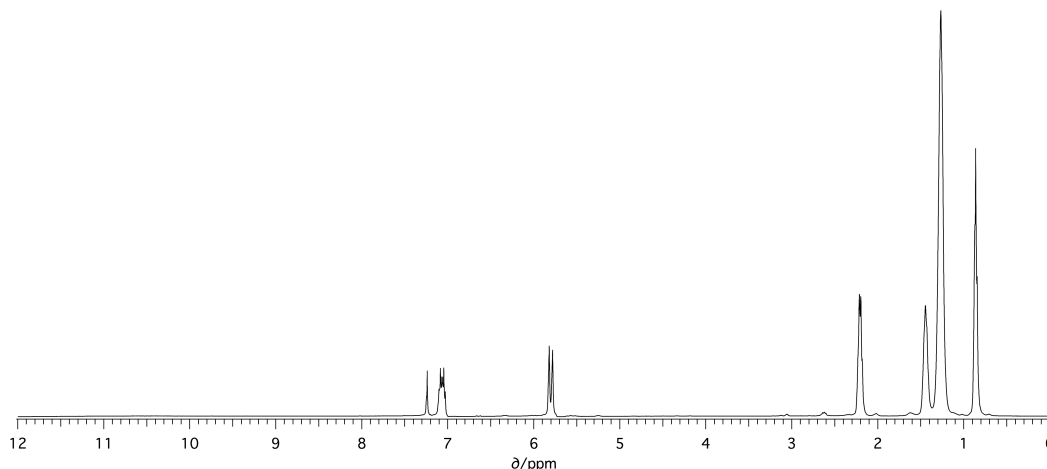
Figure 3.2 The ^{1}H NMR spectrum of the substrate 2-decenoic acid recorded at δ(400 MHz, CDCl$_3$); 0.88 (3 H, s, CH$_3$), 1.23 (8 H, s, CH$_2$), 1.42 (2 H, s, CH$_2$), 2.18 (2 H, s, CH$_2$), 5.82 (1 H, m, CH=CH), and 7.18 (1 H, m, CH=CH) confirms the purity of 2-decenoic acid.

acids of varying chain length can be present due to purification limitations and would cause the broadening of the proton signals. The headspace of 2-decenoic acid was analyzed using GC/MS in an effort to identify these breakdown constituents. However, the vapor pressure of the starting material was low and yielded a spectrum in which the breakdown products could still not be separated, as seen by a very broad, tailing peak in Figure 3.3. The solitary signal at a retention time of 20.68 min is indicative of 2-decenoic acid, with a correlation quality of 70 % to literature, which is relatively low but expected due to the broad peak. It can be concluded that although substrate 2-decenoic acid is not pure, the starting material contains molecules with the same functionality as only one broad peak is present in the spectrum.

Upon heating the substrate in PHEN for a total of 24 h, pure hydrocarbon products were obtained and confirmed. Vinyl protons were not seen in the samples taken after 8 or 24 h in PHEN, only aliphatic protons, and therefore cannot confirm the isomerization and subsequent pericyclic decarboxylation to produce pure alkenes. However, it can be confirmed that the product is not 2-decenoic acid and that thermal conversion of the substrate occurred, although the product can only be confirmed as a liquid hydrocarbon product. No further analysis was

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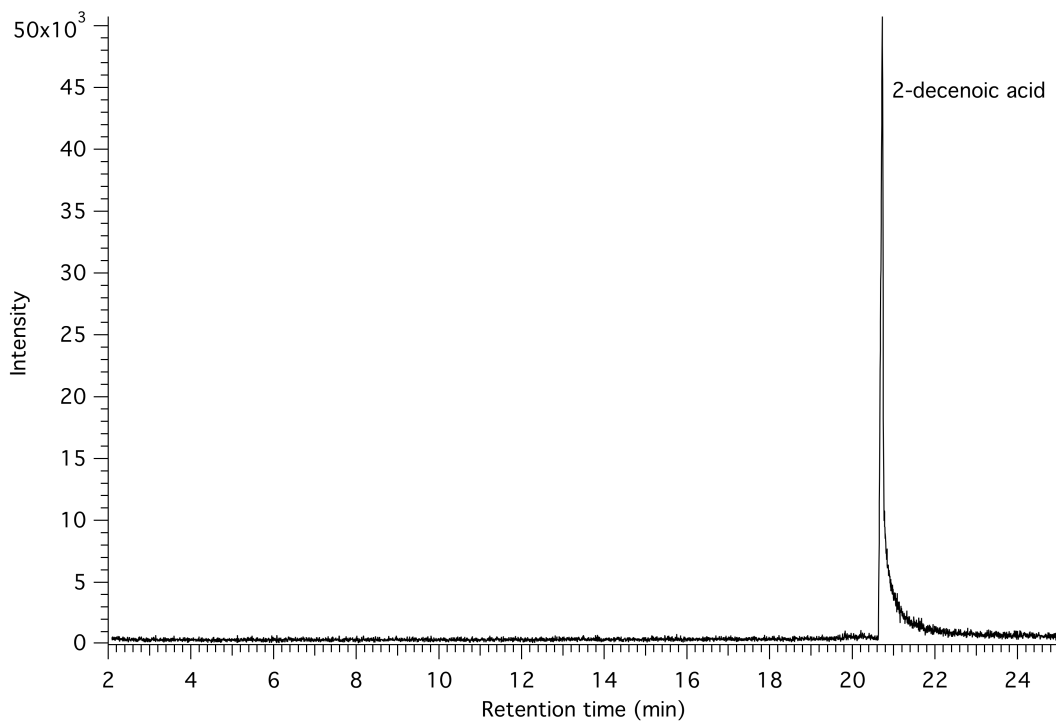
Figure 3.3 GC spectra of the starting material, 2-decenoic acid, obtained from TCI (92 %). The broad peak and tailing are indicative of impurities present. Literature ID match of 70 % 2-decenoic acid at 20.68 min was obtained.

performed using PHEN as a solvent due to limitation of materials.

The conversion of 2-decenoic acid to liquid hydrocarbons, such as alkanes/alkenes, was confirmed after heating the substrate to reflux in PYR for a total of 36 h. The condensed, liquid product collected was dissolved in CDCl₃ every 8, 24, and 36 h and analyzed using a 400 MHz NMR. The ¹H NMR spectra collected can be seen in Figure 3.4a-c. The results show that between the start of reflux and 8 h, Figure 3.4a, only liquid alkanes were produced. The lack of signals between 4.5-6.5 ppm indicates that there are no vinyl protons present in the sample and therefore a saturated, alkane product. Between 8 and 24 h of reflux, Figure 3.4b, the alkane signal was still dominant in the product however at the chemical shift, 3.47 ppm, there is a large singlet present. Signals having chemical shifts within the region of 2.4-4.5 ppm are indicative of protons residing next to a more electronegative atom instead of next to an sp² carbon, as was found within the 1.6-2.7 ppm range. Since the only electronegative atom present in the reaction

mixture is oxygen, it can be concluded that this product is not purely hydrocarbon in nature and is oxygenated. After 24 h, alkene products were produced as can be seen in Figure 3.4c. The signals found between 4.72 and 4.78 ppm are correlate to a liquid alkene product however the
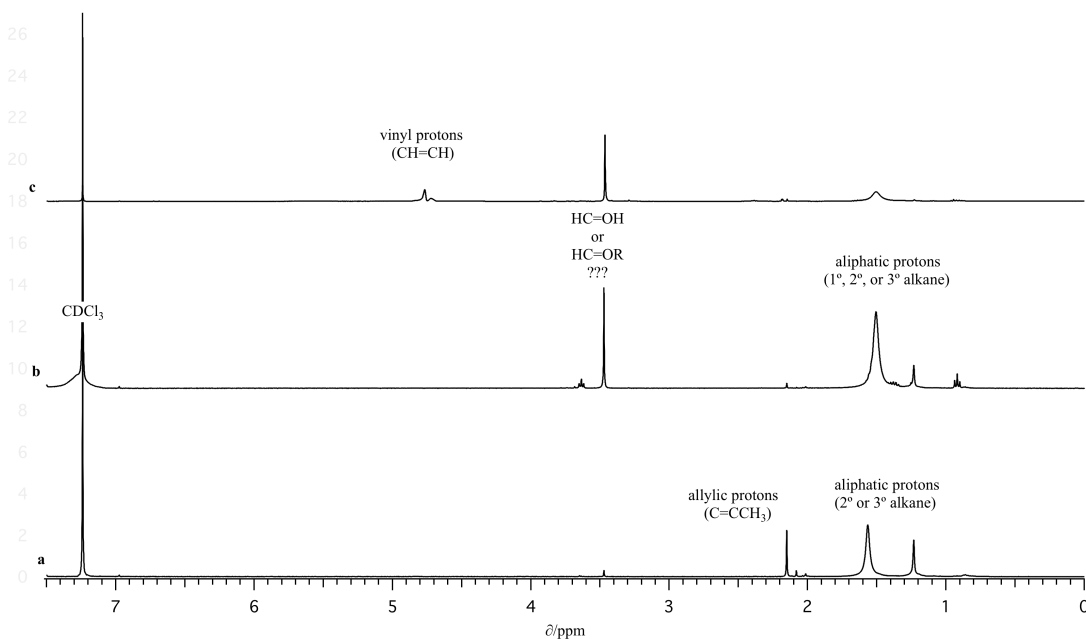
Figure 3.4 The ^{1}H NMR spectrum of the product recorded at δ (400 MHz, CDCl$_3$); a) 0.88 (3 H, s, CH$_3$), 1.57 (10 H, s, CH$_2$), 2.04 (2H, s, CH$_2$), and 5.53 (2 H, m, CH=CH) confirms the presence of 2-decenoic acid. The singlet present at 3.07 ppm is indicative of a CH$_2$ group on 3-decenoic acid, refer to Figure 2.4, between the vinyl protons and the aliphatic chain. Since the starting material is only 92 % pure, the existence of other similar, unsaturated fatty acids will exist, as separation of these closely related compounds is nearly impossible.

product still has the singlet at 3.47 ppm indicating a mixed product which may contain some oxygenated species, such as alcohols or ethers.

Due to the broad signal in the aliphatic and vinyl regions, congruent with mixed products, integration and identification beyond functional groups present was unobtainable from the data collected. PYR was determined to be an insufficient solvent system to provide the energy required for isomerization as well as decarboxylate the starting material. Not only were the results difficult to accurately conclude liquid hydrocarbon formation, the reaction was only starting to produce liquid alkenes in the 24-36 h interval. This is a much slower reaction than the decarboxylation of 3-decenoic acid, as alkenes were already produced at 8 h and 76 % complete

after 24 h. Further analysis will be required to determine if the reaction can be controlled to produce a range of alkanes/alkenes out of a mixed reactant by taking advantage of the obvious separation observed in the NMRs above.

The solvent mixture of 2:1 PHEN:PYR was used to heat the substrate, 2-decenoic acid, to reflux and was the final opportunity for one of the PAH solvent system studied to provide the energy requirements for the isomerization and decarboxylation of the substrate via the low energy pericyclic rearrangement. The liquid product was analyzed via ^{1}H NMR to determine solvent interference, if any, as well as the type of liquid hydrocarbon produced. It was found that two very different products were recovered after 24 and 48 h, Figure 3.5a and b, respectively. Liquid alkanes were produced within the first 24 h after the onset of reflux, as can be seen with the presence of aliphatic proton signals at chemical shifts of 1.23 and 1.57 ppm (2° and 3° alkanes) and no vinyl protons between 4.5 and 6.5 ppm. During the next 24 h of refluxing the reaction mixture, isomerization and pericyclic decarboxylation was confirmed by the production of 1- nonene, Figure 3.5b. This ^{1}H NMR spectrum is indicative of a terminal alkene and matches literature values reported for 1-nonene. There is a singlet present at 4.81 ppm that does not integrate for the 1-nonene product and has not been identified further using NMR. To further confirm the presence of the liquid alkene 1-nonene, GC/MS was utilized to accurately determine the side products present as seen in the unidentified signals in the ^{1}H NMR spectra obtained inherently present by the impurities found in the starting material.

The GC/MS spectra of 3-decenoic acid and 2-decenoic acid in 2:1 PHEN:PYR after 24 h are compared in Figures 3.6 and 3.7, respectively. It can be seen from the spectra that although the main product for both is 1-nonene, the amount of breakdown products formed using 2-
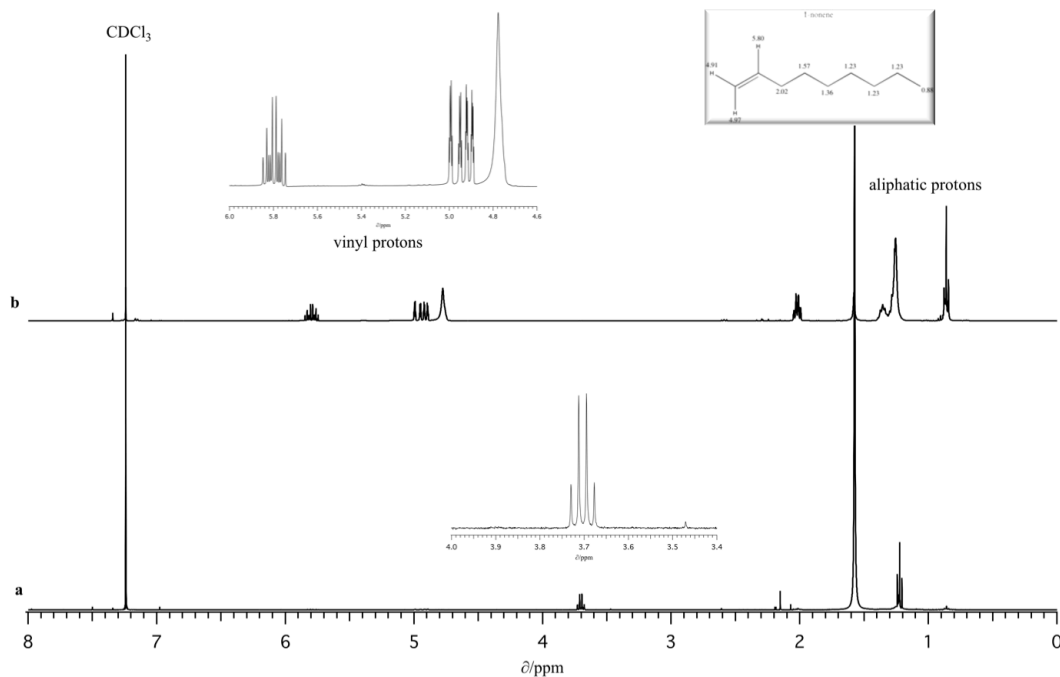
Figure 3.5 ^{1}H NMR of reaction products after 2-decenoic acid was refluxed in a solvent mixture of 2:1 PHEN:PYR for a) 24 h and b) 48 h. Insets are a magnified look at the splitting patterns of the signals corresponding to the (a) quadruplet present at 3.7 ppm and (b) the vinyl protons between 4.5-6.6 ppm. Figure 5b confirms the presence of 1-nonene as the primary liquid hydrocarbon product and the preceding pericyclic decarboxylation of 2-decenoic acid.

decenoic acid is significantly larger. As discussed in Chapter 2, the impurities found in the headspace of the product in Figure 3.6 are due to the solvent breakdown over time and the release of ortho, meta, or para substituted benzene. Since the boiling point of these molecules is around 111 °C, the contaminant in the unpurified PHEN or PYR solvent is carried over to the product. However, this is not the case for the breakdown products observed in the decarboxylation of 2-decenoic acid, Figure 3.7. It can be observed that the major product 1-nonene is found at a relative percentage that is 50 % lower that the decarboxylation product of 3-decenoic acid that does not require isomerization. Since the starting material used was determined to contain a variety of fatty acids that average to 92 % 2-decenoic acid, the large number of smaller chain alkenes/alkanes produced confirm that the isomerization and subsequent pericyclic decarboxylation of all fatty acids was successful. The presence of benzene is still

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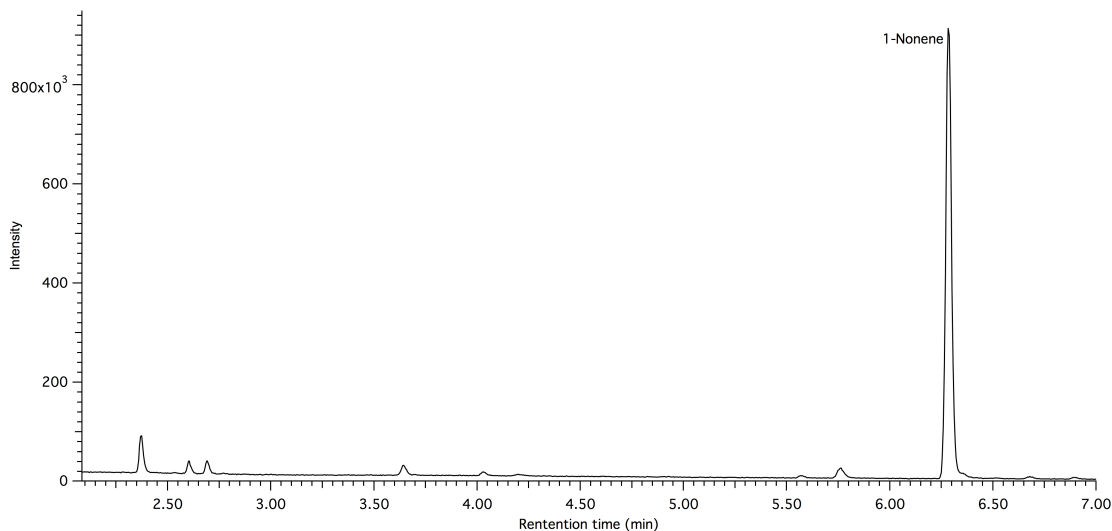
Figure 3.6 GC spectrum of products formed after 3-decenoic acid (1.0 g, 5.9 mmol) was decarboxylated in 2:1 PHEN:PYR (5.0 g, 18.7:8.2 mmol) for 24 h. Major product identified by Mass Spectroscopy (min, relative %): 1-nonene (6.29, 83.97 %); 1,3-dimethylbenzene (5.76, 2.27 %); toluene (3.64, 1.64 %); and benzene (2.37, 5.21 %). Peaks at a retention time of 2.60, 2.69, and 3.64 min could not be identified as literature ID quality was below 10 %. All major peaks are identified with an ID quality of at least 91 %.

present in this system just like the 3-decenoic acid system and is a contribution of the impurities

from the solvent.
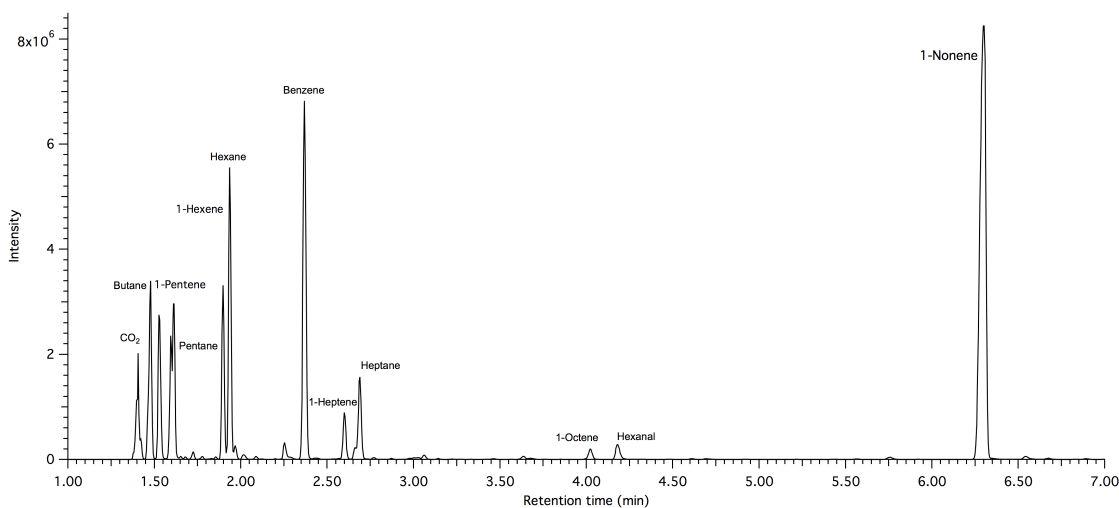
Figure 3.7 GC/MS spectrum of products formed after 1.7 g of 2-decenoic acid was decarboxylated in10.0 g of 2:1 PHEN:PYR for 48 h. Major products identified by Mass Spectroscopy (min, relative %): 1-nonene (6.30, 34.5 %); hexanal (4.16, 0.89 %); 1-octene (4.03, 0.57 %); n-heptane (2.69, 3.84 %); 1-heptene (2.60, 1.87 %); benzene (2.37, 14.42 %); n-hexane (1.94, 9.69 %); 1-hexene (1.90, 5.56 %); n-pentane (1.61, 5.16 %); 1-pentene (1.60, 3.32 %); ethanol (1.53, 5.24 %); and n-butane (1.41, 3.91 %). At least 90 % ID quality was obtained on all peaks identified.

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A significant benefit of this process is the capabilities of the solvent to handle a mixture of fatty acids ranging and produce the corresponding alkenes/alkanes, as none of these products were present in either starting material. It is predicted, given the final products, that the starting material contained fatty acids ranging from C_5 to C_{10}, although the specific unsaturation position of the fatty acid cannot be determined given the current analysis methods. The mixed solvent system of 2:1 PHEN:PYR, when used in a 5:1 solvent to substrate ratio, has proven to be a diverse and stable solvent system for the production of pure alkenes using β,γ-unsaturated fatty acids or a mixture of alkanes/alkenes using α,β-unsaturated acids. All products were liquid hydrocarbons except for hexanal and ethanol present at 0.89 and 5.24 %, respectively. Although these products are found at relatively low relative percents, the presence of an oxygenated species will require further separation before this process can claim to produce pure liquid hydrocarbons comparable to current liquid hydrocarbon fuels. However, using this unique PAH solvent system allows the reaction to be tailored towards isolating a pure product of 1-nonene through the use of 3-decenoic acid or a mixture of alkenes and alkanes such as 1-nonene, 1-octene, 1-heptene/heptane, 1-hexene/hexane, 1-pentene/pentane and butane by utilizing 2-decenoic acid as the feedstock. This demonstration of isomerization and decarboxylation of the long chain α,β-unsaturated fatty acid 2-decenoic acid has not been confirmed previously in literature, to the best of the authors knowledge.

After the isomerization and decarboxylation was confirmed using 2-decenoic acid, the decarboxylation of an even longer chain fatty acid, 2-hexadecenoic acid, was performed. Since the reflux temperature of 2-hexadecenoic acid exceeds the boiling point of PHEN, this PAH solvent cannot be used for the decarboxylation of this substrate. However, PAH solvents capable of withstanding the high reflux temperature of 2-hexadecenoic acid such as PYR, 2:1

PHEN:PYR and FA were studied. Liquid product was collected and dissolved in CDCl$_3$ after reflexing in PYR for 8, 20, and 30 hours, Figure 3.8a-c, respectively. It can be seen that although products formed, there is no indication of alkene formation throughout the entire 30-hour reaction. The presence of aromatic protons within the product at 30 hours confirms the breakdown of PYR over the reaction time and contamination of the liquid hydrocarbon product.
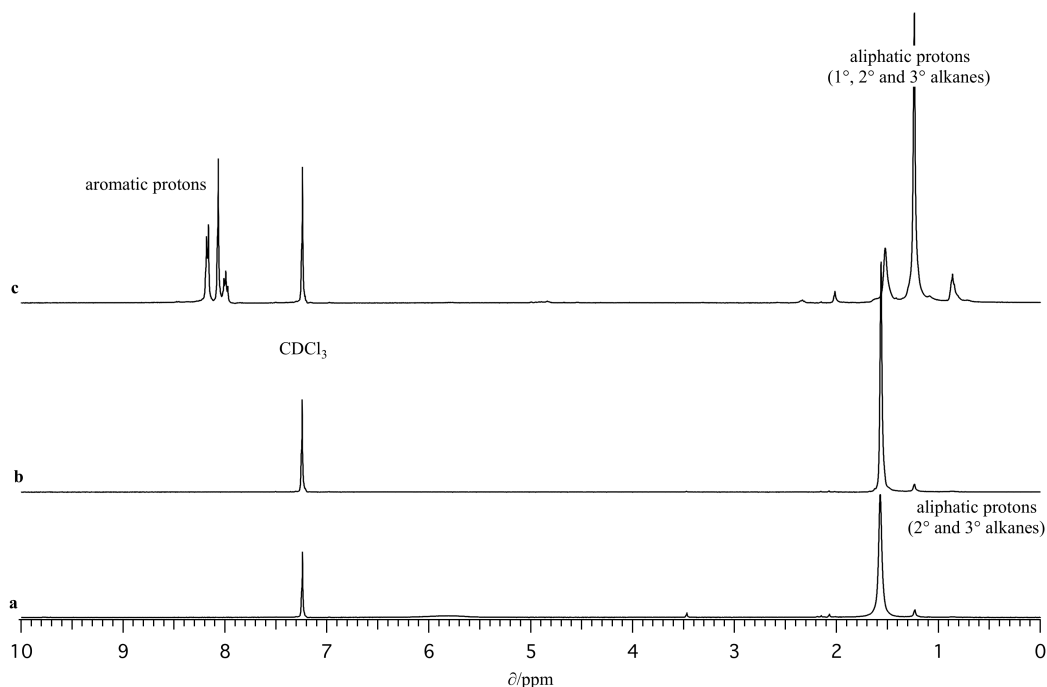
Figure 3.8 The ^{1}H NMR spectrum of the conversion products after heating 2-hexadeceonoic acid to reflux in PYR for a) 8 h, b) 20h, and c) 30h, using a 10:1 solvent to substrate ratio.

The inability of PYR to resist decomposition at these temperatures is troubling and therefore not an optimal solvent for fatty acids with reflux temperatures above 300 °C. The solvent fluoranthene (FA) was also used for the decarboxylation of 2-hexadecenoic acid due to its high boiling point. However, over time, this molecule begins to break down as well due to the 5 membered ring interrupting the delocalization of the aromatic rings surrounding it. The final product was found to contain impurities from the breakdown of the solvent as discovered by aromatic impurities found in the ^{1}H NMR spectrum. The reaction was repeated in triplicate and

each time, the solvent contaminated the liquid product after as little as 10 h. Therefore, the reaction in FA will not be described further in this chapter.

The reflux of 2-hexadecenoic acid in 2:1 PHEN:PYR successfully produced alkene products as described in Figure 3.9. It can be seen that there is a uniform breakdown of shorter chain alkenes and alkanes implying that either 2-hexadecenoic acid has a wide distribution of fatty acids, ranging from C_{11} to C_{16} or the products are breaking down under the extreme
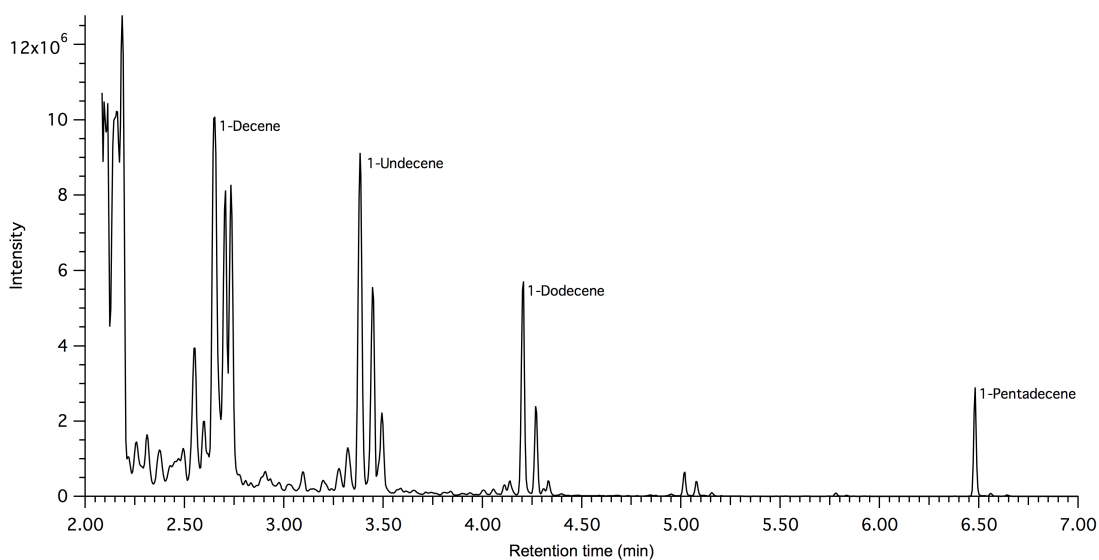
Figure 3.9 GC/MS of products formed after 2-hexadecenoic acid was refluxed in 2:1 PHEN:PYR for 24 h. The GC trace shows a mixture of alkene and alkane products that are indicative of the distribution of fatty acids found in the starting material, only 90 % pure 2-hexadecenoic acid. The retention times (min) and relative % is given for each peak: m-xylene, p-xylene, or o-xylene (2.186, .77 %); benzaldehyde (2.552, 5.13 %); 1-decene (2.653, 15.20 %); decane (2.706, 9.15 %); octanal (2.734, 9.67 %); 1-undecene (3.388, 10.58 %); undecane (3.451, 5.90 %); nonanal (3.494, 2.72 %); 1-dodecene (4.206, 5.60 %); dodecane (4.273, 2.19 %); 1-tridecene (5.019, 0.56 %); tridecane (5.081, 0.36 %); and 1-pentadecene (6.481, 2.82 %).

temperature of 375 °C as decarboxylation is occurring. Pure alkene and alkane produced were formed using this fatty acid and therefore confirming that PAH solvents have the energy density to provide the heat capacity needed fully decarboxylate fatty acids with reflux temperatures under 380 °C.

3.4 CONCLUSION

In conclusion, long chain α,β-unsaturated fatty acids, 2-decenoic acid and 2-hexadecenoic acid were successfully decarboxylated in 2:1 PHEN:PYR within 24 h. Solvent systems of PYR and FA are highly unstable at these temperatures as there was a substantial occurrence of breakdown products form the solvent systems present in the liquid hydrocarbon and headspace of the liquid producing impure alkene products and will therefore be abandoned for any future work with long chain, α,β-unsaturated fatty acids. This is the first report of α,β-unsaturated fatty acids undergoing pericyclic decarboxylation without the use of catalyst and in an inexpensive PAH solvent system.

3.5 MATERIALS AND METHODS

Solvents phenanthrene (94%) and pyrene (90%) were obtained from Sigma Aldrich. Substrate 2-decenoic acid acid (95%) was obtained from TCI as well as 2-hexadecenoic acid. All reagents were used without further purification.

Experimental solvents examined were phenanthrene (PHEN), pyrene (PYR), 2:1 PHEN:PYR and fluoranthene (FA) for 2-hexadecenoic acid, which were all used in 5:1 solvent to substrate ratios. Differing combinations of solvent and substrate, Table 4.1, were heated to reflux in a 25-mL, 3-neck pear shaped flask in a sand bath. Temperature of the reaction was monitored directly in solution. Product was collected in a receiving flask immersed in an acetone/dry ice bath held at -78 °C. Aliquots of product and reaction mixture were taken at least every 8 and 24 h. The CO_2 formed was collected in a sodium bicarbonate trap while the pure olefin condensed in the receiving flask.

The products were dissolved in $CDCl_3$ and each sample was analyzed using ^{1}H NMR on a Varian 400 MHz spectrometer using Varian programmed pulse sequences. Products were

analyzed for composition and impurities. Aliquots of the reaction mixture were also dissolved in CDCl$_3$ and analyzed using a Varian 400 MHz NMR spectrometer. ^{1}H was used to monitor the stability of the solvent over time as well as the disappearance of starting material as the reaction proceeded.

GC/MS analysis was used to accurately determine the percent yield of alkene product as well as any side products that may have formed. The headspace of the volatile product was collected via a 1 μL syringe and was subjected to an inlet temperature of 225 °C and a flow rate of 50.9 mL/min along a Zebron capillary GC column with an inner diameter of 0.25 mm at 30 m long. The sample was then heated to 180 °C at a rate of 5 °C/min after injection and the GC trace was collected. The retention time of the products were analyzed via MS and confirmed thru the digital database, Palisades Mass Spectroscopy Library, with at least 90 % confidence.

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CHAPTER 4

CONJUGATED AND MIXED UNSATURATED FATTY ACIDS UNDERGO PERICYCLIC

DECARBOXYLATION USING POLYCYCLIC AROMATIC HYDROCARBON SOLVENTS:

2,4-HEXADIENOIC ACID, 3-PENTENOIC ACID AND 3-DECANOIC ACID, AS WELL AS

2- AND 3-DECENOIC ACID

4.1 OVERVIEW

PAH solvent systems, studied in Chapter 2 and 3, were proven to provide the energy required to decarboxylate various α,β- and β,γ- unsaturated fatty acids without the use of catalysts or high pressures and temperatures. It was found that all compounds were decarboxylated to provide alkene and alkane products. However, studying the PAH solvent ability to decarboxylate conjugated fatty acids and mixed reactants of varying chain length and bond position is crucial. If the PAH solvent can handle the decarboxylation of these complicated system, the energy required to extract and purify the fatty acids from renewable sources will inevitably decrease. The conjugated system, 2,4-hexadecenoic acid (lit.[1] bp 228 °C), and mixed reactants of varying chain length such as 3-pentenoic acid and 3-decenoic acid, as well as varying bond position, 2- and 3-decenoic acid, will be discussed in this chapter. Pure, liquid hydrocarbons were produced and confirmed by ^{1}H NMR. The headspace of the product formed from the decarboxylation of the mixed reactants, 2- and 3-decenoic acid, was also analyzed via GC/MS to determine the distribution, if any, of the alkene/alkanes produced. It was found that the products for all decarboxylation reaction were purely hydrocarbon with no interference from the PAH solvent. These results prove that, regardless of isomerization before the decarboxylation, the PAH solvents studied have a high energy density capable of fully producing up to 82 % hydrocarbon products in 24 h.

4.2 INTRODUCTION

Fatty acids can exist in nature with various unsaturation positions and in differing quantities. The availability of purely β,γ-unsaturated fatty acids found in renewable sources is limited.[1] Most unsaturated fatty acids found in the chloroplast of plants are found as mixtures and therefore can be costly to extract the single, pure fatty acid desired.[2,3] Current processing techniques described in the literature have this inherent problem of requiring a pure starting material in order to produce a highly yielding liquid hydrocarbon of choice.[4-6] However, by utilizing the high energy density of the PAH solvent systems studied in Chapters 2 and 3, there is a high probability that any fatty acid containing unsaturation in the α,β- or β,γ- position will have enough energy to perform the pericyclic decarboxylation to yield the corresponding olefin.

Conjugated fatty acids, such as the commercially available 2,4–hexadienoic acid, are complex substrates that require the concerted isomerization of both double bonds before the pericyclic decarboxylation can take place, as can be seen in Figure 4.1. Sorbic acid, 2,4-hexadienoic acid, was chosen for its availability and, being a short chain fatty acid, lower
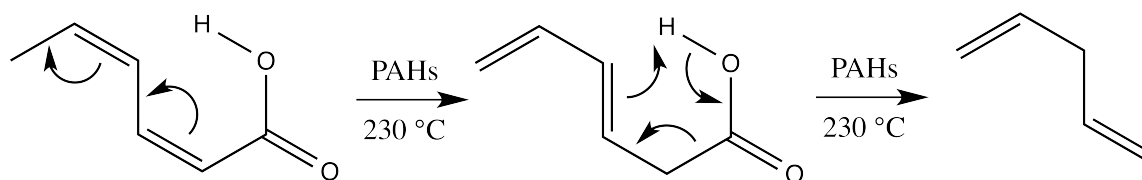
Figure 4.1 Isomerization and subsequent pericyclic decarboxylation of *cis, cis*- 2,4-hexadienoic acid in PAH solvents (PHEN, 2:1 PHEN:PYR, or PYR) resulting in terminal alkenes.

decarboxylation temperature. Besides being a synthesized additive for the food industry,[7] it is present in renewable sources such as the berries of the mountain ash and can be easily extracted from this annual feedstock.[8] The extra heat capacity present in the PAH solvents can be utilized for the isomerization of the conjugated substrate and subsequent pericyclic decarboxylation. This concerted reaction is driven forward by the removal of the carboxyl group of the fatty acid due to

its high electronegativity and elevated temperatures of the system, as described in Figure 2.1 of Chapter 2.

PAH solvents were shown to have the required energy density to facilitate pericyclic decarboxylations in α,β- or β,γ-unsaturated fatty acids of chain lengths up to C_{16}, without the use of catalyst or elevated pressures. Since 2:1 PHEN:PYR solvent provided a large yield of hydrocarbon product when using a single, at least 94% pure starting material and without contamination from the solvent it was the best solvent for studying mixed substrates. Investigation of the solvent capabilities to selectively decarboxylate mixed fatty acids of various chain lengths or unsaturation position is crucial to the overall efficacy of our solvent system towards a wider range of renewable feedstock, provided the substrates contain α,β- or β,γ-unsaturated fatty acids. A mixture of varying chain lengths, 3-pentenoic acid and 3-decenoic acid, as well as varying unsaturation, 2-decenoic acid and 3-decenoic acid, were each solubilized in 2:1 PHEN:PYR and the subsequent hydrocarbon products were confirmed using ^{1}H NMR. These mixtures are representative of the various combinations of substrates that could be present in the raw extract from renewable feedstocks.

4.3 RESULTS AND DISCUSSION

The PAH solvent system of 2:1 PHEN:PYR has proved to be a superior solvent system when compared to PHEN or PYR at reflux temperatures above 300 °C, as shown in Chapters 2 and 3. For this reason, it was the only solvent system pursued when investigating the complex substrates discussed herein. The conjugated acid described in Figure 4.1, is a short chain, α,β-unsaturated fatty acid that will require isomerization before the pericyclic decarboxylation can be permitted to form terminal alkenes. This hypothesis has been tested by using 5.0 g of 2:1 PHEN:PYR to reflux 2,4-hexadienoic acid in a 5:1 solvent to substrate ratio. This reaction

proceeded to reflux as the liquid product was collected via condensation. The product was analyzed using ^{1}H NMR, 8 and 24 hours after reflux, Figure 4.2a and b, respectively. The signals found in the ^{1}H NMR are dissimilar in the fact that after 8 hours, an alkane product has formed
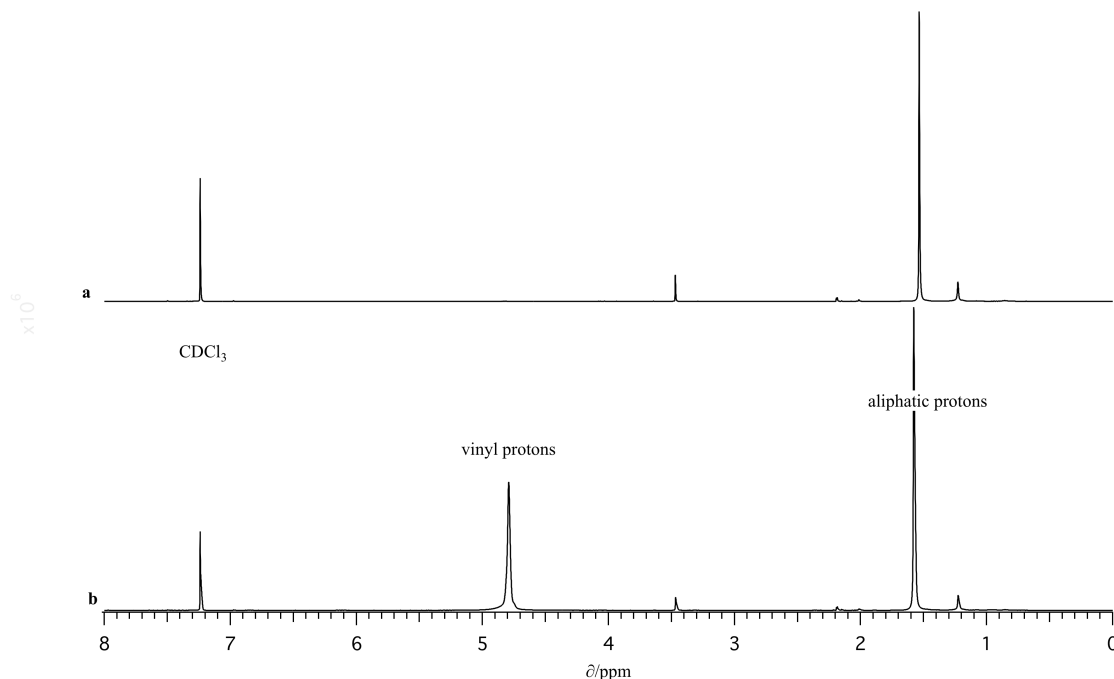
Figure 4.2 ^{1}H NMR spectra of the product formed after a) 8 and b) 24 h of refluxing 2,4-hexadienoic acid in 2:1 PHEN:PYR. The products formed are very dissimilar and imply that the alkane product was collected before the alkene product is formed. However, the unidentified product at 8 h (a) is still formed after 24 h as the proton signals at 3.46 ppm are present in both spectra.

with no peaks present within the vinyl region to confirm alkene formation. The peak at 3.46 ppm in Figure 4.2a implies a proton signal that resides next to an electron-withdrawing group. Based on the presence of this product, pericyclic decarboxylation cannot be confirmed and thermal decomposition of 2,4-hexadienoic acid is therefore likely in order to produce oxygenated products. However, within 24 hours after the onset of reflux, Figure 4.2b, alkene products were confirmed as a broad signal at 4.78 ppm appeared. This signal, since it is a large singlet, cannot be integrated to determine the exact alkene(s) present. Because of the ambiguity of the product spectrum and GC/MS being unavailable at the time of these reactions, identification of the product was unobtainable. Nonetheless, it can be concluded that alkene product formation was

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confirmed but further analysis will be required to confirm the complete identity of the products formed. It is important to note that the PAH solvent system of 2:1 PHEN:PYR provided the energy required to alter the substrate into liquid alkanes/alkenes without interfering with the product formed.

Mixed substrates of varying chain lengths were investigated using 0.3 g of 3-pentenoic acid and 0.7 g of 3-decenoic acid in 5.0 g of 2:1 PHEN:PYR. The products were analyzed using ^{1}H NMR as GC/MS was again unavailable at the time of this study. It can be seen in Figure 4.3 that the β,γ-unsaturated acids were completely converted to liquid hydrocarbon products, as there are no proton signals corresponding to protons residing next to electronegative atoms. Both Figure 4.3a and 4.3b contain signals corresponding to aliphatic protons, 0.8-1.5 ppm range, but do not have proton signals in the 2.4-4.5 ppm range confirming a purely hydrocarbon product. After 24 hours of reflux, Figure 4.3b, vinyl protons are observed at 4.8 ppm and confirm an
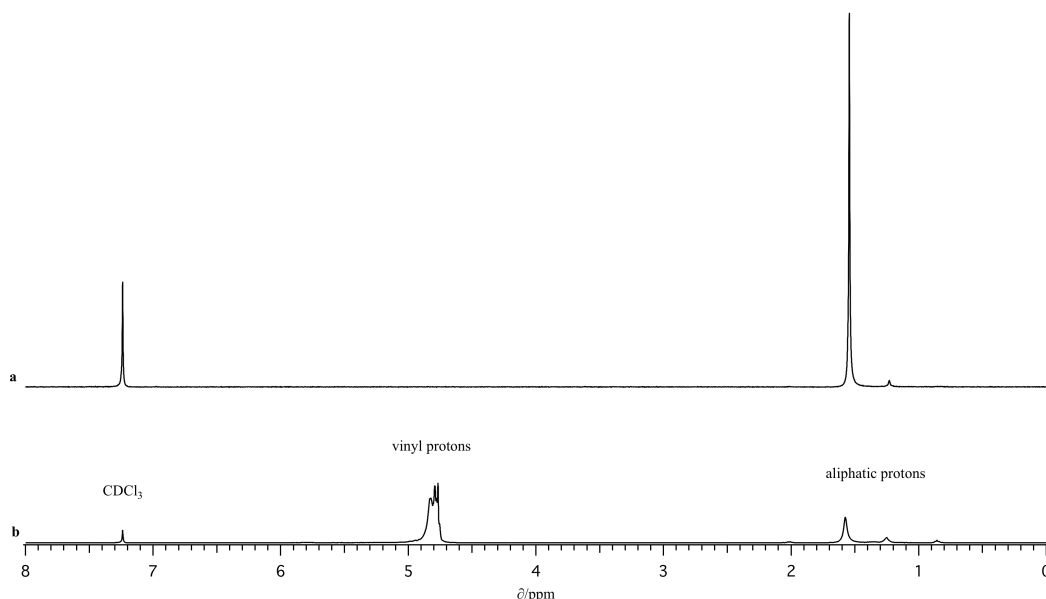
Figure 4.3 ^{1}H NMR spectra of the decarboxylated product collected at a) 8 and b) 24 h after the onset of reflux of a mixed 3-pentenoic acid and 3-decenoic acid substrate in 2:1 PHEN:PYR. Products are confirmed as mixed alkanes/alkenes of unknown chain length.

alkene product. Like 2-decenoic acid in Chapter 3, the mixed substrate produced a mixed alkene product, as the signal is broad and unsymmetrical. Since it is highly difficult to integrate a ^{1}H NMR spectra containing mixed chain lengths of the species due to the overlap of proton signals observed for each, the only conclusion that can be drawn from this data is that a mixed alkene was produced within 24 hours of the onset of reflux. Future investigation of this reaction using GC/MS is necessary before identification of these mixed products can be possible.

Understanding the ability of the solvent system, 2:1 PHEN:PYR, to selectively provide the energy required to isomerize and decarboxylate α,β- and β,γ-unsaturated fatty acids simultaneously is necessary for the controlled production of mixed alkenes. Using a larger sample size, but still a solvent to substrate ratio of 5:1, 1.0 g of both 2- and 3-decenoic acid were dissolved in 10.1 g of 2:1 PHEN:PYR. After 24 hours of reflux, the headspace of the liquid product was analyzed using GC/MS and can be found in Figure 4.4. The qualities of the product identifications have at least a 90 % correlation to Wiley Database Mass Spectral Library. The major product, 1-nonene, was 61.47 % of the total product analyzed. Minor products of 1-heptene and heptane constitute almost 15 % of the product. Although in low relative percentage (2.70 %), trans-1-butyl-2-methylcyclopropane was a surprising result as instead of forming a terminal alkene after the pericyclic rearrangement occurred, it is assumed that the migrated to form the cyclic alkene. It is uncertain if this was a product resulting from impurities in the substrates such as shorter/longer fatty acids or dimer formation as the substrates decomposes over time. Rewardingly, about 80 % of the product contains liquid hydrocarbons proving the successful pericyclic decarboxylation of substrates containing α,β- and β,γ-unsaturated fatty acids.
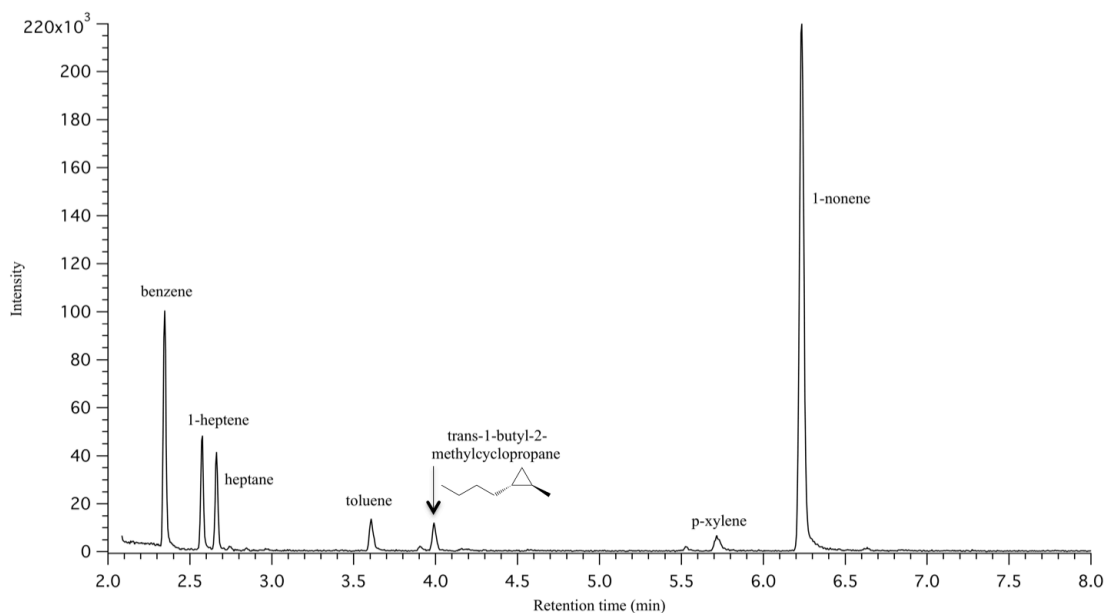
Figure 4.4 GC/MS of the product formed after refluxing 2- and 3-decenoic acid in 2:1 PHEN:PYR for 24 h. Identification of major products was possible using MS and are listed using the retention time (min) and relative % intensity: 1-nonene (6.24, 61.5 %), p-xylene (5.72, not calculated), trans-1-butyl-2-methylcyclopropane (3.99, 2.70 %), toluene (3.60, 3.55 %), heptane (2.66, 6.85 %), 1-heptene (2.58, 8.10 %), and benzene (2.34, 17.34 %).

Since all materials were used without further purification, results like these are expected. This is especially true regarding the contamination of the product with benzene, toluene, and p-xylene; percentages are described in the figure caption. All breakdown products from the solvent system have low vapor pressures and being a closed system will inevitably collect in the product flask. The remaining products are confirmed to be the same breakdown products observed when 3- and 2-decenoic acid were decarboxylated in 2:1 PHEN:PYR individually, Figure 2.8 and 3.6, respectively. ¹H NMR was not collected for the product and therefore it cannot be confirmed whether these aromatic products are dissolved in the liquid product or only part of the headspace above the liquid as in previous studies. Given the resemblance to the fatty acid products found when individually decarboxylated, it is safe to assume these products would not be dissolved in the liquid hydrocarbon product.

As there were limitations on analytical techniques chosen and used in this chapter, there are answers that are still unobtainable when only one analysis technique was run for each

reaction. However, hydrocarbon product formation can be confirmed from all analysis methods but GC/MS proved to be a more powerful technique as it allows for the full picture of the major products and their breakdown instead of a general confirmation of mixed alkenes/alkanes.

4.4 CONCLUSIONS

The successful decarboxylation of complex, mixed substrates allows for the declaration that the solvent system, 2:1 PHEN:PYR, is an exceptional system for facilitating the isomerization and pericyclic decarboxylation of α,β- or β,γ-unsaturated fatty acids with carbon chains of C_{10} and larger. To the best of the author's knowledge, documentation of the isomerization and decarboxylation in 2:1 PHEN:PYR solvents has not been reported previously. However, as these are just commercially obtained, pure fatty acids, testing fatty acids obtained from renewable sources such as mountain ash (sorbic acid), *Acacia* (3-dececnoic acid and 3-methyldecenoic acid), or *Arabidopsis thaliana* (2- and 3-decenoic acid in the form of 3-*trans*-hexadecenoyl) will still need to be studied to determine the fate of this process when competing with catalytic liquid hydrocarbon production.

4.5 MATERIALS AND METHODS

Solvents phenanthrene (99 %) and pyrene (98 %) were obtained from Sigma Aldrich. Substrate 3-pentenoic acid (95 %), 2-decenoic acid (>90 %), 3-decenoic acid (>90 %) and sorbic acid (99 %) were all obtained from TCI.. All reagents were used without further purification.

The experimental solvent, 2:1 PHEN:PYR, as used to solubilize and facilitate reflux was acids mentioned above. Reaction mixtures were heated to the reflux of the parent acid in a 25-mL, 3-neck pear shaped flask in a sand bath. Temperature of the reaction was monitored directly in solution. Product was collected in a receiving flask immersed in an acetone/dry ice bath held

at -78 °C. Aliquots of product were taken every 8 and 24 hours. The CO_2 formed was collected in a sodium bicarbonate trap while the pure olefin condensed in the receiving flask.

The products were dissolved in $CDCl_3$ and each sample was analyzed using ^{1}H NMR on a Varian 400 MHz spectrometer using Varian programmed pulse sequences. Products were analyzed for composition and impurities. GC/MS analysis was used to accurately determine the percent yield of alkene product as well as any side products that may have formed. The headspace of the volatile product was collected via a 1 μL syringe and was subjected to an inlet temperature of 225 °C and a flow rate of 50.9 mL/min along a Zebron capillary GC column with an inner diameter of 0.25 mm at 30 m long. The sample was then heated to 180 °C at a rate of 5 °C/min after injection and the GC trace was collected. The retention time of the products were analyzed via MS and confirmed thru the Wiley digital database, Palisades Mass Spectroscopy Library, with at least 90 % confidence.

4.6 REFERENCES

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Chapters 2 and 3 references pertain to the ideas presented in this chapter.

CHAPTER 5

SUMMARY

This work investigated the pericyclic decarboxylation of β,γ- and α,β-unsaturated fatty acid to produce liquid alkene hydrocarbons capable of competing with current transportation fuels. PAH solvent systems not only allow for compete decarboxylation of many different β,γ- and α,β-unsaturated fatty acid but also contain enough energy density to fully produce alkene products without the use of catalysts of extreme temperatures and pressures. This is important as the need for transportation fuels from renewable sources that can mimic petroleum products used today is highly desired due to depleting resources of petroleum with an ever increasing demand for fuel.

The substrates 3-pentenoic acid and 3-decenoic acid were converted to alkene hydrocarbon products after 24 hours in the solvent systems, PHEN, PYR, and 2:1 PHEN:PYR following the reaction scheme in Figure 2.1. Products formed after refluxing 3-pentenoic acid were identified as liquid hydrocarbons, although the determination of the specific alkene products formed was difficult in the PYR solvent, Figure 2.2c. However, using the thermally stable PAH solvent, PHEN, the product formed can be confidently identified as 1-butene, Figure 2.2a. Refluxing the longer chain β,γ-unsaturated fatty acid in PAH solvents also produced alkene hydrocarbon products, especially when using PHEN and 2:1 PHEN:PYR. It can be seen in Figure 2.8 that the product, analyzed by GC/MS is 84 % 1-nonene. This result is the first time long chain, β,γ-unsaturated fatty acids in PAH solvents has been reported to successfully produce liquid alkene hydrocarbons, such as 1-nonene, after refluxing for 24 hours.

Since the successful decarboxylation of 3-decenoic acid was confirmed, investigating the decarboxylation of the thermodynamically stable α,β-unsaturated fatty acids that are more

prevalent in nature must be addressed. Although the PAH solvents have the required energy density to decarboxylate β,γ-unsaturated fatty acids and produce alkene hydrocarbon products, it is necessary to determine the solvent stability when isomerization is required before the subsequent decarboxylation. This isomerization could hinder the formation of terminal alkenes if not enough energy is provided in the systems for this reaction. Upon decarboxylating 2-decenoic acid in 2:1 PHEN:PYR for 24 hours, the liquid product was collected and analyzed using ^{1}H NMR and GC/MS to identify all products present in the headspace above the liquid product. As can be seen in Figure 3.5, the ^{1}H NMR spectra of the alkene product after 2-decenoic acid was refluxed in 2:1 PHEN:PYR for a) 24 and b) 48 h. Sharp splitting patterns on the vinyl proton signals confirm the presence of a pure, terminal hydrocarbon product however the presence of the broad singlet at 5.75 ppm is indicative of a mixed alkene product as well.

To further confirm this result, the product was analyzed with GC/MS after 24 hours of reflux and the data is presented in Figure 3.7. The major product, at 34.5 % relative abundance, was 1-nonene however; other alkenes/alkanes were present in the spectrum and are described in Figure 3.7. The confirmation of the terminal alkene, 1-nonene, proves the isomerization is occurring before the pericyclic decarboxylation happens resulting in the product predicted. Small chain alkenes and alkanes are also present in the spectrum and can be attributed to the variety of fatty acids present in the starting material as depicted by the GC/MS of the substrate, 2-decenoic acid shown in Figure 3.6. This spectrum shows mixed reactants containing the same carboxyl groups but with varying chain length, and is confirmed by the manufacturer. The ability of the solvent system to facilitate the isomerization and subsequent decarboxylation of α,β-unsaturated fatty acids of various chain lengths is intriguing and discussed in Chapter 4.

Longer chain unsaturated fatty acids usually exist in the thermodynamically stable α,β-form and therefore have been explored using 2:1 PHEN:PYR solvent systems as well as PYR and FA. It was determined that the PYR and FA solvent systems could not withstand the higher temperatures and contaminated the product significantly. However, when refluxed in 2:1 PHEN:PYR a result similar to the one for 2-decenoic acid was obtained and can be seen in Figure 3.9. The GC/MS of the product shows a significant breakdown of shorter chain alkenes/alkanes as well as the presence of the expected alkene, 1-pentadecene. This uniform GC trace of the product is indicative of selectively decarboxylating each unsaturated acid found in the substrate, be it β,γ- and α,β- unsaturated fatty acids present. This result allows for the conclusion that the PAH solvent system of 2:1 PHEN:PYR provides the required energy density to facilitate isomerization and pericyclic decarboxylation of any unsaturated fatty acid of chain lengths C_5-C_{16}.

To further test the ability of 2:1 PHEN:PYR to facilitate decarboxylation in these systems, complex substrate mixtures of conjugated acids, mixed fatty acids of varying chain length and mixed fatty acids of varying bond position were studied in Chapter 4. The data collected for sorbic acid and the mixed substrates of 3-pentenoic acid and 3-decenoic acid were inconclusive and require GC/MS analysis to further identify the products formed. However, GC/MS was used to analyze the product after the mixed substrate, 2- and 3- decenoic acid, was refluxed for 24 hours in a 2:1 PHEN:PYR solvent system and is provided in Figure 4.4. The alkene products formed totaled ~80 % of the relative area within the spectrum, of which 61.5 % was the hypothesized product, 1-nonene.

These results, in conjunction with the data provided in previous chapters, confirm the solvent stability of 2:1 PHEN:PYR over time and the ability of this solvent system to provide the

necessary energy to facilitate pericyclic decarboxylations, regardless of the starting material present. To the best of the author's knowledge, this is the first report of PAH solvent systems being used to facilitate the decarboxylation of β,γ- and α,β-unsaturated fatty acids without the use of catalysts or extreme temperatures and pressures. By utilizing potential renewable feedstocks with β,γ- and α,β-unsaturated fatty acids, the energy required for producing liquid hydrocarbon fuels can potentially be much lower. Using PAH solvent systems, the high activation energy barrier is overcome and the exothermic decarboxylation proceeds rapidly to produce liquid alkene products capable of competing with current transportation fuels.

MONITORING THE REFLUX OF 3-PENTENOIC ACID USING NON-PAH SOLVENTS:

NO SOLVENT (NEAT), IONIC LIQUIDS, AND GRAPHITE

Since most high boiling point PAH solvents cannot be used due to their carcinogenic nature, alternative solvents were pursued that were "green' solvents that are not carcinogenic. Ionic liquids are known for being a "green" solvent for many chemical reactions. However, the ionic liquid (1-Butyl-3-methylimidazolium hexafluorophosphate) provided no product regardless of the solvent to substrate ratios used. This solvent was deemed inappropriate for this system and reactions regarding no solvent (neat) and graphite solvents were pursued.

The neat reaction of 1.0 g of 3-pentenoic acid was placed in a 10 mL round bottom flask heated to 180 °C and connected to a condenser which allowed the product to collect in a flask held at -78 °C. A miniscule amount of product was produced after 8 hours and the reaction could not be continued, as the reaction flask was charred and ceased to produce more product. A ^{1}H NMR spectrum was obtained by swirling the flask with $CDCl_3$ in an effort to gather as much product as possible and is provided in the figure on the next page. The absence of vinyl protons indicates that the substrate did not undergo pericyclic decarboxylation but instead thermally decomposed to an alkane product with oxygen still present, as the proton signal at 3.471 ppm indicates a proton next to an electronegative atom.

Graphite as a solvent, did not produce a large amount of decarboxylated products either, as shown in the GC/MS of the product collected after 1.0 g of 3-pentenoic acid was injected into 5.0 g of graphite heated to 180 °C. Product was collected in the same manner as all products in

this dissertation. The GC/MS, found on page 3, did contain 1-butene but a large concentration of oxygenated products as well. There is a minimal indication of graphite having the required energy needed to overcome the large activation barrier.
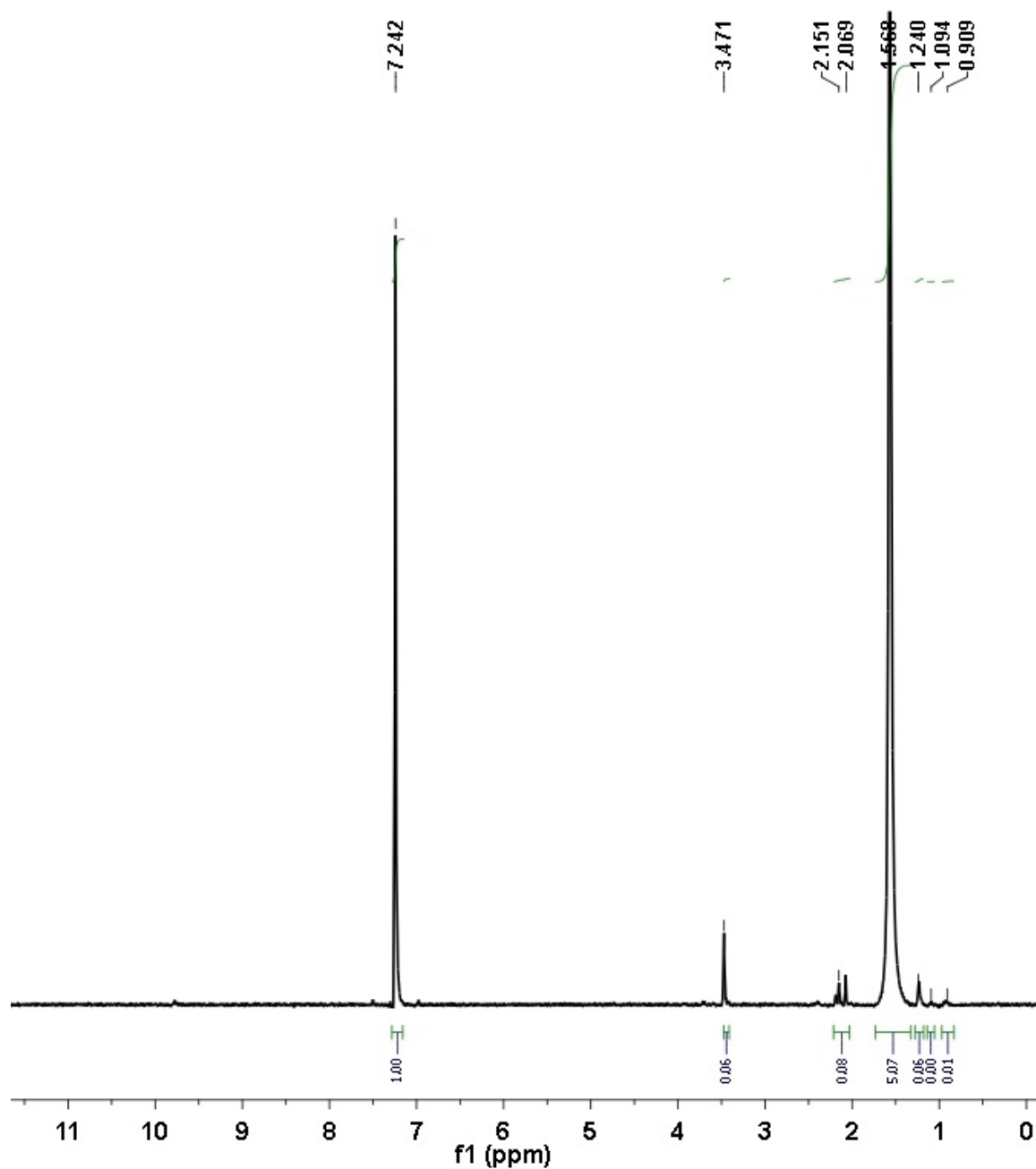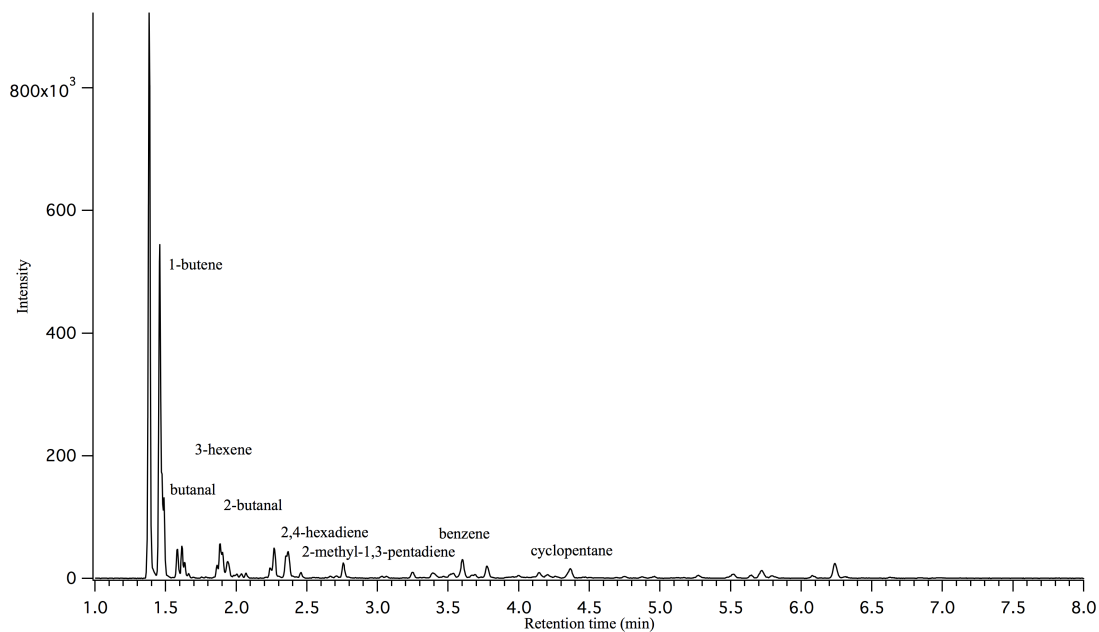
To conclude, PAH solvents are necessary to facilitate the pericyclic decarboxylation in order to produce liquid hydrocarbon product. Although 3-pentenoic acid produced liquid products when heated in graphite, they are not the desired products of this dissertation.

MODIFICATION OF HETEROGENEOUS METAL OXIDE CATALYSTS TO PRODUCE

RAW MATERIALS FROM CELLULOSIC ETHANOL (BIOETHANOL)

A research fellowship performed during the summer 2012 at the National Institute for Advanced Industrial Science and Technology in Tsukuba, Japan is described. A synopsis of the author's 9-week fellowship in which heterogeneous, metal-oxide catalysts were synthesized and used in the catalytic conversion of bioethanol to chemicals such as propylene and acetone, currently produced from petroleum feedstocks. The author's participation in the Isao Nakamura laboratory, under the supervision of Tadahiro Fujitani, has advanced the laboratory's database of catalysts by synthesizing and characterizing twenty-one mixed metal-oxide catalysts, in ratios varying from 1-5%. The catalytic conversion of bioethanol to raw materials such as propylene and acetone was studied and quantified using GC/MS. Furthermore, an alternative mechanism than what is currently understood for the catalytic conversion of bioethanol to acetone was discovered. This alternate mechanism is still under investigation in the Nakamura group.

Date: July 19, 2012

AIST Internship Program
Research Report

1. Name: Michelle Romanishan

    Host Researcher: Dr. Isao Nakamura

2. Title of Research in Japan:

    Modification of heterogeneous metal oxide catalysts to produce raw materials from cellulosic ethanol (bioethanol)

3. Internship Period: From May 21, 2012   To July 20, 2012

4. Research Implementation and Results:

    Commercial chemicals, such as propylene, acetone and iso-butene, are typically made from petroleum sources. However, due to dwindling resources over the past decade, numerous institutes have been researching methods to produce these chemicals from renewable sources such as biomass or syngas. Dr. Nakamura's group is currently pursuing converting bioethanol, a biomass from eucalyptus trees, to propylene via a catalytic process. Zirconium oxide (ZrO_2) catalysts have typically been used for this conversion and are currently being optimized to increase the percent production of certain chemicals, specifically propylene. ZnO_2 catalysts can be modified to increase the number of acidic or basic catalytic sites to selectively increase production of these products.

    During my time at AIST, I have modified ZnO_2 catalysts by adding various metals oxides in different ratios to the primary catalyst. This was done to introduce more acidic or basic sites onto the catalyst in order to improve the raw material production from bioethanol. Specifically, metals such as Yttrium, Lanthanum, Bismuth, Cesium, Strontium, Magnesium, and Zinc were added to ZrO_2 in ratios of 1, 3, 5, and 10 mol percent (mol %). These heterogeneous metal oxide catalysts were prepared and characterized using XRD, TPD, and BET techniques to determine the crystalline phase, amount of acidic or basic sites, and the

pore size and volume of each catalyst, respectively. Each catalyst was reacted with an ethanol/water/N_2 mixture to measure the catalytic activity to produce propylene and other chemicals such as ethylene, acetone and iso-butene. These reactions were carried out in a high-pressure reactor at 450 °C and 10 atm for 4 h. Through GC analysis, we determined the products present and their corresponding conversion yields. Ethylene production is fairly common in these reactions but the propylene production was our primary target when determining the activity of these catalysts. These percentages were then compared to the catalytic performance of calcined ZrO_2.

The data collected was tabulated and the results discussed with Fujitani-san and Takahashi-san. It was shown that the addition of 3 mol % of the metal Yttrium, Y, produced the highest yield of propylene at 44 %. The crystallinity of this compound differed from ZrO_2 and was primarily tetragonal in nature instead of a mixture of tetragonal and monoclinic like ZrO_2. Lanthanum metal, La, also had a very high yield of propylene production at 42 % conversion when 1 mol % was added and also showed a crystal phase that was mainly tetragonal. Both of these metals produced a large yield of ethylene as well, but not as high as strontium, Sr. The Sr metal additive acted very similar to ZrO_2 in the production of all conversion products reported. Surprisingly, 1 mol % of the zinc, Zn, additive converted ethanol to propylene poorly at only 4 % however, produced acetone at a very high yield of up to 60 % and at an average of 50 %. The crystalline phase was monoclinic which was very different from the ZrO_2 catalyst as well as all other mixed metal oxide catalysts at this percentage. More investigation and characterization is being done to determine why this species behaved so differently than the others. From researching the literature and observing the reaction trends, the data seems to point in the direction of the

catalyst having more selective basic sites that would facilitate this type of raw material production. However, until the TPD using CO_2 carrier gas is completed, these claims are purely speculation on my part. The remaining metal additives studied showed little change or lower activities when compared to the activity of ZrO_2 in the conversion of bioethanol to propylene, as will be explained in the final presentation.

To conclude, modifying ZrO_2 with various mixed metal oxides has proven to have some benefit in increasing the production of raw materials such as propylene and acetone. I hope the results found here can be useful towards furthering the scope of this project, including expanding new reaction pathways and exploring metal oxides with similar physical characteristics as that of Y, La and Zn.

5. Comments and suggestions to AIST, especially concerning the AIST Internship program (If you visited related researchers in Japan, please mention it)

The AIST internship program has been a wonderful experience. The program was set up so that the transition from America to Japan was very stress-free and welcoming. I was very informed and everything I needed was made available to me or at least easily obtained. The flexibility of allowing me to participate and reorganize everything, including a new host researcher, after the natural disaster last year was very reassuring that this program would be helpful and knowledgeable and allowed for a smooth transition into the group. The host researcher selected was a wonderful fit for me as well as allowed me to pursue important research in my field of interest and add to my knowledge of the current field. Having this internship will add significantly to my future plans as a researcher in this field. I hope the friendships and collaborations I have made here will continue to grow as research in this field develops along with my career in biofuels.

I had the fortunate opportunity to meet the Deputy Director of the Biomass Technology Research Center at AIST Chugoku thanks to Dr. Fujitani and his director coordinating the trip to Higashi-Hiroshima City. Deputy Director Satoshi Hirata was kind enough to show us around the bioethanol production plant where biomass from the cellulose found in eucalyptus trees is converted to bioethanol in a batch process. He also described their gasification operations and showed us around the Fisher-Tropsch reactor similar to ours but much larger in scale. This experience added significantly to my already overwhelming interest in the biomass industry.

The following pages contain the data collected and presented to the AIST International Division who sponsored the fellowship.

Modification of heterogeneous metal oxide catalysts to produce raw materials from cellulosic ethanol (bioethanol)

Michelle Romanishan

July 19, 2012

Hosted by Dr. Isao Nakamura

National Institute of Advanced Industrial Science and Technology (AIST)

Background

Due to the global energy crisis and the increasing demand for propylene, much attention has been paid to alternative resources to petroleum. We focus on bioethanol conversion into lower olefin such as ethylene and propylene, which are important raw materials for chemical industry.
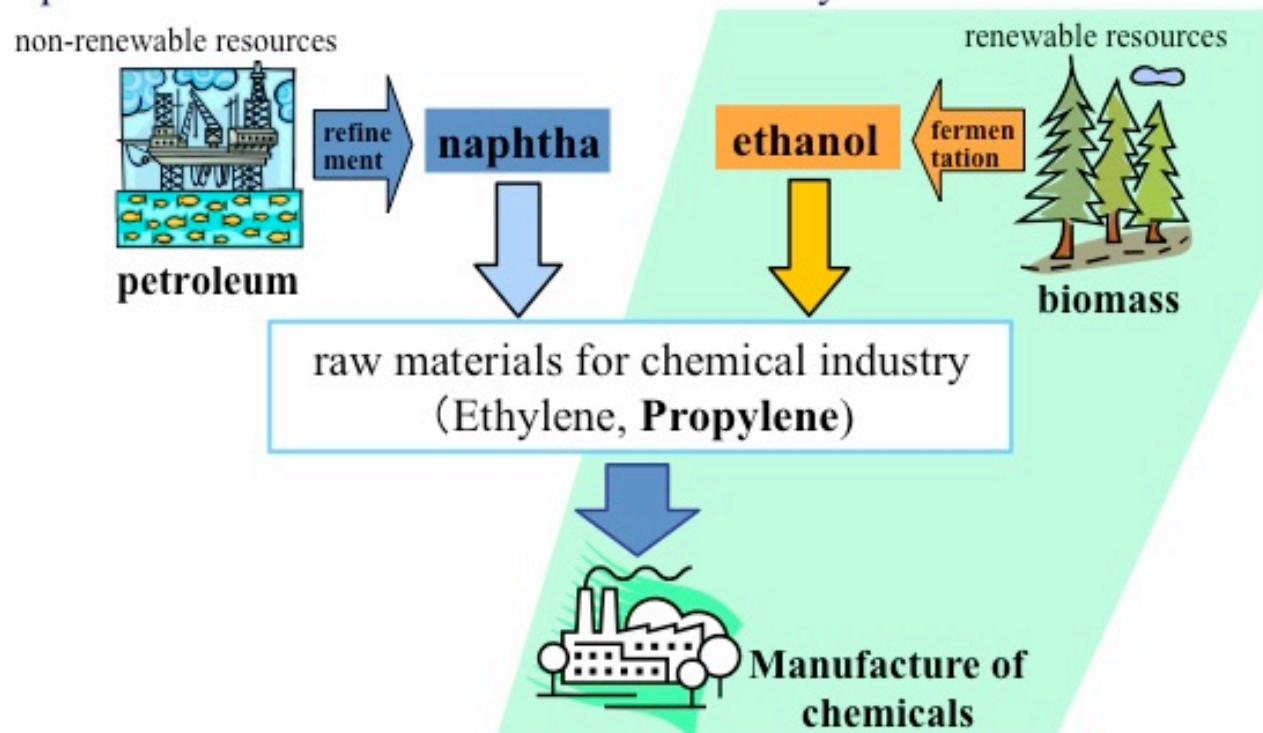
Plausible reaction mechanism from ethanol to propylene for zeolite catalysts

$$3C_2H_5OH \xrightarrow{\text{dehydration}} 3C_2H_4 \xrightarrow{\text{oligomerization}} 2C_3H_6$$
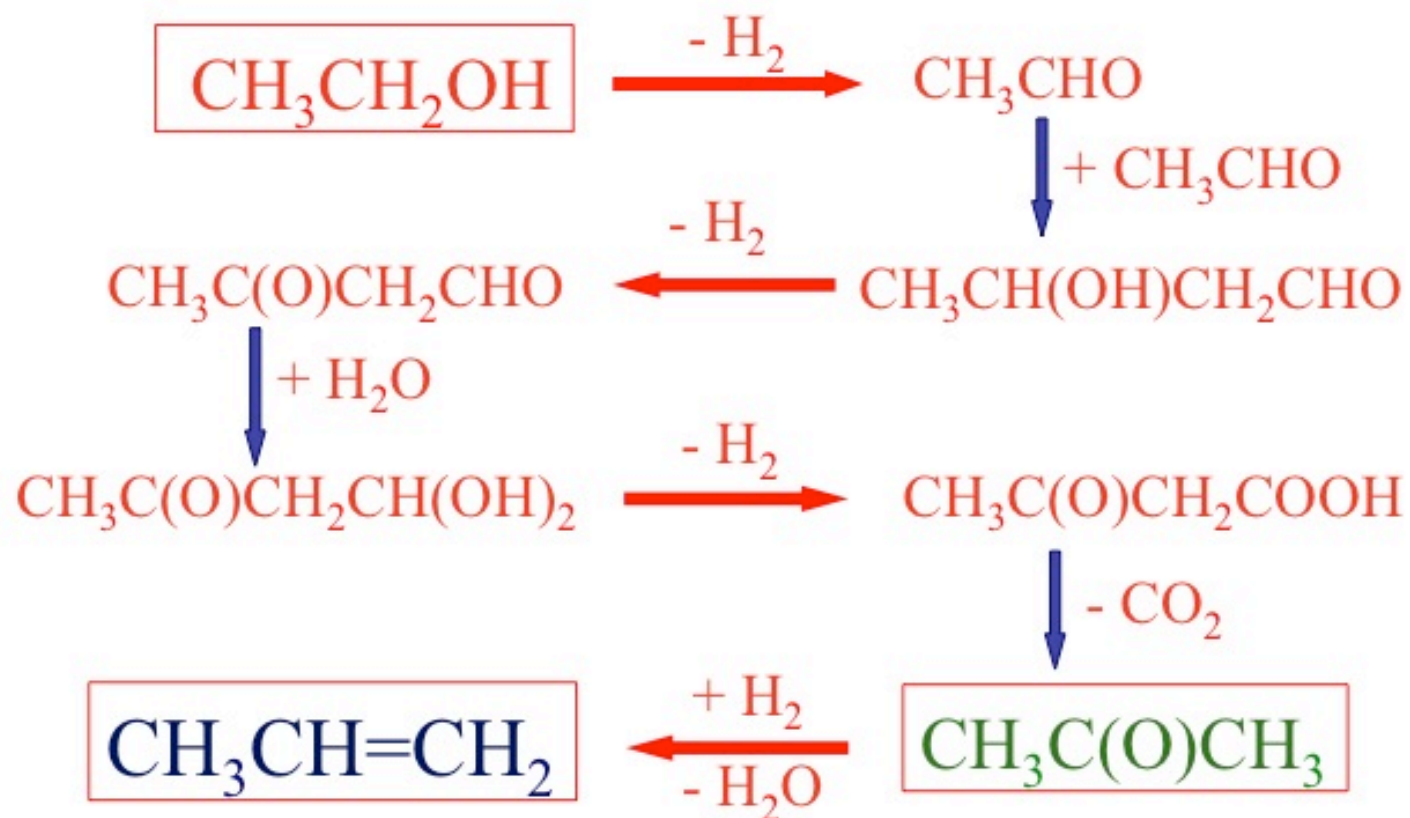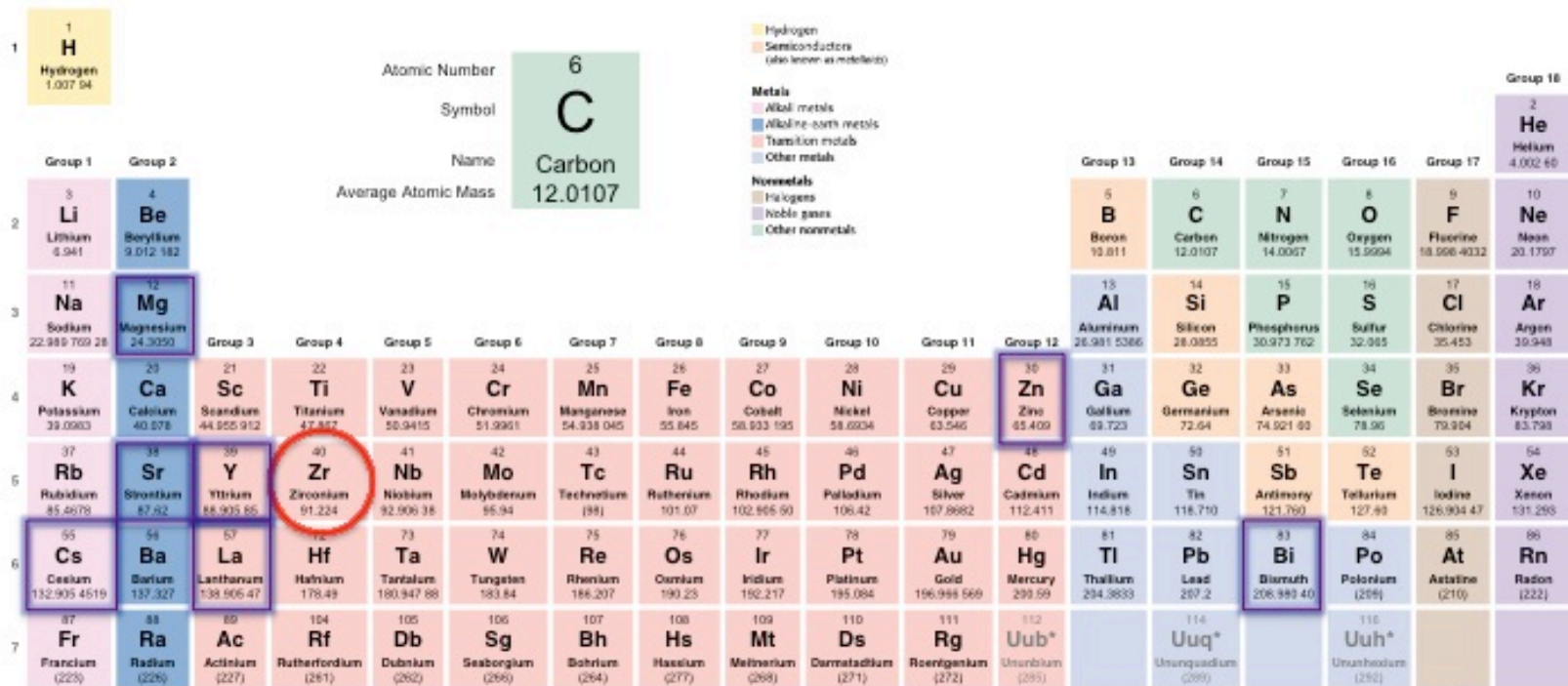
$$H_2O$$
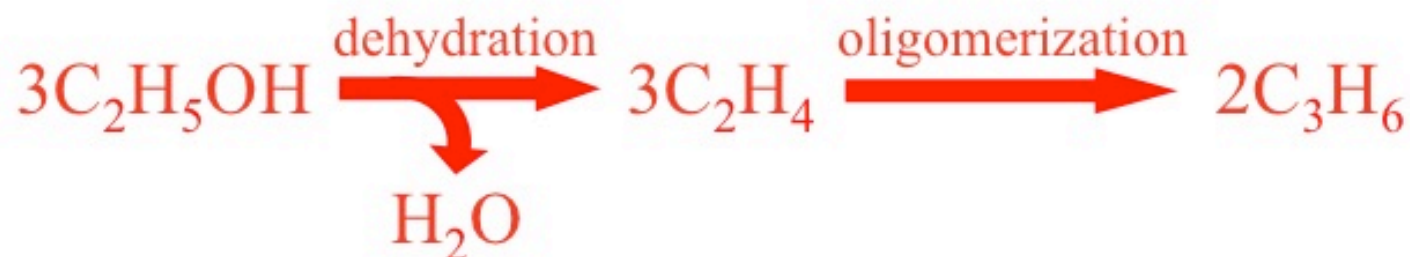
Acidic sites act as an active species.

Zeolite catalysts have been found to have short lifetimes and low activities towards propylene production

Plausible reaction mechanism from ethanol to acetone and propylene using heterogeneous ZrO_2 catalysts

$$CH_3CH_2OH \xrightarrow{-H_2} CH_3CHO$$

$$\downarrow +CH_3CHO$$

$$CH_3C(O)CH_2CHO \xleftarrow{-H_2} CH_3CH(OH)CH_2CHO$$

$$\downarrow +H_2O$$

$$CH_3C(O)CH_2CH(OH)_2 \xrightarrow{-H_2} CH_3C(O)CH_2COOH$$

$$\downarrow -CO_2$$

$$CH_3CH=CH_2 \xleftarrow[-H_2O]{+H_2} CH_3C(O)CH_3$$

Basic sites can also act as an active species.

Periodic Table of the Elements

Analysis Techniques

- BET monolayer
  - Named after Braunauer, Emmett, and Teller in 1938
  - Measures specific gas adsorption on surfaces of particles
  - Obtain surface area and pore size of catalyst

- Temperature Programmed Desorption (TPD)
  - Measures the desorption of an absorbed gas species on the surface by mass spectrometry while simultaneously increasing the substrate temperature
  - Obtain the strength of acidic or basic sites on the catalyst, depending on the amount of NH_3 or CO_2 desorbed, respectively

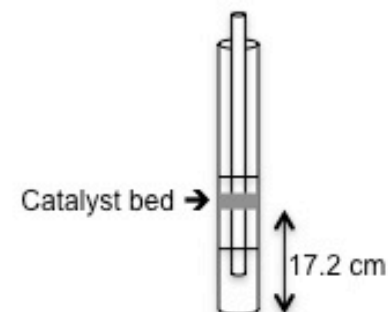- X-Ray Diffraction (XRD)
  - Measures crystallinity of catalyst powder

Additive	Content	Surface area	Pore volume	Average pore diameter	NH_3 adsorption amount	CO_2 adsorption amount	NH_3/CO_2	Crystal phase	C_2H_4 Yield	C_3H_6 Yield	Acet aldehyde Yield	IPA + acetone Yield
	(mol%)	(m²/g)	(cm³/g)	(Å)	(10⁵/g)	(10⁵/g)			(C-%)	(C-%)	(C-%)	(C-%)
Y	1	59.7	0.145	72.2	9.82	14.78	0.664	T+M	35.1	41.9	0.0	1.3
Y	3	79.8	0.145	51.8	11.74	19.54	0.601	T	31.3	44.0	0.9	3.3
Y	4	75.6	0.121	45.0	11.52	17.79	0.648	T	27.0	41.3	0.0	1.8
Y	5	85.9	0.125	40.2	12.11	21.00	0.577	T	30.7	39.2	2.3	4.2
La	1	74.6	0.161	63.0	12.24	19.38	0.632	T+M	33.5	42.3	0.0	1.8
La	3	97.5	0.128	36.8	13.77	26.52	0.519	T	26.6	40.8	0.0	2.3
La	5	92.7	0.103	32.9	12.25	26.09	0.470	T	21.0	35.3	0.7	3.8
Bi	1	58.9	0.144	70.0	8.74	14.12	0.619	T+M	40.5	36.9	0.0	1.7
Bi	3	70.4	0.151	58.2	7.62	15.02	0.507	T+M	28.3	38.3	1.6	2.2
Bi	5	55.6	0.136	66.4	3.48	11.99	0.290	T+M	13.5	30.5	1.7	4.8
Cs	1	26.2	0.154	186.4	4.41	6.65	0.663	M	44.3	29.1	1.3	3.7
Cs	3	27.7	0.160	180.2	5.17	7.22	0.716	M	45.4	28.5	0.0	3.0
Cs	5	26.8	0.146	177.5	4.29	8.11	0.529	M	43.4	22.3	0.0	7.0
Sr	1	49.0	0.152	94.4	8.63	12.90	0.669	T+M	47.4	33.4	0.0	1.7
Sr	3	64.7	0.149	69.4	9.83	17.40	0.565	T+M	40.4	37.1	0.0	4.0
Sr	5	71.8	0.148	60.7	10.50	21.28	0.493	T+M	41.9	37.9	0.0	3.1
Mg	3	51.9	0.156	88.0	8.65	14.10	0.613	T+M	42.1	34.0	0.0	1.2
Mg	5	53.6	0.165	89.4	8.84	16.15	0.547	T+M	37.0	34.9	0.0	1.3
Zn	1	34.5	0.160	149.7	5.69	8.84	0.644	M	4.0	8.1	1.4	49.5
Zn	3	26.5	0.155	184.2	4.92	7.95	0.619	T+M	2.0	8.9	0.0	42.6
Zn	5	26.0	0.158	188.0	5.16	8.63	0.598	T+M	2.5	14.2	0.0	25.6
ZrO(NO₃)₂		43.5	0.181	158.9				M + T	45.1	29.8	1.2	2.1

Additive	Content	C_2H_4 Yield	C_3H_6 Yield	Acet aldehyde Yield	IPA + acetone Yield
	(mol%)	(C-%)	(C-%)	(C-%)	(C-%)
Y	1	35.1	41.9	0.0	1.3
Y	3	31.3	44.0	0.9	3.3
Y	4	27.0	41.3	0.0	1.8
Y	5	30.7	39.2	2.3	4.2
La	1	33.5	42.3	0.0	1.8
La	3	26.6	40.8	0.0	2.3
La	5	21.0	35.3	0.7	3.8
Bi	1	40.5	36.9	0.0	1.7
Bi	3	28.3	38.3	1.6	2.2
Bi	5	13.5	30.5	1.7	4.8
Cs	1	44.3	29.1	1.3	3.7
Cs	3	45.4	28.5	0.0	3.0
Cs	5	43.4	22.3	0.0	7.0
Sr	1	47.4	33.4	0.0	1.7
Sr	3	40.4	37.1	0.0	4.0
Sr	5	41.9	37.9	0.0	3.1
Mg	3	42.1	34.0	0.0	1.2
Mg	5	37.0	34.9	0.0	1.3
Zn	1	4.0	8.1	1.4	49.5
Zn	3	2.0	8.9	0.0	42.6
Zn	5	2.5	14.2	0.0	25.6
$ZrO(NO_3)_2$		45.1	29.8	1.2	2.1

Analysis and Reaction Data

| Additive	Content	Surface area	Pore volume	Average pore diameter	NH$_3$ adsorption amount	CO$_2$ adsorption amount	NH$_3$/ CO$_2$	Crystal phase	C$_2$H$_4$ Yield	C$_3$H$_6$ Yield	Acet aldehyde Yield	IPA + acetone Yield
	(mol%)	(m^2/g)	(cm^3/g)	(Å)	(10^5/g)	(10^5/g)			(C-%)	(C-%)	(C-%)	(C-%)
Y	1	59.7	0.145	72.2	9.82	14.78	0.664	T+M	35.1	41.9	0.0	1.3
Y	3	79.8	0.145	51.8	11.74	19.54	0.601	T	31.3	44.0	0.9	3.3
Y	5	85.9	0.125	40.2	12.11	21.00	0.577	T	30.7	39.2	2.3	4.2
La	1	74.6	0.161	63.0	12.24	19.38	0.632	T+M	33.5	42.3	0.0	1.8
La	3	97.5	0.128	36.8	13.77	26.52	0.519	T	26.6	40.8	0.0	2.3
La	5	92.7	0.103	32.9	12.25	26.09	0.470	T	21.0	35.3	0.7	3.8
Sr	1	49.0	0.152	94.4	8.63	12.90	0.669	T+M	47.4	33.4	0.0	1.7
Sr	3	64.7	0.149	69.4	9.83	17.40	0.565	T+M	40.4	37.1	0.0	4.0
Sr	5	71.8	0.148	60.7	10.50	21.28	0.493	T+M	41.9	37.9	0.0	3.1
Zn	1	34.5	0.160	149.7	5.69	8.84	0.644	M	4.0	8.1	1.4	49.5
Zn	3	26.5	0.155	184.2	4.92	7.95	0.619	T+M	2.0	8.9	0.0	42.6
Zn	5	26.0	0.158	188.0	5.16	8.63	0.598	T+M	2.5	14.2	0.0	25.6
ZrO(NO$_3$)$_2$		43.5	0.181	158.9				M + T	45.1	29.8	1.2	2.1

XRD of calcinated ZrO_2
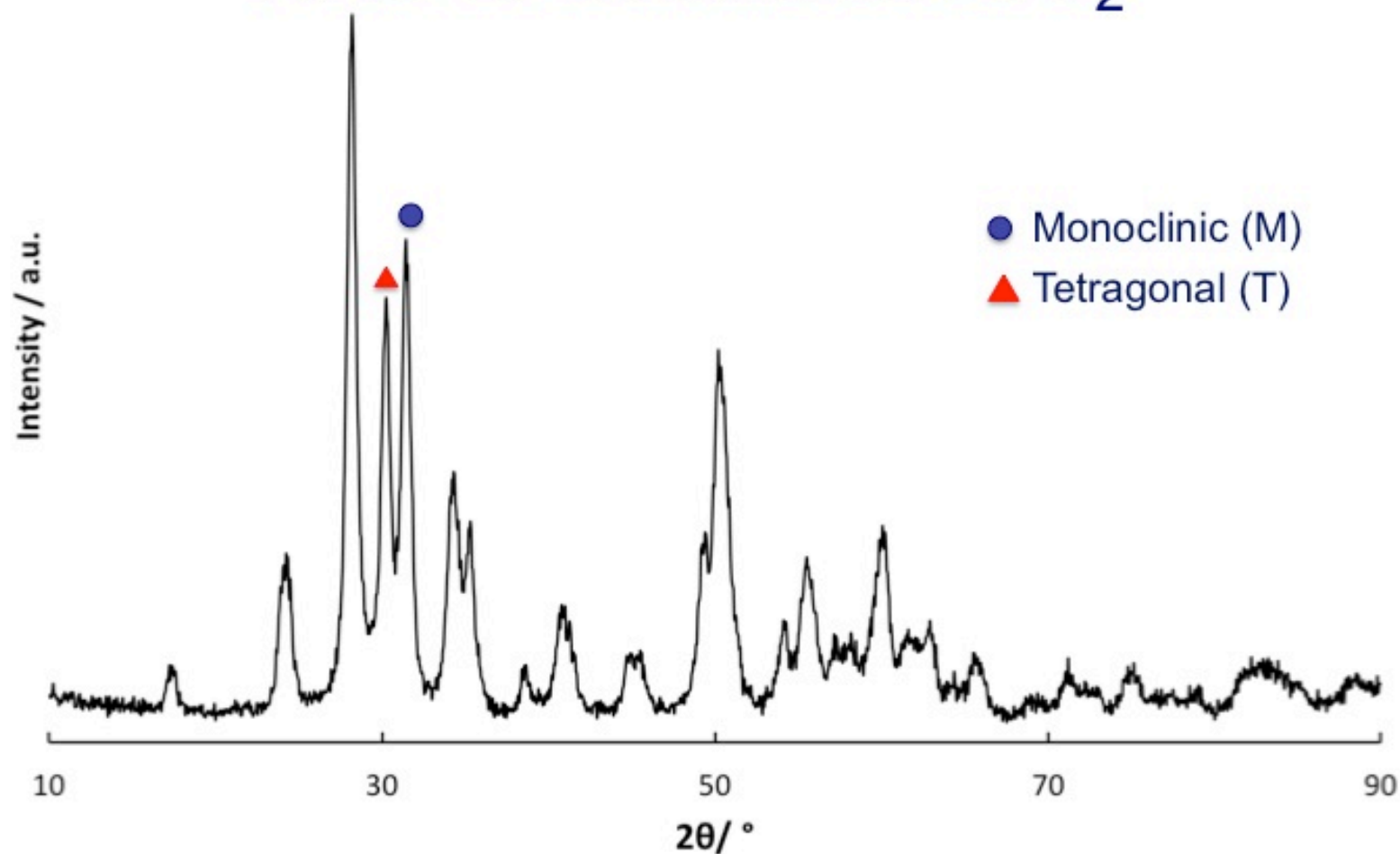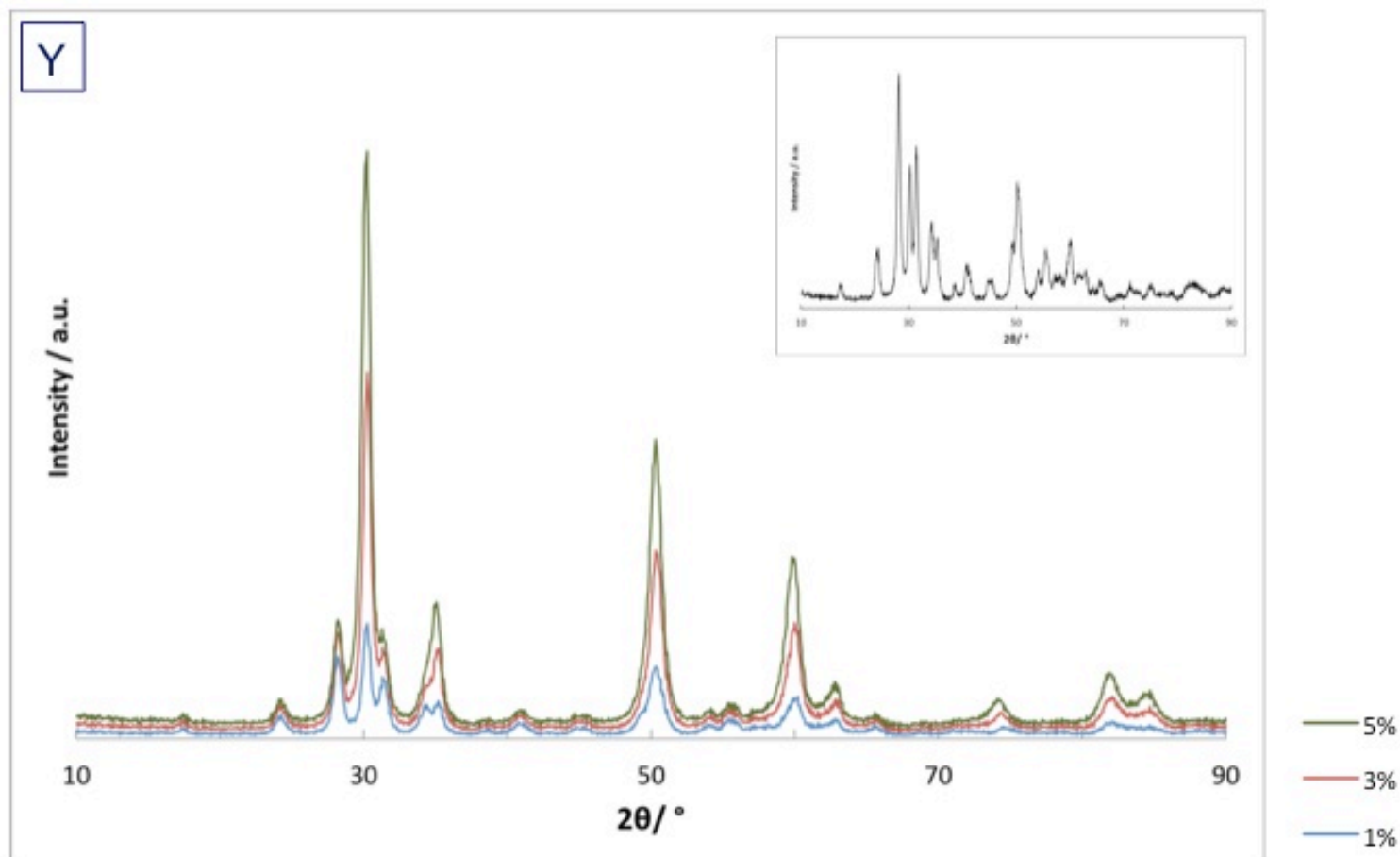
● Monoclinic (M)
▲ Tetragonal (T)
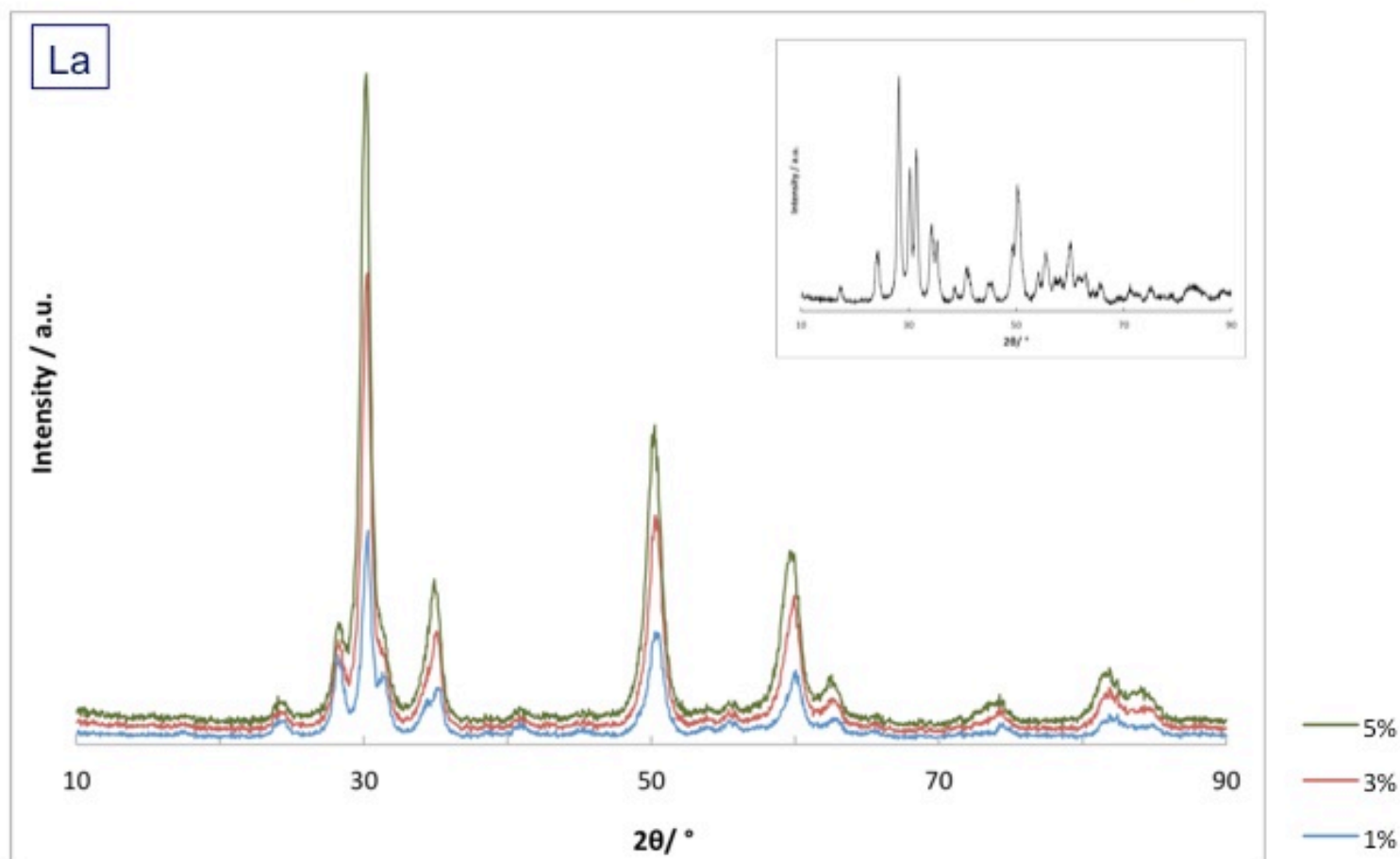
XRD of mixed metal oxide catalysts

XRD of mixed metal oxide catalysts

XRD of mixed metal oxide catalysts
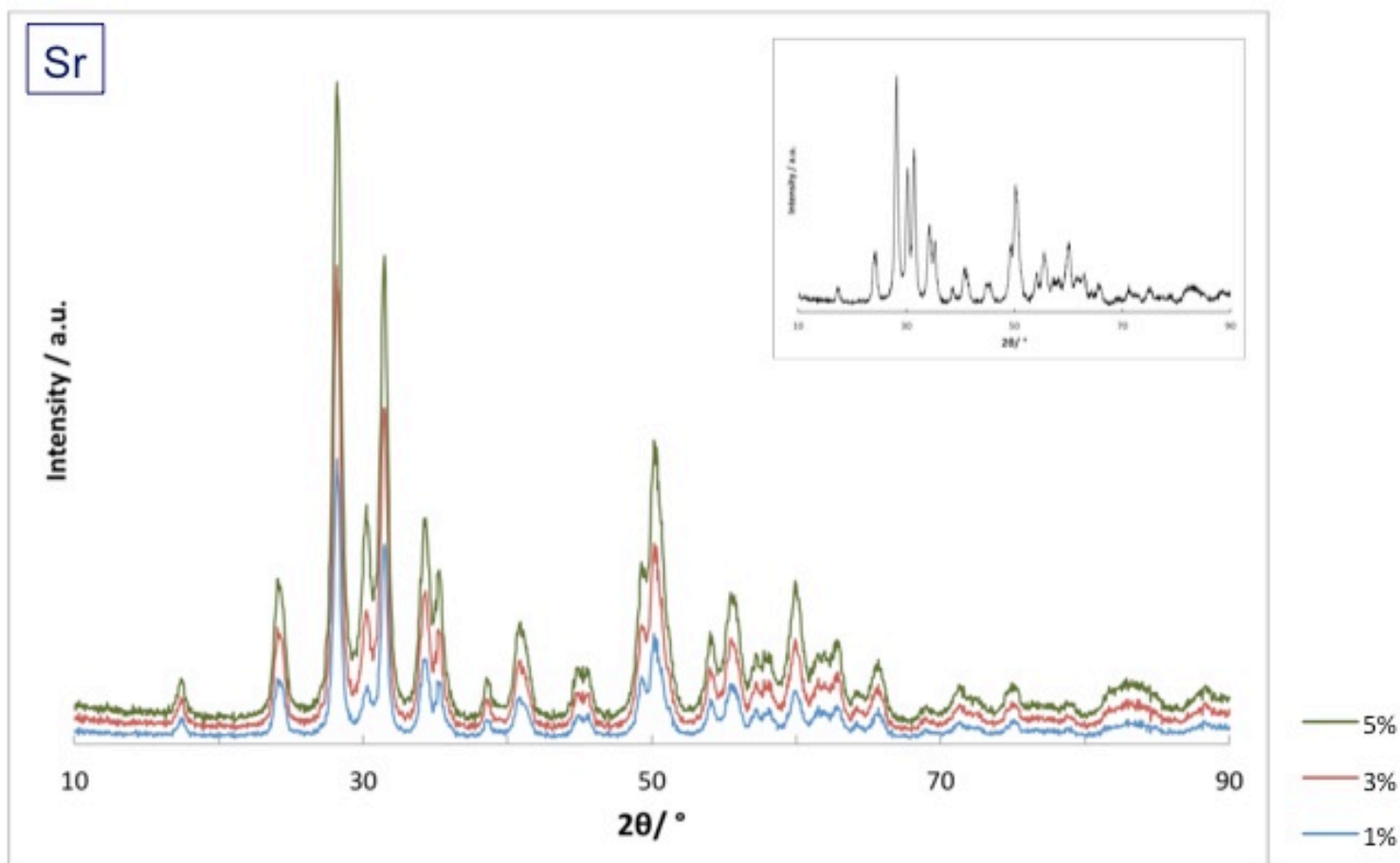
XRD of mixed metal oxide catalysts
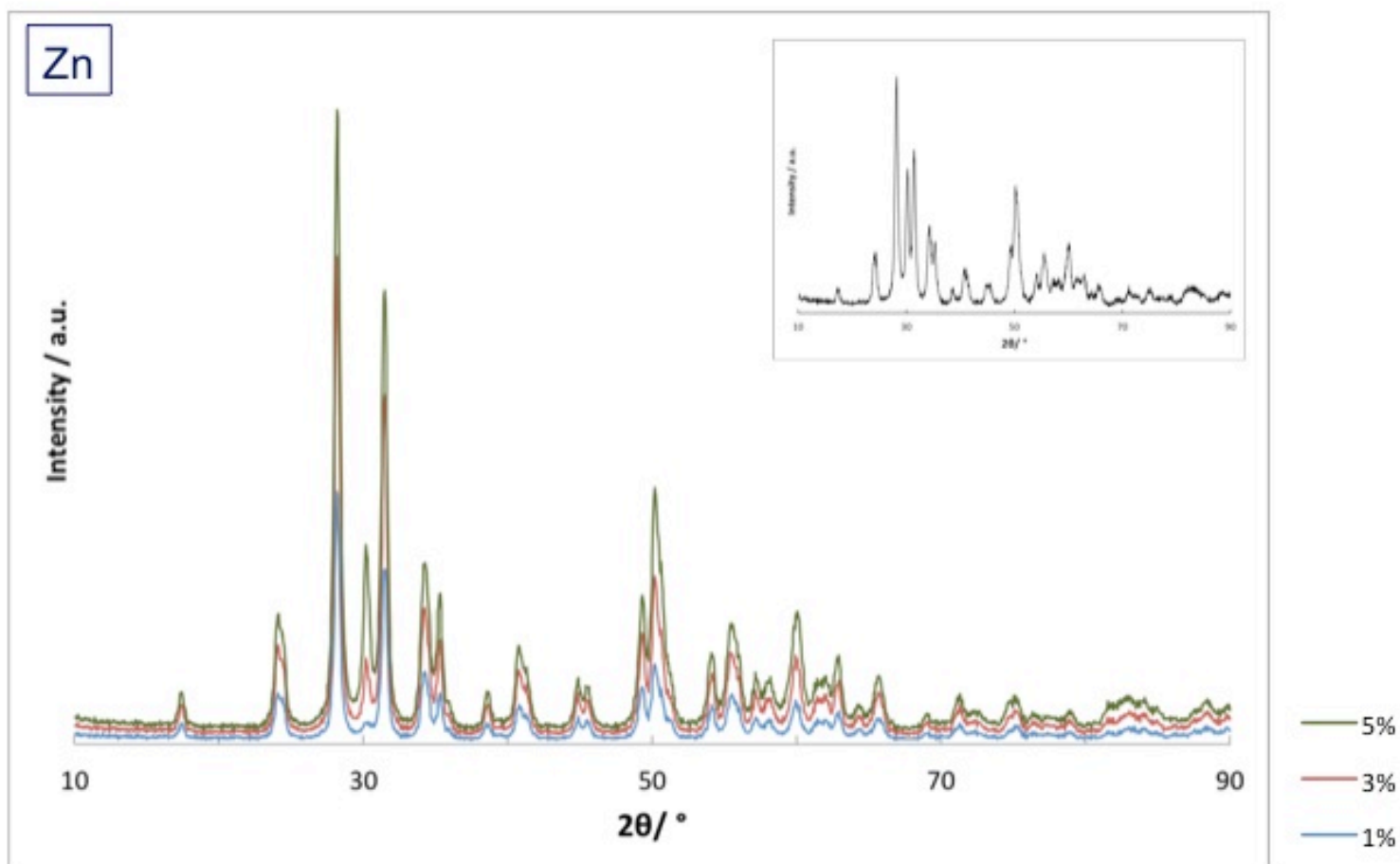
Conclusions

- Mixed metal oxides were developed, analyzed and reacted to increase raw material production from bioethanol

- Y and La additives
  - yielded the highest conversions of ethanol to propylene

- Sr additives
  - highest yields of ethylene production and better propylene conversion than ZrO_2

- Zn additives
  - produced unexpected results with the production of acetone in high yield
  - TPD analysis needs to be completed to get a better understanding of this catalyst

- Bi, Cs, and Mg additives showed no significant improvement for conversion of ethanol to propylene

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No 調製済	Zr出発原料	沈殿剤	容器	熟成温度 (℃)	熟成時間 (h)	焼成温度 (℃)	仕込量 (wt%Si)	表面積 (m²/g)	細孔体積 (cm³/g)	平均細孔径 (Å)	NH₃吸着 (m mol/g)	CO₂吸着 (-)	NH₃/CO₂	結晶構造	強度比 T/M	相変化温度 (℃)	C2H4収率 (C-%)	C3H6収率 (C-%)	Acetaldehyde収率 (C-%)	IPA+acetone収率 (C-%)
済	Y2O3ZrO2	NH4OH	Glass	室温	24	600	1	59.7	0.145	72.2	0.164	0.247	0.663	T+M			35.1	41.9	0.0	1.3
済	Y2O3ZrO2	NH4OH	Glass	室温	24	600	3	79.8	0.145	51.8	0.196	0.327	0.599	T			31.3	44	0.9	3.3
済	Y2O3ZrO2	NH4OH	Glass	室温	24	600	4	75.6	0.121	45.0	0.193	0.298	0.648	T			27.0	41.3	0.0	1.8
済	Y2O3ZrO2	NH4OH	Glass	室温	24	600	5	85.9	0.125	40.2	0.203	0.351	0.578	T			30.7	39.2	2.3	4.2
済	La2O3ZrO2	NH4OH	Glass	室温	24	600	1	74.6	0.161	63.0	0.205	0.324	0.633	T+M			33.5	42.3	0.0	1.8
済	La2O3ZrO2	NH4OH	Glass	室温	24	600	3	97.5	0.128	36.8	0.231	0.444	0.520	T			26.6	40.8	0.0	2.3
済	La2O3ZrO2	NH4OH	Glass	室温	24	600	4	102.7	0.132	36.8				T						
済	La2O3ZrO2	NH4OH	Glass	室温	24	600	5	92.7	0.103	32.9	0.205	0.437	0.469	T			21.0	35.3	0.7	3.8
済	La2O3ZrO2	NH4OH	Glass	室温	24	600	10	43.5	0.044	31.4				T						
済	Bi2O3ZrO2	NH4OH	Glass	室温	24	600	1	58.9	0.144	70.0	0.146	0.236	0.619	T+M			40.5	36.9	0.0	1.7
済	Bi2O3ZrO2	NH4OH	Glass	室温	24	600	3	70.4	0.151	58.2	0.128	0.251	0.510	T+M			28.3	38.3	1.6	2.2
済	Bi2O3ZrO2	NH4OH	Glass	室温	24	600	5	55.6	0.136	66.4	0.058	0.201	0.289	T+M			13.5	30.5	1.7	4.8
済	Cs2OZrO2	NH4OH	Glass	室温	24	600	1	26.2	0.154	186.4	0.074	0.111	0.667	M			44.3	29.1	1.3	3.7
済	Cs2OZrO2	NH4OH	Glass	室温	24	600	3	27.7	0.160	180.2	0.086	0.121	0.711	M			45.4	28.5	0.0	3.0
済	Cs2OZrO2	NH4OH	Glass	室温	24	600	5	26.8	0.146	177.5	0.072	0.136	0.529	M			43.4	22.3	0.0	7.0
済	SrOZrO2	NH4OH	Glass	室温	24	600	1	49.0	0.152	94.4	0.144	0.216	0.667	T+M			47.4	33.4	0.0	1.7
済	SrOZrO2	NH4OH	Glass	室温	24	600	3	64.7	0.149	69.4	0.164	0.291	0.564	T+M			40.4	37.1	0.0	4.0
済	SrOZrO2	NH4OH	Glass	室温	24	600	5	71.8	0.148	60.7	0.176	0.356	0.494	T+M			41.9	37.9	0.0	3.1
済	MgOZrO2	NH4OH	Glass	室温	24	600	3	51.9	0.156	88.0	0.145	0.236	0.622	T+M			42.1	34.0	0.0	1.2
済	MgOZrO2	NH4OH	Glass	室温	24	600	5	53.6	0.165	89.4	0.148	0.270	0.548	T+M			37.0	34.9	0.0	1.3
済	ZnOZrO2	NH4OH	Glass	室温	24	600	1	34.5	0.160	149.7	0.096	0.148	0.649	M			4	8.1	1.4	49.5
済	ZnOZrO2	NH4OH	Glass	室温	24	600	3	26.5	0.155	184.2	0.082	0.133	0.616	T+M			2.0	8.9	0.0	42.6
済	ZnOZrO2	NH4OH	Glass	室温	24	600	5	26.0	0.158	188.0	0.086	0.144	0.389	T+M			2.5	14.2	0.0	25.6
	ZrO(NO3)2					600		43.5	0.181	158.9				M+T	0.28		45.1	29.8	1.2	2.1

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