Microwave Specific Effects on Heterogeneous Catalyzed and Homogeneous Solution Claisen Rearrangement

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MICROWAVE SPECIFIC EFFECTS ON HETEROGENEOUS CATALYZED AND HOMOGENEOUS SOLUTION CLAISEN REARRANGEMENT

By

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I would like to dedicate this dissertation to my parents, and my fiancé Xiaowei Liu for their love and encouragement.
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ABSTRACT

Microwave has been for their ability to heat water and food rapidly. And thanks to scientific technology and global marketing, the microwave oven was invented and got widely used in 1970’s and 1980’s. Microwave radiation has specific characteristics: it is an electromagnetic waves that contains an electric magnetic component. As electromagnetic radiation, it can move in the vacuum as light speed, it has no mass, and cannot collide with each other; the most important property of microwave is it can generate energy. Recently more and more scientists are using microwave machines as heating sources due to its high efficiency in heating solutions.

Claisen rearrangements are long-established, well-understood reactions that have proved highly utilitarian in the area of synthetic organic chemistry. In particular, the Claisen and related Cope rearrangements provide a stereo-specific method of carbon-carbon bond formation through a concerted [3,3]-sigmatropic shift. In this study, this reaction is chosen to show the microwave enhancement in heterogeneous catalysis and the chaperone effect. The constant temperature reaction method is used in the microwave reactions that helps to compare to the thermal reactions with the corresponding temperature. In chaperone reactions, constant power is used based on its high effect on microwave radiation absorption and the temperature stabilization.
CHAPTER 1

INTRODUCTION

1.1 Microwave and Microwave Heating

Microwave has been used for its ability to heat water and food rapidly. And thanks to scientific technology and global marketing, the microwave oven was invented and got widely used in 1970’s and 1980’s\(^1\). Microwave radiation has specific characteristics: it is an electromagnetic wave that contains an electric magnetic component. As electromagnetic radiation, it can move in the vacuum at light speed, it has no mass, and cannot collide with each other; the most important property of microwave is it can generate energy. The frequency of microwave is from 300MHz to 300GHz, between the radiowave and infrared\(^2\) (Figure 1.1).

![Spectrum of electromagnetic waves.](image)

**Figure 1.1** Spectrum of electromagnetic waves.

Historically, high-frequency induction heating was used before the discovery of microwaves. In 1946, the interaction between microwaves and materials was found from the
melting of chocolate, and the first commercial microwave oven was invented in 1952 by the Raytheon Company. And in 1970’s, a domestic and microwave oven was developed by Japanese scientist which generally operated at a frequency of 2.45GHz, corresponding to a wavelength of 12.24cm and the energy of $1.02 \times 10^{-5}$ ev. Since then, microwave ovens are widely used not only in heating foodstuffs, but also in chemistry synthesis\(^1\).

Based on its low frequency, microwaves cannot break molecular bonds. Heating of molecules in solution takes place through the process described by Debye in which the dipole moment of the molecule couples to the oscillating electric field of the radiation. Collisional hinderance of the relaxation of the molecules results in loss processes which give rise to heat. In solids, there are two fundamental types of loss processes: conduction loss and Debye-type loss. Conduction loss, occurs through electron migration induced by the electric field of the microwaves. This can lead to Joule-type heating and space-charge separation; in the latter, loss processes leading to heating will occur because of charge trapping by defect sites that hinders recombination leading to heat loss. For highly conductive materials such as metals, the radiation will mostly be reflected from the metal surface which prevents heating. In insulators, the permanent or induced dipoles of molecules can give rise to heating. In magnetic materials loss processes associated with the interaction of the magnetic field of the radiation with the magnetic moment of the materials can also result in heating. Overall, the thermal energy, $P$, which generated by microwave radiation is defined and the relationship between $P$ and microwave is given by Equation (1.1):

$$ P = \frac{1}{2} \sigma E^2 + \pi f \varepsilon_0 \varepsilon_r'' E^2 + \pi f \mu_0 \mu_r'' H^2 $$  \hspace{1cm} (1.1)\(^3\)

In this equation, $E$ and $H$ are the strength of the electric and magnetic fields of the microwave; $\sigma$ is the electric conductivity; $f$ is the frequency of microwave; $\varepsilon_0$ is the permittivity
in vacuum; $\varepsilon_r''$ is the relative dielectric loss factor; $\mu_0$ is the magnetic permeability in vacuum; and $\mu_r''$ is the relative magnetic loss. The first part of the equation expresses conduction loss heating, the second part demonstrates dielectric heating and the third part explains the magnetic loss heating.

1.1.1 Conduction Loss Heating

Electronic conduction plays a most important role in the microwave heating of metal or semiconductors. And highly conductive materials or insulating materials heat less effectively than molecules or materials with moderate conductivity. When the frequency of microwave changes, the electronic conductivity of the material does not change dramatically. The conduction loss happens largely in those materials which have a large amount of ionic salts. In many oxide ceramics like Al$_2$O$_3$, the dielectric loss is relatively small, but it has strong conduction loss which thermally activates the electrons and the temperature gets increased in the microwave radiation. In large conductivity materials, the ionic conduction loss dominates the temperature variations, and ionic conductivity does not vary much from the change of microwave frequency since the conductivity is highly dependent on temperature and ions get activated and flow faster with the increase of temperature$^4$.

1.1.2 Dielectric Heating

Insulating materials or nonconductive materials interact with microwave radiation due to their permanent dipoles. In other words, only polar molecules can absorb microwave radiation and generate heat, but nonpolar molecules would hardly absorb microwave radiation. When microwave radiation interacts with the dipolar molecules, the molecular dipoles will realign with
themselves, and move with the microwave oscillation which forms molecular rotations (Fig. 1.2). However, as the electric field of the microwave oscillates, the motions of the molecules, including rotations and vibrations, will lag behind the microwave frequency, which is described as dielectric loss and causes energy absorption from the electric field. These motions of the molecules generate heat mostly through the friction of the molecules. In this case, many solutions and small polar molecules can be heated in microwave system and generate a huge amount of heat.

![Molecular rotation of a dipole molecule in an electric field.](image)

**Figure 1.2** Molecular rotation of a dipole molecule in an electric field.

**1.1.2.1 Loss Tangent.** The process by which microwave radiation interacts with a molecule in solution and generates heat is through dielectric loss, which was first described by Debye and called “Debye heating process”. There are two parameters that describe the dielectric properties of the material in solution: the relative permittivity or the dielectric constant $\varepsilon'$, and the loss factor in the microwave heating process $\varepsilon''$. And the relationship between these two parameters can be described in Eq. (1.2):

$$\varepsilon^* = \varepsilon' - j\varepsilon''$$

(1.2)
Table 1.1 shows some dielectric properties of some common solvents at different frequency.

Table 1.1  Dielectric constant and dielectric loss for common solvents at different frequencies

<table>
<thead>
<tr>
<th>Solvent</th>
<th>3×10^8 Hz</th>
<th>3×10^9 Hz</th>
<th>3×10^10 Hz</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ε'</td>
<td>ε''</td>
<td>ε'</td>
</tr>
<tr>
<td>Water</td>
<td>77.5</td>
<td>1.2</td>
<td>76.7</td>
</tr>
<tr>
<td>0.1M NaCl</td>
<td>76</td>
<td>59</td>
<td>75.5</td>
</tr>
<tr>
<td>Heptane</td>
<td>1.97</td>
<td>N/A</td>
<td>1.97</td>
</tr>
<tr>
<td>Methanol</td>
<td>30.9</td>
<td>2.5</td>
<td>23.9</td>
</tr>
</tbody>
</table>

In this table, we can see that the heat loss (ε'') of water increases when the frequency grows from 0.3 GHz to 30GHz, but other polar solvent like methanol, shows best heat at 3GHz and the ε'' will decrease whether we increase or decrease the frequency of electromagnetic waves. Since the frequency of microwave that we commonly use is 2.45GHz, which corresponds or is similar to the 3×10^9Hz data in Table 1.1, which turns out that many polar solvents contain high dielectric loss in this frequency and absorb microwave energy well.

The ratio of the loss factor and the relative permittivity (ε'')/ ε' = tan δ is defined as The Loss Tangent which commonly describes the ability of a material to convert electromagnetic energy into heat energy under specific microwave frequency and temperature conditions. The higher the loss tangent is, the better the heating efficiency would be. Figure 1.3 shows the variation of the permittivity and the loss factor of a solvent with frequency. Generally, the loss
factors of many solvents including water would reach to the climax when the permittivity of them starts decreasing. And in this figure, we can see that the highest loss factor of water is near the frequency of 9GHz, and the loss tangent reaches climax at this frequency\(^5\).

\[\text{Figure 1.3} \text{ The variation of } \varepsilon' \text{ and } \varepsilon'' \text{ with frequency changes}\]

1.1.2.2 Relaxation Time of Molecules. For polar liquids, the frequency dependent \(\varepsilon'\) and \(\varepsilon''\) can be described by Debye equations:

\[
\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + j\omega\tau} \quad (1.3)
\]

\[
\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + \omega^2\tau^2} \quad (1.4)
\]

\[
\varepsilon'' = \frac{(\varepsilon_0 - \varepsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \quad (1.5)
\]
Where \( \tau \) is the relaxation time and \( \varepsilon_0 \) and the \( \varepsilon_\infty \) are the value of permittivity at frequencies \( \ll \tau^{-1} \) and \( \gg \tau^{-1} \) respectively, \( \omega \) is the angular frequency of the incident radiation. The interaction between the electric field and the solution will cause the realignment of the molecules corresponds to the direction of the electric field. Since the electric field is oscillating or the outer field is turned off, the motivations of the molecules do not return to their original positions or alignments immediately. The relaxation time, \( \tau \), is the measure of the time taken to achieve this randomised state\(^6\).\(^7\).

For a spherical molecule, the relaxation time is highly related to the volume or the size of the molecules, the viscosity and the temperature of the medium since the continuing molecular rotations, and the relaxation time can be interpreted by using the equation below:

\[
\tau = 4\pi r^3 \eta / kT
\]

(1.6)\(^7\)

Where \( \eta \) is the viscosity of the solvents, \( r \) is the radius of the spherical dipole molecules, \( k \) is the Boltzman’s constant, and \( T \) is the temperature of the medium. Combine the equations 1.2-1.6, we can see that the longer the relaxation time, the less the loss tangent will be, which turns out that decreasing the relaxation time will increase the dielectric heating. The examples that demonstrate the relationship between these parameters are shown in the table below.

In this table, all these alcohols have similar dipole moments. And we can see that as the chain lengths of the alcohols grow, the relaxation time increases, and the loss tangent decreases. This data also fits well in equation 1.6, that the relaxation time will increase with the growth of molecular volume and viscosity.
Table 1.2 Relaxation times at 20°C and dielectric properties of alcohols.  

<table>
<thead>
<tr>
<th>Compound</th>
<th>Relaxation time</th>
<th>Dipole moment</th>
<th>Viscosity</th>
<th>Loss tangent</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH</td>
<td>51.5</td>
<td>1.70</td>
<td>5.45</td>
<td>.0659</td>
</tr>
<tr>
<td>EtOH</td>
<td>170</td>
<td>1.69</td>
<td>10.8</td>
<td>0.941</td>
</tr>
<tr>
<td>Propan-1-ol</td>
<td>332</td>
<td>1.68</td>
<td>20</td>
<td>0.757</td>
</tr>
<tr>
<td>propan-2-ol</td>
<td>237</td>
<td>1.66</td>
<td>17.7</td>
<td>0.799</td>
</tr>
<tr>
<td>Butan-1-ol</td>
<td>538</td>
<td>1.66</td>
<td>22.7</td>
<td>0.571</td>
</tr>
<tr>
<td>Pentan-1-ol</td>
<td>792</td>
<td>1.80</td>
<td>33.5</td>
<td>0.427</td>
</tr>
<tr>
<td>Hexan-1-ol</td>
<td>976</td>
<td>1.67</td>
<td>N/A</td>
<td>0.344</td>
</tr>
</tbody>
</table>

1.1.3 Magnetic Loss Heating  
In magnetic materials such as iron oxides and other spinels, magnetic loss heating dominates in microwave heating. These materials are affected by the magnetic field of the microwave as the magnetic field couples to the magnetic moment: loss processes (heating) occur because oscillations of the magnetic moments are act of phase with the applied radiation. For example, magnetic iron oxide, \( \text{Fe}_3\text{O}_4 \), can absorb microwave radiation and generate heat but non-magnetic iron oxide, \( \text{Fe}_2\text{O}_3 \), cannot be heated well.  

1.1.4 Penetration Depth  
Penetration depth \( D_p \) is a measure of the depth that electromagnetic wave can penetrate into a material and the power usually decrease to half of its original value which is the power at
Sometimes a material has relatively high loss tangent, but it still has low heating efficiency due to its low penetration depth. When microwave radiation reaches the material’s surface, part of the radiation would be reflected, and the other would be transmitted into the material and interacts with atoms and the electrons inside the material (Figure 1.4). The penetration depth depends on the nature of the material, and it can be estimated by the following equation:

\[ D_p = \frac{\lambda}{4\pi} \left[ \frac{2}{\varepsilon' \left( 1 + \frac{\varepsilon''}{\varepsilon'} \right)^2 - 1} \right]^{1/2} \]  

(1.7)

Where \( \lambda \) is the radiation wavelength, and at microwave frequency (2.45 GHz), \( \lambda = 12.24 \text{ cm} \). Since there are dielectric constant and loss factor in the equation, which are temperature dependence, we can say that the penetration depth is also temperature dependent.

Figure 1.4. Electromagnetic radiation penetrates into a material.
When microwave radiation interacts with nonpolar solvents, the penetration depth is very deep compared to polar solvents. This demonstrates that nonpolar solvents could not absorb microwave radiation well and has low heating efficiency compared to the polar solvents. Measuring the penetration depth of microwave into a material is essential to help us promote the heating efficiency and achieve optimal microwave heating.

1.2 Microwave Selective Heating

1.2.1 Advantages of Microwave Heating

Chemical reactions are typically carried out by conventional heating in which a resistively heated source (i.e. hot plate). Recently, more and more researchers are using microwaves to heat solutions due to the high efficiency of microwave heating\textsuperscript{10}. Figure 1.5 shows the comparison between microwave heating and conventional heating, and the advantages of microwave assisted heating. In conventional heating, the energy transfers from oil bath or heater to the beaker, or the vessel wall, then transfers into the solution. In a reaction, the temperature of the reactants would be almost the same with the temperature of the solution, or sometimes lower than the solution temperature. But in microwave heating, the vessel wall and the solvent are transparent to the microwave radiation, which means the microwave radiation would directly interact with the reactants inside the solution, and result in the localized superheating\textsuperscript{11}. 
**Figure 1.5** Heat transfer and simulation images of microwave and conventional heating: a) conventional heat transfer; b) microwave heating energy transfer; c) simulation of conventional heating; d) simulation of microwave heating.

The simulation images in Figure 1.5 c and d shows that in conventional heating, the temperature inside the solution is lower than the outside temperature, which turns out that the energy is transferred from outside to inside; but in microwave heating, the inside temperature (temperature of the reactants) is much higher than the bulk temperature, or the solution temperature, which proves that in microwave heating, heat is transferred from reactants to solution, and explains why microwave heat more efficiently than conventional heating.
When the reaction finished, in conventional heating, we usually take our vessels from the oil bath, and let it cool down to room temperature. During which time, the bulk temperature is still high enough to support the continuation of the reaction. But in microwave reactions, when the reaction finished, microwave energy no longer be supplied, and the reaction would be fully stopped, which increase the accuracy of measuring actual reaction time and conversion.

1.2.2 Heat Storage

The model for selective heating in slow-moving liquids by using a low frequency electric field was brought up by Huang and Richard and showed in Figure 1.6 \textsuperscript{12,13}. In this model, a dipolar molecule is dissolved in a nonpolar solvent, which does not absorb the microwave radiation. Only the polar molecule absorb the microwave energy and generate heat. Based on this, the polar molecules, or the domains, absorb microwave radiation, generate and store heat, and the heat is transferred from the domain to the medium.

Since the amount of energy is absorbed and stored by a domain, and achieve microwave specific rate enhancement, the amount of heat is generated by the interaction between the microwave and the domain which depends on several affects, including the penetration depth and the frequency of the microwave. This results in the temperature of the domain \(T_{\text{dom}}\) being higher than the temperature of the medium \(T_{\text{med}}\), and heat storage, \(q\), can be described as the equation below:

\[ q = h_{\varepsilon}(T_{\text{dom}} - T_{\text{med}}) \]  
(1.8)
The energy that a domain can store mostly depends on the temperature difference between the domain and the medium. In other words, the higher the temperature difference between the domains and the solution, the higher heat stores, and the higher the microwave specific effect. Also, the heat would transfer from the medium to the outside from the vessel wall, which in case, would decrease the temperature of the medium ($T_{\text{med}}$) and decrease the heat storage of the domain. In this case, a sealed system would be better to increase the heat storage and increase the microwave specific heating effect.
1.2.3 Microwave Selective Heating in Heterogeneous Catalysis

Microwave loss processes in solids, such as heterogeneous catalysis, are more complex than for molecules in solution. For a heterogeneous catalyst, the heat transfer process is shown in Figure 1.7. In a heterogeneous catalysis, only the catalyst absorbs the microwave radiation and generates heat, but all the other parts, including the solvent, the vessel, and the reactants are non-absorbing. In this system, the localized superheating occurs on the heterogeneous catalyst, and the heat transfers from the catalyst to the medium. It is apparently that the temperature of the catalyst ($T_{\text{cat}}$) would be much higher than the temperature of the medium ($T_{\text{med}}$), and the heat stored by the catalyst would be $q$, which depends on the difference between these two temperatures.

![Microwave selective heat process in heterogeneous catalysis.](image)

**Figure 1.7** Microwave selective heat process in heterogeneous catalysis.
When reaction occurs, the cold reactant molecules would attach on the hot catalysts’ surface, getting catalyzed and converted to product, and the product molecules would leave the active sites on the catalysts’ surface and give place to other reactant molecules. This process demonstrates how microwave-specific catalysis works that results in the microwave effects and reaction rate enhancement.

1.3 Applications in Microwave Assisted Synthesis

In recent years, microwaves have become a common heating source in laboratories, especially in organic synthesis due to its high efficiency in heating up solutions and, more recently, in its ability to selectively heat reactants. However, in the former theory, people usually consider microwave machine simply as a “faster heater” which only generates heat more rapidly and decreases the time of synthesis compared to oil bath heating. There are no other effects due to the microwave radiation itself. Recent publications has begun to show microwave specific effects in both homogeneous and heterogeneous catalyzed reactions and showed the results that microwave was not only a “faster heater”. For example, some organic synthesis requires long reaction time, such as 20 hours or more to get high conversion. However, it only takes one or two hours to achieve the similar conversion by using microwave oven. These microwave assisted synthesis are always used in high temperature reactions.

Here are some examples and applications that shows the advantages of microwave heating and microwave effects in both homogeneous and heterogeneous catalysis.
1.3.1 Microwave Selective Heating in Organic Synthesis

A most classical application in homogeneous catalysis is Diels-Alder reaction. Knoevenagel provided the conversion and rate constant comparisons between microwave reactions and thermal reactions of coumarin synthesis\(^{16,17}\) (Figure 1.8) in the following tables:

![Diels-Alder Reaction](image)

**Figure 1.8** Diels-Alder Reaction

**Table 1.3** Conversion comparison of Diels-Alder reactions at 95°C.

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>Solvent: Xylene</th>
<th>Solvent: Dibutyl Ether</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Microwave Conversion</td>
<td>Thermal Conversion</td>
</tr>
<tr>
<td>1</td>
<td>22%</td>
<td>8%</td>
</tr>
<tr>
<td>2</td>
<td>49%</td>
<td>14%</td>
</tr>
<tr>
<td>3</td>
<td>70%</td>
<td>20%</td>
</tr>
<tr>
<td>4</td>
<td>83%</td>
<td>26%</td>
</tr>
<tr>
<td>5</td>
<td>92%</td>
<td>30%</td>
</tr>
</tbody>
</table>
Table 1.4 Rate constants comparison of Diels-Alder reaction.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Xylene k (mol L s(^{-1}))</th>
<th>Ethanol k (mol L s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Microwave</td>
<td>Thermal</td>
</tr>
<tr>
<td>60</td>
<td>5.7×10(^{-3})</td>
<td>2.2×10(^{-3})</td>
</tr>
<tr>
<td>80</td>
<td>12.2×10(^{-3})</td>
<td>3.7×10(^{-3})</td>
</tr>
</tbody>
</table>

In the tables above, we can see that in both non-polar solvent and polar solvents systems, the conversions and the rate constants in microwave reactions are higher than the ones in thermal reactions. Comparing these two different solvent systems, we can see that in Table 1.3, the conversion enhancement in xylene microwave reaction is about 62% higher than the thermal reaction after 5 hours; but in ether solvent, the conversion enhancement in microwave is 40% more than the thermal one. This phenomenon also appears in the rate constant comparison (Table 1.4), that is the rate constant enhancement in xylene solvent reaction is nearly tripled in microwave reaction, but it is only 1.5 times higher in the ethanol solvent reaction.

The results turn out that in non-polar solvent, this Diels-Alder reaction has more microwave enhancement than in polar solvent, and this is called “solvent effect”\(^{18}\). Using non-polar solvent is more strikingly to observe microwave effect because non-polar solvents are transparent to the microwave radiation, only the reactants would absorb the microwave energy and generate heat, then transfer to the medium, which results in microwave selective heating (\(T_{\text{dom}} \gg T_{\text{med}}\)). But in polar solvents, both solvent and reactants absorb microwave energy and generate heat (\(T_{\text{dom}} \geq T_{\text{med}}\)), which decrease the microwave selective heating which results in lower microwave enhancement\(^{19}\). However, the solvent effect is highly dependent on the reaction itself, in other words, not all the reactions have solvent effect\(^{20}\).
1.3.2 Microwave Applications in Heterogeneous Catalysis

Compared to microwave driven homogeneous catalysis, microwave driven heterogeneous catalysis is more intuitive to observe microwave effect and less controversial since only the heterogeneous catalyst absorbs microwave energy. This effect is more obvious in the gas-solid phase catalysis. Here’s the example that shows microwave enhancement in gas-solid heterogeneous reaction, the Boudouard reaction\textsuperscript{21-23} (equation 1.9):

\[ \text{C} + \text{CO}_2 \rightarrow 2\text{CO} \quad \Delta H = 172 \text{ kJ/mol} \quad (1.9) \]

This reaction is highly endothermic, and it takes high temperature to form CO (\( > 700 ^\circ \text{C} \)). The kinetic and Arrhenius parameters of microwave driven Boundouard reaction was measured by Hunt and Stiegman, shown in the table below\textsuperscript{24}:

**Table 1.5** Rate of Boundouard reaction under microwave and thermal conditions.

<table>
<thead>
<tr>
<th>Power (W)</th>
<th>Temperature ((^\circ\text{C}))</th>
<th>Rate (mmol/min)</th>
<th>Temperature ((^\circ\text{C}))</th>
<th>Rate (mmol/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>813</td>
<td>0.908</td>
<td>850</td>
<td>0.291</td>
</tr>
<tr>
<td>100</td>
<td>912</td>
<td>1.32</td>
<td>900</td>
<td>0.549</td>
</tr>
<tr>
<td>125</td>
<td>958</td>
<td>1.50</td>
<td>950</td>
<td>0.804</td>
</tr>
<tr>
<td>150</td>
<td>992</td>
<td>1.66</td>
<td>1000</td>
<td>1.30</td>
</tr>
</tbody>
</table>

\[ \text{Ea} = 38.5 \text{ kJ/mol} \quad A = 1.09 \times 10^{-3} \text{ s}^{-1} \]

\[ \text{Ea} = 118.4 \text{ kJ/mol} \quad A = 1.57 \text{ s}^{-1} \]

In the microwave reaction, the temperature of the carbon surface is much higher than the gaseous medium which turns out to be the microwave selective heating. Also, in microwave
reactions, the rate constants at different power are higher than the thermal reactions with the corresponding temperature, and the activation energy decreases dramatically in the microwave reactions. These kinetic data proved a huge rate enhancement under the microwave irradiation compared to thermal reactions and shows the microwave effect.

Not only in kinetic analysis, they also observed the changes of thermodynamics of the reaction in microwave irradiation. And the results are shown below:

| Table 1.6 Thermal dynamic parameters in microwave and thermal conditions\(^1\) |
|---|---|---|---|---|---|
| **Microwave** |  |
| T (K) | T (K) gas | \(K_p\) | \(\Delta G\) (kJ/mol) | \(\Delta H\) (kJ/mol) | \(\Delta S\) (J/mol) |
| 1086 | 267 | 68.3 | -38.1 | 33.4 | 65.6 |
| 1185 | 380 | 85.2 | -43.8 |  |
| **Thermal** |  |
| 1086 | 1086 | 21.6 | -27.7 | 183.3 | 194.3 |
| 1185 | 1185 | 117.4 | -47.0 |

In the microwave driven reactions, the temperature dependence is weaker than the thermal reactions, therefore, upon the table, the thermodynamics of the reaction in microwave changes dramatically, which reflects in the decrease of \(\Delta H\) and \(\Delta S\), and the increase of \(\Delta G\). The combination of kinetic and thermodynamic results proved that microwave radiation does not simply act as a “heater” in the reactions, but it does interact with the molecules and causes the specific microwave effect.
2.1 Introduction

Claisen rearrangements are long-established, well-understood reactions that have proved highly utilitarian in the area of synthetic organic chemistry. In particular, the Claisen and related Cope rearrangements provide a stereo-specific method of carbon-carbon bond formation through a concerted [3,3]-sigmatropic shift\(^{25}\). The prototypical example of an aromatic Claisen rearrangement is the conversion of allyl phenyl ether to ortho-allyl phenol (Figure 2.1). This and many other claisen rearrangements often require high temperatures (150-200 °C) for the rearrangement to occur. In the case of reaction in the Figure 2.1, temperatures greater than 200°C are required to effect reaction in a reasonable period of time. As such, there has been much interest in finding suitable catalysts for the reaction that will allow it to occur efficiently at much lower temperatures\(^{26,27}\).

\[ \text{O} \quad \text{Δ} \quad \text{T} > 200 \text{ °C} \]

**Figure 2.1.** Claisen rearrangement of allyl phenyl ether
In general, most effective catalysts have been Lewis acids, such as BCl$_3$, which increase the rate of aryl Claisen rearrangements by as much $10^{10}$ relative to the thermal reaction. In addition, a large number of transition metal complexes also catalyze the Claisen rearrangement, also through Lewis acid interactions$^{28}$. In the case of transition metal complex catalyst, the effect of these catalysts on the stereochemistry of the product has been a major source of interest. A notable aspect of this work is that, with few exceptions (zeolites being one of them), there are very few are heterogeneous catalysts. Clearly, there would potentially be advantages to have an efficient, low temperature heterogeneous catalyst that can be easily separated from the solution.

While finding improved methods for heterogeneously catalyzing the Claisen rearrangement is a significant goal, the reaction, due to its simple kinetics, has been of considerable utility in understanding and quantifying microwave effects in homogeneous solution$^{29,30}$. In this study Chen used para-nitro-allyl phenyl ether (ApNE) as starting material and self-catalyst to form nitro-allyl phenol (ANP) and made the first-order kinetic data (Figure 2.2, 2.3). He showed the rate constant increase in different concentrations of ApNE by using constant power in microwave oven compared to thermal reactions, which proved the dramatic microwave enhancement or microwave effect in homogeneous reactions.

![Reaction diagram](image)

**Figure 2.2.** Claisen rearrangement of nitro-allyl phenyl ether
Figure 2.3. First-order kinetic plots of ApNE in microwave and thermal conditions

2.2 Experimental

2.2.1 Thermal Synthesis of 2-Allylphenol and 2, 3-dihydro-2-methylbenzofuran

2-allylphenol (AP) was synthesized by Claisen rearrangement of allyl phenyl ether (APE). In preparation of 0.5 M APE solution, measure 1.372 mL APE by pipet, and put into 20mL vial, then add 20mL tridecane into this vial. In uncatalyzed thermal reactions, measure 3 mL 0.5 M APE-tridecane solution by pipet and transfer to 10 mL pyrex tube then add magnetic stirring bar inside. Repeat this procedure three more times to make four reaction samples. Put
these four samples in the preheated silicone oil which is heated by hot plate and wait for about 5 min to heat up to 190°C. Take out one pyrex tube every 30 min (30 min, 60 min, 90 min, 120 min) and wait to cool down to room temperature. Measure 300 µL solution by pipet and transfer to the 10 mL volumetric flask, add 1 M naphthalene in toluene solution into the 10mL volumetric flask (naphthalene is the internal standard for gas chromatography (GC) measurement, toluene is the solvent for GC samples) so that the reacted solution is diluted to 10 mL. Take 1mL diluted solution to the GC vial for the GC measurement.

In catalyzed thermal reactions, weigh 200 mg Fe₃O₄ nanoparticles and put in the pyrex tube, add 3 mL 0.5 M APE solution which prepared above and the stirring bar into the pyrex and follow the same procedure above to get 30min, 60min, 90min, 120min reaction. After taking out the pyrex tubes, filter out the Fe₃O₄, then use the same procedure above to prepare for the GC samples.

In the catalyzed cyclizations, measure 1.372 mL 2-allylphenol (AP) by pipet, and put into 20mL vial, then add 20mL tridecane into this vial to make 0.5 M AP solution in tridecane. Weigh 200 mg Fe₃O₄ nanoparticles and put into 10 mL pyrex tube. Measure 3 mL 0.5 M AP-tridecane solution by pipet and transfer to the pyrex tube containing magnetite. Repeat this procedure three more times to make four reaction samples. Put these four samples in the preheated silicone oil which is heated by hot plate and wait for about 5 min to heat up to 190°C. Take out one pyrex tube every 30 min (30 min, 60 min, 90 min, 120 min) and let it cool down to room temperature. Filter off the Fe₃O₄ to get pure liquid solutions. Measure 300 µL product solution by pipet and transfer to the 10 mL volumetric flask, add 1 M naphthalene in toluene solution into the 10mL volumetric flask (naphthalene is the internal standard for GC measurement,
toluene is the solvent for GC samples) so that the solution is diluted to 10 mL. Take 1 mL diluted solution to the GC vial for the GC measurement.

2.2.2 Gas Chromatography Measurements of 2-Allylphenol and 2, 3-dihydro-2-methylbenzofuran

2.2.2.1 Calibration Curves of Allyl Phenyl Ether, 2-Allylphenol and 2, 3-dihydro-2-methylbenzofuran. In preparation of 10 mL 1 mol/L bulk allyl phenyl ether solution, measure 1.305 mL pure allyl phenyl ether (APE) by pipet and transfer to the 10mL volumetric flask, add 1 mol/L naphthalene in toluene solution into the flask to reach 10 mL (naphthalene is the internal standard). In preparation of 0.2 mol/L APE solution, measure 2 mL 1 mol/L APE bulk solution and transfer into the 10 mL volumetric flask and diluted to 10 mL by adding 1 mol/L naphthalene in toluene solution, then measure 1 mL diluted solution and put into the GC vial. Use the similar procedures to make the 0.1 mol/L, 0.05 mol/L, 0.02 mol/L 0.01 mol/L and 0.005 mol/L APE samples. The same whole procedures are used to make 2-allylphenol and 2, 3-dihydro-2-methylbenzofuran samples.

The calibration curves of these three compounds are analyzed by using Perkin Elmer Clarus-400 gas chromatography, and the curves are used for determining the concentrations of the reactants and products in the actual reactions. Figure 2.4 to 2.6 below shows the calibration curves of these compounds which are peak areas versus concentrations.
Figure 2.4. Calibration curve of allyl phenyl ether.

Figure 2.5. Calibration curve of 2-allylphenol.
2.2.2.2 Gas Chromatography of Allyl Phenyl Ether, 2-Allylphenol and 2, 3-dihydro-2-methylbenzofuran. The concentrations of Allyl Phenyl Ether, 2-Allylphenol and 2, 3-dihydro-2-methylbenzofuran are all measured by gas chromatography. The diluted samples prepared in 2.2.1 are injected into Clarus 400 gas chromatography equipped with DB-5 high resolution column with internal diameter 0.32 mm, film thickness of 0.25 µm, length of 30 m and the temperature limitation is from -60 °C to 325 °C. Figure 2.7 shows the gas chromatography of these three compounds.

Figure 2.6. Calibration curve of 2, 3-dihydro-2-methylbenzofuran.

Figure 2.7. Full gas chromatography Claisen rearrangement.
The method in the measurement is: hold at 40°C for 4 min, then raise at 10°C per min to reach 70°C and hold for 2 min, then raise at 45°C to reach 250°C and hold for 2 min, then drop to 40°C at the rate of 45°C per min. In this GC figure, the x-axis is the retention time (min) and the y-axis is the intensity of the peaks (µV). The peaks shown before 7.0 min are the peaks of toluene, the solvent and the impurities in the toluene; the peak shown at 9.7 min is the reactant, allyl phenyl ether; the peak shown at 10.1 min is 2, 3-dihydro-2-methylbenzofuran; the peak shown at 10.8 min is the internal standard, naphthalene; the peak shown at 11.0 min is 2-allylphenol; the peak shown at 11.5 min is the reaction solvent, tridecane.

2.2.3 Microwave Synthesis of 2-Allylphenol and 2, 3-dihydro-2-methylbenzofuran

In the microwave kinetic analysis, all the reactants, solvent and the container must not absorb or slightly absorb any microwave radiation, only the catalyst absorbs the microwave energy and generates heat. Based on this, 10 mL quartz tubes are used instead of glass tubes, and tridecane, the non-polar and high boiling point solvent is used. In the heterogeneous catalyzed Claisen rearrangement, 0.5 M APE in tridecane solution is used, and the 200 mg Fe₃O₄ nanoparticles is added. Measure 3 mL 0.5M APE in tridecane solution by pipet and put into the 10 mL quartz tube, then add 200 mg magnetite nanoparticles. Insert the quartz tube into the CEM microwave machine, sealed with fiber optic thermometer which could monitor the temperature inside the solution. After the preparation, set the microwave to constant temperature, and the temperature is set to 170 °C, and the time is set to 30min. After the reaction finish, cool down the solution and filter off the magnetite solid and gain pure liquid solution, then take 300 µL mixture solution into 10 mL volumetric flask. The volumetric flask is then filled to 10 mL by adding 1
mol/L naphthalene in toluene solution, and 1 mL of the solution is taken from the volumetric flask to the GC vial which would be ready for the GC injection. Repeat this procedure four times to calculate errors and standard deviation. To generate kinetic data in a specific temperature, the 30 min, 60 min, 90 min, 120 min reactions should be repeated. And five temperature sets of reactions should be done.

In heterogeneous catalyzed cyclization, the same reaction conditions are used except using 0.5 M 2-allylphenol as starting material for three temperatures.

2.3 Results and Discussions in Claisen Rearrangement

2.3.1 Uncatalyzed Claisen Rearrangement

Compared to homogeneous catalysis, the microwave assisted heterogeneous catalysis is more selectively heated since only the catalyst absorbs microwave radiation. In my study, I chose Claisen rearrangement to probe microwave effects in solid-substrated interfaces. My fundamental hypothesis, based on prior studies, is that by using catalysts that have large microwave absorption cross sections we can potentially alter reaction rates, change product selectivity and alter the position of chemical equilibria due to microwave-specific effects\textsuperscript{31,32}. The underlying basis of these microwave specific effects arise from the effects of different microwave loss heating processes on chemical processes at the surface.

We have recently observed striking microwave-specific catalytic enhancement using a series of magnetic spinel nanoparticles that were effective in the oxidation of methanol to formaldehyde in aqueous methanol solutions. Direct comparison of the conventional thermal
reactivity with that of the microwave heated solution showed that conventional thermal catalysis was, at best, around 4% of what was obtained in the microwave\textsuperscript{33}.

In this study, we report the heterogeneous catalysis of the aryl Claisen rearrangement of allyl phenyl ether (APE) over magnetic ferrite spinels under both convective and microwave conditions. The reaction rates and the product distribution are found to differ significantly between the catalyzed and uncatalyzed reactions and between the two methods of heating. (Figure 2.10)

![Figure 2.8. Heating curve of 0.5 M allyl phenyl ether in tridecane, 300W.](image)

To confine microwave heating exclusively to the catalyst the reaction conditions are selected so that the only significant microwave absorber in the reaction is the catalyst. This is accomplished by selecting non-absorbing solvents and reactants. In particular, tridecane was used as the solvent, due to its transparency to microwave radiation and its high boiling point. The
reactant, APE has a very small dipole moment and shows only minimal heating (Figure 2.8), and only the specific catalyst absorbs microwave energy and generate heat (Figure 2.9). Under the conditions of this study it cannot directly rearrange in the microwave as temperatures necessary to do that cannot be reached.

**Figure 2.9.** Heating curve of microwave catalyzed Claisen rearrangement, 190 °C.

For purposes of comparison with the catalyzed reactions, the disappearance of uncatalyzed homogeneous solutions of APE in tridecane were measured as a function of time at five different temperatures between 195 and 215°C in 5°C increments over a period of 120 minutes. The thermal rearrangement of APE follows the expected first order decay kinetics (Figure 2.10, a). An Arrhenius plot (Figure 2.11) shows an activation energy of 98.51 kJ/mol. Analysis of the solution after the reaction has taken place shows it to be was quite clean and the only product observed was the rearrangement product 2-allylphenol (AP).
Figure 2.10. Disappearance of APE in Claisen rearrangements: a) thermal uncatalyzed reaction; b) thermal catalyzed reaction; c) microwave catalyzed reaction.
2.3.2 Catalyzed Claisen Rearrangement

From our prior studies we established that magnetic spinel nanoparticles represented a potentially useful class of microwave catalysts. These materials generally are strong microwave absorbers due to permittivity and permeability loss processes. In the oxidation of methanol to formaldehyde, the most effective catalyst was a series of chromites, MCr$_2$O$_4$, where CuCr$_2$O$_4$ was the most active catalyst, though the Co$^{2+}$ and Fe$^{2+}$ chromite compositions were also active. For the Claisen rearrangement, which will not involve an oxidation process, the catalytic activity will arise from specific interactions with the surface that facilitate the rearrangement process. Initial studies were carried using magnetite, Fe$_3$O$_4$, because of its pronounced microwave heating and known catalytic reactivity.
2.3.2.1 Thermal Catalysis. The disappearance of APE as a function of temperature in the presence of magnetite is shown in Figure 2.10 b. As can be seen, there is a rapid decrease in APE concentration that increases with temperature. A direct comparison to the homogeneous thermal reaction (Figure 2.10 a) shows that comparable disappearance rates take place over a much lower temperature range in the presence of Fe$_3$O$_4$. In particular, at 215 °C in the absence of Fe$_3$O$_4$, 43.4% of the APE reacts by the end of reaction time (120 min). Conversely, in the presence of Fe$_3$O$_4$ a similar conversion (43.7%) is observed over the same reaction time at 190 °C suggesting that the magnetite is a very active catalyst.

2.3.2.2 Microwave Catalysis. The reaction was carried out under microwave radiation under conditions of constant temperature. Under these conditions the microwave heats the solution to a predetermined solution temperature, as measure through an internal fiber optic thermometer. Once the temperature is attained it is maintained by the microwave through a feedback loop that modulates the applied power to maintain the prescribed temperature. In the experiments described here the preset temperatures are the same as those used in the convectively heated catalyzed reaction. Notably, since the solvent is non-absorbing, it is the magnetite catalyst that absorbed the radiation and then convectively heats the solution.

The decay of APE under microwave conditions is shown in Figure 2-10 c. Comparisons with the convectively heated catalyzed reaction (Figure 2.10 b) indicates that the microwave driven reaction is dramatically faster. For example at 170 °C the percent of APE reacted during the duration of the experiment (120 min) in the microwave is 60.2% compared to 26.6% under convective heating. At the higherst temperature, 190 °C, 72% of the APE has reacted compared to 43% under convective heating.
2.3.2.3 Products of the Catalyzed Reaction. What differs dramatically between the homogeneous thermal reaction and the catalyzed reactions are the products produced. Analysis of the isolated products by NMR indicate that two products are produced in the presence of magnetite: the expected 2-allyl phenol (AP) and the cyclization product 2,3-dihydro-2-methylbenzofuran (DHMBF) (Figure 2.12).

![Chemical Structures](image)

Figure 2.12. Catalyzed Claisen rearrangement and cyclization

The generation of the cyclization product is not unusual and has been observed in aryl Claisen rearrangements catalyzed homogeneously by transition metal salts and heterogeneously mesoporous aluminium silicates and zeolites. Appearance of the two products as a function of time at 190 °C under convective and microwave heating is shown in Figure 2.13 a and b.
Figure 2.13. the appearance of (■) 2-allylphenol and (●) 2,3-dihydro-2-methylbenzofuran at 190 °C catalyzed by 200 mg of Fe₃O₄ under (a) convective and (b) microwave heating.

As can be seen, under convective heating AP and DHMBF initially form in almost equal quantities under convective heating. Over the time of the reaction, the amount of DHMBF grows steadily while the amount of AP produced starts to diminish. Under microwave heating, the product distribution is dramatically different with DHMBF being the dominant product while the
AP is produced in much smaller amounts and exhibits an approximately steady state concentration over the duration of the experiment. This difference in the product distribution is observed across the range of temperatures studied. As shown in Figure 2.14, the product distribution under convective heating is roughly 1:1 AP and DHMBF under convective heating. At higher temperatures, the product distribution favors DHMBF where the composition is 58.7% DHMBF to 41.3% AP at 190 °C. For the microwave driven reaction, the product distribution strongly favors the cyclization product, DHMBF, accounting for approximately 90% of the product. As in the convectively heated case, the DHMBF product becomes slightly more favored at higher temperatures.

![Figure 2.14](image)

**Figure 2.14.** Percent composition of AP and DHMBF in the solution after 120 min of reactions time as a function of temperature under convective (ther) and microwave (μW) heating.
2.3.3 Conclusion

The comparison between thermal catalyzed and thermal uncatalyzed Claisen rearrangement shows that the magnetite is a good catalyst that can accelerate the reaction and generate more product. Moreover, the catalyzed reaction and form one more product instead only AP generated in uncatalyzed thermal reactions. In comparisons of catalyzed microwave reaction and catalyzed thermal reactions, we found that the microwave reaction accelerates the Claisen rearrangement a lot and the disappearance of APE is dramatically more than the thermal catalyzed Claisen rearrangement. More interestingly, in the microwave reaction, DHMBF is the main product and AP would remain in low concentration compared to both products grow continuously in thermal catalyzed Claisen rearrangement. This result proves that there is a huge microwave enhancement in Claisen rearrangement and got completely different product proportions compared to the thermal reactions of Claisen rearrangement.

2.4 Microwave Acceleration in Catalyzed Cyclization

2.4.1 Introduction of Langmuir Isotherm and Deduction of Rate Equations

Former studies proved that the generation of DHMBF occurs directly from the cyclization of the AP and its synthesis from APE is generally thought to be a tandem reaction where AP is generated initially through the Claisen rearrangement and then cyclized to produce DHMBF. The formation of Claisen rearrangement and cyclization products on a solid surface, showing the possible pathways for product formation is shown in Figure 2.15.
Since this is a heterogeneous catalysis, and based on the former result, both the catalyzed Claisen rearrangement and the cyclization reactions do not follow first-order kinetics, and since there is a procedure containing chemical adsorption and desorption on the catalysts’ surface, the Langmuir model\textsuperscript{39-42} is referred and used to resolve the kinetic calculations (Figure 2.16).

In Langmuir theory, the molecules can only adsorb on the specific sites of the catalyst’s surface, which formed the “chemisorbed” molecules. Also, one active site (*) on the catalyst’s surface can only adsorb one molecule, and the chemisorbed molecules would not interact with each other. Moreover, this is a single layer adsorption, and each active site has the same adsorbing energy. So in Langmuir isotherm theory, the rate constants of adsorption and desorption can be expressed as $k_{\text{ads}}$ and $k_{\text{des}}$ (Figure 2.16).
Based on this theory, the mechanism of the Claisen Rearrangement should be described below in consideration of chemical adsorption and desorption:

**Figure 2.16.** Langmuir isotherm theory model.

**Figure 2.17.** Kinetic model of Claisen rearrangement
In this figure, K is the equilibrium constant of chemical adsorption process; $k_1$ is the rate constant of APE converting to AP, and $k_2$ is the rate constant of APE to DHMBF, and $k_3$ is the rate constant of AP converting to DHMBF. Combining Figure 2.16 and Figure 2.17, we can write the rate equation and reaction equations of Claisen rearrangement by using Langmuir isotherm theory which would be shown below.

$$
\begin{align*}
\text{A} + \ast & \xrightarrow{k_A} \text{A}^* \\
\text{A}^* & \xrightarrow{k_1} \text{B} + \ast \\
\text{A}^* & \xrightarrow{k_2} \text{C} + \ast \\
\text{B} + \ast & \xrightarrow{k_B} \text{B}^* \\
\text{B}^* & \xrightarrow{k_3} \text{C} + \ast
\end{align*}
$$

**Figure 2.18.** Langmuir isotherm equations.

Where A is APE, B is AP and C is DHMBF, $k_1, k_2$ and $k_3$ are the rate constants of the reactions that have been mention above; $[^*]_0$ is the concentration of total active sites on the catalyst’s surface, $[^*]$ is the concentration of unoccupied active sites, $[^*]$, $[^*]$ are the concentrations of chemisorbed APE, AP or the occupied active sites, and $K_A$, $K_B$ are the equilibrium constant of chemisorption.
Since the model of cyclization is simpler, let's use cyclization which only contains B converting to C as an example, and the rate equation of cyclization can be written as:

\[ r = \frac{d[B]}{dt} = -k_B[B][\text{*}] + k_{-B}[B^\ast] = -k_3[B^\ast] \]  

(2.1)

When the chemisorption reaches equilibrium, the concentration of chemisorbed AP should remain constant, in other words, the rate of \([B^\ast]\) should be zero, so we have:

\[ \frac{d[B^\ast]}{dt} = k_B[B][\text{*}] - k_{-B}[B^\ast] - k_3[B^\ast] = 0 \]  

(2.2)

Combined equations in Figure 2.18 and equation 2.2, we can solve the intermediate of two types of active sites \([B^\ast]\) and \([\text{*}]\):

\[ \begin{align*} 
[B^\ast] &= \frac{k_B[B][\text{*}]}{k_{-B} + k_3} = \frac{k_B[B][\text{*}]}{1 + \frac{k_3}{k_{-B}}} = \frac{k_B[B][\text{*}]}{1 + \frac{k_3}{k_{-B}}} \\
[\text{*}] &= \frac{[\text{*}]}{1 + k_B[B]} 
\end{align*} \]  

(2.3)

(2.4)

In the equation, the ratio \(k_3/k_{-B}\) can be considered the comparison of \(B^\ast\) converting to C vs. \(B^\ast\) desorbing to B. And the rate equation of cyclization is based on the assumption that the chemisorption process reaches equilibrium. In other words, \(k_{-B}\) would be much greater than \(k_3\), and \(k_3/k_{-B}\) can be ignored in the equation. So equation 2.3 can be simplified as:

\[ [B^\ast] = K_B[B][\text{*}] \]  

(2.5)

Substituting eq. 2.4, 2.5 into eq. 2.1, we can solve the rate equation which is shown below:

\[ r = \frac{d[B]}{dt} = \frac{-k_3K_B[B]}{1 + K_B[B]}[\text{*}]_0 \]  

(2.6)

Equation 2.6 is the rate equation of decrease of AP in heterogeneous catalyzed cyclization, and the integration of equation 2.6 would show the relationship between [B] and t which is shown in eq. 2.7:
\[ t = -\frac{1}{k_3K_B[\star]_0} (\ln[B] + K_B[B] + c) \] (2.7)

As we can’t directly solve B in the equation, but we can solve t, we’ll use the change of [B] and t to get the curve as time as function of concentration. This equation will be used in the later kinetic calculations and solve the non-linear fit problems.

After calculating the concentration equation of B, let’s start the more complex model which is the whole reaction of Claisen rearrangement.

In this reaction, we should consider the reaction that A to B, B to C and A to C, which is shown in Figure 2.18, and when the chemisorption reaches equilibrium, both \([A^\star]\) and \([B^\star]\) should remain constant and be considered as steady state. So the reaction of these parameters as function of time should be written as:

\[ \frac{d[A^\star]}{dt} = k_A[A][\star] - k_{-A}[A^\star] - k_1[A^\star] - k_2[A^\star] = 0 \] (2.8)

\[ \frac{d[B^\star]}{dt} = k_B[B][\star] - k_{-B}[B^\star] - k_3[B^\star] = 0 \] (2.9)

By using the same method, we can calculate the rate equations of APE and AP:

\[ \frac{d[A]}{dt} = \frac{-(k_1+k_2)K_A[A]}{1+K_A[A]+K_B[B]} [\star]_0 \] (2.10)

\[ \frac{d[B]}{dt} = \frac{k_1K_A[A]-k_2K_B[B]}{1+K_A[A]+K_B[B]} [\star]_0 \] (2.11)

Since these two rate equations contains too many parameters, they cannot be integrated and solve the clean [A], [B] or t. We can’t use these equations to fit the data.

2.4.2 Results and Discussions of Catalyzed Cyclizations

2.4.2.1 Conversion Comparison. The disappearance of AP as a function of temperature in the presence of magnetite is shown in Figure 2.18 (thermal) and Figure 2.19 (microwave). In
the thermal reactions, five temperatures are used from 180 °C to 200 °C and in microwave reactions, the three temperatures are used from 185 °C to 195 °C by using internal fiber optic thermometer as an internal temperature monitor under the condition of constant temperature. Since the solvent is non-absorbing, only reactant, AP, and the catalyst, magnetite absorbs microwave radiation and generates heat.

**Figure 2.19.** Disappearance of 2-allylphenol in thermal heterogeneous catalysis.
Figure 2.20. Disappearance of 2-allylphenol in microwave heterogeneous catalysis.

In the figures, it is obvious to find out that decrease of AP increases dramatically in the microwave reactions compared to thermal reactions which indicates that the microwave driven reactions are notably faster. For example, at 195 °C the conversion during the duration of the experiment (120 min) in the microwave is 91.25% compared to 58.48% under convective heating. And more directly, the conversion in the highest temperature of convective heating (200 °C) over longest duration of time (120 min), 64.07%, is still lower than the conversion of lowest temperature (185 °C) over shortest reaction time (30 min) in the microwave reaction which is 75.10%.
2.4.2.2 Kinetic Parameter of Catalyzed Cyclizations. Since the heterogeneous catalyzed cyclization of 2-allylphenol to 2, 3-dihydro-2-methylbenzofuran is not a first-order reaction, but follows Langmuir isotherm, the regular kinetic calculations cannot be used to analyze the data. Instead, the Langmuir equation (Eq. 2.6) is used to characterize the data.

To integrate Eq. 2.6 and solve the rate constant, non-linear least square algorithm is used\(^4^3\). In this algorithm, the data should be put into the equation first, and the original parameters are set to iterate into the equation to find the approaching parameters that can cause minimum errors, in other words, the numbers of the parameters would best fit the data and the equation\(^4^4,4^5\). The software that used to do the calculation is “Rstudio”, and name of the package is “nls.lm \{minpack.lm\}” which mostly used to minimize the sum square of the vector returned by the function by using a modified Levenberg-Marquardt algorithm and solve the non-linear least square fitting problems\(^4^6\). The rate constants of both convective and microwave reactions are shown in Table 2.1, and the fitting curves are shown in Appendix B.

Table 2.1. Rate constants of thermal reactions and microwave reactions.

<table>
<thead>
<tr>
<th>T</th>
<th>(K_B)</th>
<th>(-k_3K_B[^*]_0)</th>
<th>(k_3[^*]_0)</th>
<th>(K_B)</th>
<th>(-k_3K_B[^*]_0)</th>
<th>(k_3[^*]_0)</th>
</tr>
</thead>
<tbody>
<tr>
<td>180 °C</td>
<td>1.5(±0.010)</td>
<td>-1.1(±0.007)E-04</td>
<td>7.3E-05</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>185 °C</td>
<td>1.6(±0.010)</td>
<td>-1.4(±0.020)E-04</td>
<td>9.3E-05</td>
<td>1.8(±0.003)</td>
<td>-5.1(±0.008)E-04</td>
<td>2.9E-04</td>
</tr>
<tr>
<td>190 °C</td>
<td>1.6(±0.007)</td>
<td>-1.6(±0.039)E-04</td>
<td>1.0E-04</td>
<td>1.8(±0.004)</td>
<td>-5.5(±0.021)E-04</td>
<td>3.1E-04</td>
</tr>
<tr>
<td>195 °C</td>
<td>1.6(±0.011)</td>
<td>-1.9(±0.021)E-04</td>
<td>1.2E-04</td>
<td>1.7(±0.003)</td>
<td>-5.8(±0.008)E-04</td>
<td>3.4E-04</td>
</tr>
<tr>
<td>200 °C</td>
<td>1.6(±0.006)</td>
<td>-2.2(±0.024)E-04</td>
<td>1.4E-04</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>
The equilibrium constant \( K_B \) remains stable that oscillates around 1.6 and 1.7, demonstrating that in both microwave and thermal reactions, the chemi-adsorption is larger than the chemi-desorption during the reaction, which proceeds the reaction goes from reactant to product. Since in both thermal and microwave reactions, the same amount of catalyst is used, the \( [\cdot]_0 \) should be the same in these reactions. In this table, the rate constant times the concentration of total active sites in microwave reactions are apparently three times larger than the data in thermal reactions with the same temperature, 180 °C, 190 °C and 195 °C, which indicates that there is a specific microwave enhancement inside that accelerate the heterogeneous cyclization.

The Arrhenius plot of AP in both convective and microwave reactions (Figure 2.20 and 2.21) can be generated by using the rate constants in Table 2.1 with the Arrhenius Equation (Eq. 2.7).

\[
k = A e^{-E_a/(RT)}
\]

(2.7)

Where \( k \) is the rate constant that equals to \( k_3[\cdot]_0 \), \( A \) is the pre-exponential factor, \( E_a \) is the activation energy, \( R \) is the universal gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)).

![Figure 2.21. Arrhenius plot of thermal Fe\(_3\)O\(_4\) catalyzed cyclization.](image)
Figure 2.22. Arrhenius plot of microwave Fe$_3$O$_4$ catalyzed cyclization.

The activation energies can be calculated from the plots that are: 56.36 kJ/mol in conventional heating, and 27.23 kJ/mol in microwave heating. It turns out that in the microwave reactions, the activation energy decreases approximately as half as the activation energy in convective reactions, which proved that there is a specific microwave enhancement in the microwave driven catalysis that accelerates the reaction.

2.5 Parameters of Different Spinels in Catalyzing Claisen Rearrangement

In former studies, it is understood that magnetite, Fe$_3$O$_4$, is a very good heterogeneous catalyst that accelerate Claisen rearrangement and form two product. In microwave, magnetite works much better than thermal reactions that it catalyzes APE mostly to DHMBF. Based on this result, some other spinel nano particles are tested to figure out if they could also act as catalyst and generate differenent products in the Claisen Rearrangement.
2.5.1 Experimental

In this test, several ferrite spinels such as MnFe$_2$O$_4$, CoFe$_2$O$_4$, NiFe$_2$O$_4$, and other spinels like CuCr$_2$O$_4$, Co$_3$O$_4$ and Mn$_3$O$_4$ are used in the heterogeneous catalysis. The amount of these catalysts are as the same as the amount of Fe$_3$O$_4$, 200 mg, and the experimental conditions are exactly the same in Fe$_3$O$_4$ catalyzed microwave reactions, which is 0.5 M APE in tridecane, and 190 °C in constant temperature. The duration of the reactions are two hours, and the solutions are analyzed by GC.

2.5.2 Result and Discussion

The conversion of these spinels catalyzed microwave reactions are shown in Table 2.2. The reactions are under microwave conditions in two hours, and the results show the conversion of two different products.

In this table, it is found that all these spinels except Mn$_3$O$_4$ can form two products (AP and DHMBF). However, the proportion of AP : DHMBF are much different between those spinels catalyzed reactions. The ferrite spinels, MnFe$_2$O$_4$, CoFe$_2$O$_4$, NiFe$_2$O$_4$, can catalyzed to form both products and the proportion of AP and DHMBF are close to 1.0, but the proportions of CuCr$_2$O$_4$ and Co$_3$O$_4$ catalysis are 7.61 and 24.63, which indicates that these reactions forms mostly AP, but only convert to a small concentration of DHMBF. In detail, compared to MnFe$_2$O$_4$ and Mn$_3$O$_4$, which has the same cation, Mn$^{2+}$, but has different anions, it is shown that the ferrite spinel gives rise to the conversion of DHMBF, but manganese oxide does not catalyze...
the conversion of DHMBF, but only AP. This phenomenon also appears in the comparison of CoFe$_2$O$_4$ and Co$_3$O$_4$. This result indicates that in the spinel catalyzed Claisen rearrangement, the amount of DHMBF is dominated by the magnetic part or the anions, and the ferrite spinels are better than other spinels to generate DHMBF.

Table 2.2. Conversions of different spinels catalysed Claisen rearrangement.

<table>
<thead>
<tr>
<th>MW 190 °C 2h</th>
<th>AP</th>
<th>DHMBF</th>
<th>AP : DHMBF</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnFe$_2$O$_4$</td>
<td>12.1(±0.004)%</td>
<td>11.7(±0.003)%</td>
<td>1.03</td>
</tr>
<tr>
<td>CoFe$_2$O$_4$</td>
<td>14.5(±0.003)%</td>
<td>11.5(±0.001)%</td>
<td>1.26</td>
</tr>
<tr>
<td>NiFe$_2$O$_4$</td>
<td>14.5(±0.001)%</td>
<td>11.9(±0.001)%</td>
<td>1.21</td>
</tr>
<tr>
<td>CuCr$_2$O$_4$</td>
<td>18.2(±0.003)%</td>
<td>2.4(±0.001)%</td>
<td>7.61</td>
</tr>
<tr>
<td>Co$_3$O$_4$</td>
<td>20.3(±0.002)%</td>
<td>0.8(±0.001)%</td>
<td>24.63</td>
</tr>
<tr>
<td>Mn$_3$O$_4$</td>
<td>19.8(±0.001)%</td>
<td>0%</td>
<td>N/A</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>5.9(±0.002)%</td>
<td>57.4(±0.004)%</td>
<td>0.10</td>
</tr>
<tr>
<td>Fe$_3$O$_4$ Thermal</td>
<td>11.3(±0.007)%</td>
<td>16.0(±0.002)%</td>
<td>0.70</td>
</tr>
<tr>
<td>Uncat. Thermal</td>
<td>18.3(±0.006)%</td>
<td>0%</td>
<td>N/A</td>
</tr>
</tbody>
</table>

However, even these spinels can catalyze the Claisen rearrangement and form two products, compared to magnetite catalyzed reactions, there are still a huge difference in the conversion and proportion of the products. In magnetite catalyzed microwave reactions, the total conversion is 63.25% which is much higher than the total conversion of nickle ferrite catalyzed microwave reaction, 26.40%, which is the highest conversion among those other spinel catalyzed reactions. More directly, the conversion and the proportion of this nickle ferrite catalysis looks
more close to the thermal magnetite catalysis, which is 27.2% total conversion and 0.70 in proportion of AP : DHMBF. Moreover, the total conversion of other spinels except ferrites are around 21%, which is between the conversion of uncatalyzed thermal reactions and Fe$_3$O$_4$ catalyzed thermal reactions. Combining all the data and comparisons above, we can conclude that these except manganese oxide do act as catalyst that forms two different products, and the ferrite spinels are better in converting to DHMBF, but others are better in forming AP. However, these spinels act more likely heater that generate heat by absorbing microwave radiation then transfer the heat to the surrounding solutions, but has no other microwave-specific effect. Fe$_3$O$_4$ is the only catalyst that shows the microwave enhancement in this heterogeneous catalyzed Claisen rearrangement.
CHAPTER 3

THE CHAPERONE EFFECT IN MICROWAVE DRIVEN REACTIONS

3.1 Introduction

Recently we reported the existence of microwave-specific effects on the rates of organic reaction\textsuperscript{29-32}. The origin of these effects, where reactions proceed a rates greater than what would be predicted from the temperature of the solution through the Arrhenius parameters, was shown to arise from selective heating of the molecules. The reaction systems used to quantify the effect consisted of microwave absorbing polar reactant molecules in a non-polar solvent. The solvent shell around the absorber forms a domain that stores energy so that the reactant experiences a temperature that is higher than the surrounding medium. One of the limitations of microwave driven chemistry is that reactant species must be polar to absorb radiation. Obviously this can be overcome by using absorbing solvents, however, microwave-specific rate enhancement is unlikely to be observed under those conditions. In our prior study of the microwave driven aryl Claisen rearrangement of allyl p-nitrophenyl ether, it was found that the concentration of the absorbing species in a non-polar solvent has a dramatic effect on the degree of microwave-specific enhancement with higher concentration resulted in greater rate enhancement even when the microwave power is lower\textsuperscript{28}. This suggests that the association and agglomeration of the dipole species, which occurs at higher concentration, can create efficient domains for absorption and storage of energy. Our hypothesis is that if microwave absorbing dipolar molecules can associate with non-absorbing reactant molecules to form domains, then the reactant molecules
can experience rate enhancement from the heat stored in the domain. In effect, the dipolar species can “chaperone” the reactant into the selectively heated domain.

We tested this hypothesis with the aryl Claisen rearrangement of allyl phenyl ether (APE). This is a well understood unimolecular reaction following first order kinetics (Figure 3.1). Under convective heating conditions, the reaction occurs at relatively high temperature, c.a. 200 °C. For purposes of comparison with the microwave reactions, the disappearance of APE in tridecane solvent was measured as a function of time at four different temperatures between 200 and 215 °C. An arrhenius plot was constructed from the temperature dependent first order rate constants. Obtained from the plot was an activation energy of 98.51 kJ/mol. Since APE has a very small dipole moment and shows only minimal heating in the microwave, it cannot directly rearrange in the microwave as temperatures necessary to do that cannot be reached.

![Figure 3.1. Claisen rearrangement of allyl phenyl ether.](image)

The “chaperone” added in the Claisen Rearrangement that helps generate heat in the microwave is 1-nitronaphthalene (nNAP). With a higher concentration of nNAP compared to
lower concentration of APE, the nNAP molecules would surround the APE molecule and aggregate together by $\pi-\pi$ bondings (Figure 3.2), forming cluster-like larger molecule groups. Since nNAP is the only dipolar molecule in the solution, it will absorb microwave radiation and generate heat, and transfer to the bonded APE immediately that helps the reaction to rearrange.

The microwave enhancement in this process compared to convective reactions is called the “chaperone effect”.

**Figure 3.2.** Higher concentration of 1-nitronaphthalene molecules surround and aggregate to lower concentration of allyl phenyl ether molecules that forming “clusters”.
3.2 Experimental

3.2.1 Thermal Synthesis of 2-Allylphenol with 1-Nitronaphthalene

In this synthesis, 0.05 mol/L APE in tridecane solution is used and different concentrations of nNAP are used. In preparation of 0.05 M APE solution, measure 0.137 mL APE by pipet, and put into 20 mL vial, then add 20 mL tridecane into this vial. Measure 3 mL 0.5 M APE-tridecane solution by pipet and transfer to 10 mL pyrex tube then add magnetic stirring bar inside. For 1 : 9 APE : nNAP solution, weigh 0.2338 g 1-nitronaphthalene and put into the 3 mL APE in tridecane solution to form 0.45 mol/L nNAP solution. Repeat this procedure three more times to make four same reaction samples. Put these four samples in the preheated silicone oil which heated by hot plate and wait for about 5 min to heat up to 210°C. Take out one pyrex tube every 30 min (30 min, 60 min, 90 min, 120 min) and wait to cool down to room temperature. Measure 300 µL solution by pipet and transfer to the 10 mL volumetric flask, add 1 M naphthalene in toluene solution into the 10mL volumetric flask (naphthalene is the internal standard for gas chromatography (GC) measurement, toluene is the solvent for GC samples) so that the reacted solution is diluted to 10 mL. Take 1mL diluted solution to the GC vial for the GC measurement. The first-order kinetic plot is shown in Figure 3.3.

Since we have measured the rate constants in thermal uncatalyzed reactions before, we can make comparison of these two rate constants which turns out that there is not much difference between the thermal uncatalyzed rate constant and thermal chaperone rate constant. This result demonstrates that there would be no chaperone effect in the thermal reactions.
3.2.2 Microwave Synthesis of 2-Allylphenol with 1-Nitronaphthalene

In microwave synthesis, the same concentration of APE is used as in the convective reactions, which is 0.05 mol/L. For 1 : 9 APE : nNAP solution, weigh 0.2338g nNAP and put into 3 mL 0.05 mol/L APE in tridecane solution to form 0.45 mol/L nNAP solution. Put the quartz tube containing 1 : 9 chaperone solution in the microwave machine with stirring bar, sealed with fiber optic thermometer, and heat up with 250 W constant power for 2 hours, 3 hrs, 4hrs, hrs and 5 hrs, then take out and prepare the GC with the same procedure above. The kinetic plot is shown in Figure 3.4.

Besides 1 : 9 APE : nNAP solution, other proportions of chaperone solutions are used for the microwave reaction, which are 1 : 15 APE : nNAP (0.05 M APE, 0.75 M nNAP) and 1 : 6 APE : nNAP (0.05 M APE, 0.30 M nNAP). In order to reach the close temperature to the 1 : 9
microwave chaperone reactions, 120 W constant power is used for 1 : 15 reactions and 300 W constant power is used for 1 : 6 reactions. The kinetic plots are shown in Figure 3.5 (1 : 15 APE : nNAP) and Figure 3.6 (1 : 6 APE : nNAP).

**Figure 3.4.** First-order kinetic plot of 1 : 9 APE : nNAP microwave Claisen rearrangement.

**Figure 3.5.** First-order kinetic plot of 1 : 15 APE : nNAP microwave Claisen rearrangement.
Moreover, in spite of using aromatic molecule as “chaperone”, non-aromatic but high polarity molecule, DMSO, is used. In this reaction, 213 µL DMSO is added to form 1 : 20 APE : DMSO in tridecane solution (0.05 M APE : 1 M DMSO), the power in microwave is 300 W constant power and the first-order kinetic is shown in Figure 3.7.

Figure 3.7. First-order kinetic plot of 1 : 20 APE : DMSO microwave Claisen rearrangement.
3.3 Result and Discussion

3.3.1 Characteristics of Microwave Absorbance in Chaperone Solution

Since it is microwave selective heating, only chaperone (nNAP) absorbs microwave radiation and generate heat. Figure 3.8 is the heating curves of different concentration in 50 W constant microwave power that shows the relationship between the temperature and the nNAP concentration.

Figure 3.8. Heating Curves of 0.05 M APE, 0.05 M APE- 0.45M nNAP and 0.05 M APE- 0.75 M nNAP under the condition of microwave heatings, 50 W constant power.
In this figure, we can see that in 50 W fix power, the temperature increase of 0.05 M APE solution is less than 20 °C after 120 min, which turn out that APE in tridecane solution slightly abosrbs microwave radiation; the temperature of 0.05 M APE- 0.45 M nNAP solution reaches 126 °C, and the temperature of 0.05 M APE- 0.75 M nNAP solution reaches 151 °C, which indicates that the higher the nNAP concentration, the higher the temperature would be, and nNAP is a good chaperone that generate heat in the solution.

3.3.2 Kinetic Parameter Analysis of Chaperone Effect

In order to make comparion between the kinetics of microwave reactions and the kinetics of thermal reactions, similar temeratures should be reached which is about 205 °C. In microwave reactions, different powers should be set with different concentrations of nNAP solutions to reach similar temperatures. Appendix C shows the heating curves of Claisen rearrangement under microwave conditions with different powers. The average temerature is calculated in the microwave reactions and the rate constants of both convective and microwave reactions are shown in Table 3.1.

In this table, the rate constants are calculate from the Arrhenius Plot in thermal Claisen rearrangement in Figure 2.11. The comparison of thermal reactions between 1 : 9 APE : nNAP reaction at 210 °C and regular APE in tridecane reaction at 210 °C shows that there is only slightly rate constant increase which is within the standard error, this indicates that in there is no chaperone effect in the thermal reactions. But in microwave reaction, the rate constant increase can be observed compared to thermal reactions. For example, in 1 : 9 APE : nNAP reaction, the average temperature is 215 °C, and the rate constant is $1.02\times10^{-4}$ s$^{-1}$, which is 1.5 times to the
rate constant in 215 °C thermal reaction \( (7.70 \times 10^{-4} \text{ s}^{-1}) \). Also, for 1 : 6 APE : nNAP and 1 : 15 APE : nNAP microwave reactions, the rate constants are between 1.5 to 2 times to the rate constants in thermal reactions with the corresponding temperatures. The result demonstrates that there is a specific chaperone effect in the microwave reactions that nNAP aggregates with APE and accelerates the reaction.

**Table 3.1.** Rate constants of thermal and microwave Claisen rearrangement with corresponding temperatures.

<table>
<thead>
<tr>
<th></th>
<th>Thermal (calculated from Arrhenius equation)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>No nNAP added Claisen Rearrangement</td>
</tr>
<tr>
<td>T (°C)</td>
<td>181</td>
</tr>
<tr>
<td>( k ) (s(^{-1}))</td>
<td>1.3E-05</td>
</tr>
<tr>
<td>Microwave</td>
<td>1:6 APE:nNAP</td>
</tr>
<tr>
<td>( T_{ave} ) (°C)</td>
<td>206.90</td>
</tr>
<tr>
<td>( k ) (s(^{-1}))</td>
<td>9.3(±0.27)E-05</td>
</tr>
</tbody>
</table>

In order to discover if other dipolar molecule without aromatic groups could bond with APE and has the chaperone effect, DMSO is chosen since its high polarity and high solubility. However, the result shows that there is no dramatic rate constant enhancement compared to the thermal reaction with the same temperature, which turns out that there is no chaperone effect inside, and DMSO can only act like a heater, but cannot accelerate the reaction.
In the study, we believe that with the chaperone molecules which could bond to the reactant with specific intermolecular forces, there would be microwave enhancement that helps reactions to go faster. And the overall study demonstrates the reality of microwave specific effect on molecules and chemical reactions do occur and they can arise from selective heating processes that microwave interacts with molecules and solutions.
APPENDIX A

KINETIC PLOTS AND PRODUCTS FORMATION OF CLAISEN REARRANGEMENT AND CYCLIZATION

A.1 First-order kinetic and rate constants of 0.5M APE in tridecane solution, 195 °C

A.2 First-order kinetic and rate constants of 0.5M APE in tridecane solution, 200 °C
A.3 First-order kinetic and rate constants of 0.5M APE in tridecane solution, 205 °C

\[
y = 4.97 \times 10^{-1} e^{-4.68 \times 10^{-5} x} \\
R^2 = 9.97 \times 10^{-1}
\]

\[
y = 4.94 \times 10^{-1} e^{-4.54 \times 10^{-5} x} \\
R^2 = 9.92 \times 10^{-1}
\]

\[
y = 5.04 \times 10^{-1} e^{-5.02 \times 10^{-5} x} \\
R^2 = 9.96 \times 10^{-1}
\]

\[
y = 5.00 \times 10^{-1} e^{-4.71 \times 10^{-5} x} \\
R^2 = 1.00 \times 10^{0}
\]

A.4 First-order kinetic and rate constants of 0.5M APE in tridecane solution, 210 °C.

\[
y = 4.95 \times 10^{-1} e^{6.48 \times 10^{-5} x} \\
R^2 = 9.93 \times 10^{-1}
\]

\[
y = 4.96 \times 10^{-1} e^{6.32 \times 10^{-5} x} \\
R^2 = 9.96 \times 10^{-1}
\]

\[
y = 4.89 \times 10^{-1} e^{6.48 \times 10^{-5} x} \\
R^2 = 9.87 \times 10^{-1}
\]

\[
y = 4.88 \times 10^{-1} e^{6.17 \times 10^{-5} x} \\
R^2 = 9.87 \times 10^{-1}
\]
A.5 First-order kinetic and rate constants of 0.5M APE in tridecane solution, 215 °C.

A.6 Arrhenius plot of 0.5M APE in tridecane solution.
A.7 Thermal reaction of 0.5M APE in tridecane solution, 200 mg Fe$_3$O$_4$, 170 °C, product growth.

A.8 Thermal reaction of 0.5M APE in tridecane solution, 200 mg Fe$_3$O$_4$, 175 °C, product growth.
A.9 Thermal reaction of 0.5M APE in tridecane solution, 200 mg Fe$_3$O$_4$, 180 °C, product growth.

A.10 Thermal reaction of 0.5M APE in tridecane solution, 200 mg Fe$_3$O$_4$, 185 °C, product growth.
A.11 Thermal reaction of 0.5M APE in tridecane solution, 200 mg Fe₃O₄, 190 °C, product growth.

A.12 Microwave reaction of 0.5M APE in tridecane solution, 200 mg Fe₃O₄, 170 °C, constant T.
A.13 Microwave reaction of 0.5M APE in tridecane solution, 200 mg Fe$_3$O$_4$, 175 °C constant T.

A.14 Microwave reaction of 0.5M APE in tridecane solution, 200 mg Fe$_3$O$_4$, 180 °C constant T.
A.15 Microwave reaction of 0.5M APE in tridecane solution, 200 mg Fe$_3$O$_4$, 185 °C constant T.

A.16 Microwave reaction of 0.5M APE in tridecane solution, 200 mg Fe$_3$O$_4$, 190 °C constant T.
APPENDIX B

NON-LINEAR LEAST SQUARE FITTING CURVES

\[ R^2 = 0.9589 \]

B.1 Non-linear least square fitting curves of 0.5M AP in tridecane solution, 200 mg Fe_3O_4, 180 °C, thermal.

\[ R^2 = 0.9455 \]

B.2 Non-linear least square fitting curves of 0.5M AP in tridecane solution, 200 mg Fe_3O_4, 185 °C, thermal.
$R^2 = 0.9242$

**B.3** Non-linear least square fitting curves of 0.5M AP in tridecane solution, 200 mg Fe$_3$O$_4$, 190 °C, thermal.

$R^2 = 0.9341$

**B.4** Non-linear least square fitting curves of 0.5M AP in tridecane solution, 200 mg Fe$_3$O$_4$, 195 °C, thermal.
R²=0.9398

B.5 Non-linear least square fitting curves of 0.5M AP in tridecane solution, 200 mg Fe₃O₄, 200 °C, thermal.

R²=0.7812

B.6 Non-linear least square fitting curves of 0.5M AP in tridecane solution, 200 mg Fe₃O₄, 185 °C, microwave.
\( R^2 = 0.7533 \)

**B.7** Non-linear least square fitting curves of 0.5M AP in tridecane solution, 200 mg Fe\(_3\)O\(_4\), 190 °C, microwave.

\( R^2 = 0.7319 \)

**B.8** Non-linear least square fitting curves of 0.5M AP in tridecane solution, 200 mg Fe\(_3\)O\(_4\), 195 °C, microwave.
APPENDIX C

HEATING CURVES OF MICROWAVE DRIVEN CHAPERONE REACTIONS

C.1 Heating curve of 0.05M APE, 0.30M nNAP in tridecane solution, 300W constant power.

C.2 Heating curve of 0.05M APE, 0.45M nNAP in tridecane solution, 250W constant power.
C.3 Heating curve of 0.05M APE, 0.75M nNAP in tridecane solution, 120W constant power.

C.4 Heating curve of 0.05M APE, 1.0M DMSO in tridecane solution, 300W constant power.
REFERENCES


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