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Activation Energy of the Formation of the Allylic Carbocation in the Acid Catalyzed Dehydration of 4-Methylcyclohexanol

Dequina Nicholas

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Southern Scholars Honors Program
Senior Project Proposal Information Sheet

Name: Decima Nicholas  Date: 9-10-08

Major: Chemistry (Biochemistry)

A significant scholarly project, involving research, writing, or special performance, appropriate to the major in question, is ordinarily completed the senior year. The project is expected to be of sufficiently high quality to warrant a grade of "A" and to justify public presentation.

Under the guidance of a faculty advisor, the Senior Project should be an original work, should use primary sources when applicable, should have a table of contents and works cited page, should give convincing evidence to support a strong thesis, and should use the methods and writing style appropriate to the discipline.

The completed project, to be turned in as a duplicate, must be approved by the Honors Committee in consultation with the student's supervising professor four weeks prior to the last day of class for the semester the project is turned in. Please include the advisor's name on the title page. The 2-3 hours of credit for this project is usually done as directed study or as a research class.

NOTE: Senior Project Proposal Due Date: The senior project proposal is due in the Honors Program Director's office two weeks after the beginning of the semester the project will be completed. The proposal should be a detailed description of the Honors Project's purpose and proposed methodology.

Keeping in mind the above senior project description, please describe in as much detail as you can the project you will undertake. Attach a separate sheet of paper.

Signature of faculty advisor: [Signature]

Expected date of completion: March 27, 2009

NOTE: An advisor's final project approval does not guarantee that the Honors Faculty Committee will automatically approve the project. The Honors Faculty Committee has the final vote.

Approval to be signed by faculty advisor when the project is completed:

[ ] This project has been completed as planned (date): April 2, 2009

[ ] This is an "A" project: [ ]

[ ] This project is worth 2-3 hours of credit: [ ]

Advisor's Final Signature: [Signature]  Date: April 2, 2009

Chair, Honors Committee: Mark peach  Data Approved: May 09

Dear Advisor,

(1) Please write your final evaluation on the project on the reverse side of this page. Comment on the characteristics that make this "A" quality work.

(2) Please include a paragraph explaining your specific academic credentials for advising this Senior Project.
Final Evaluation

Southern Scholars project and report, Winter 2009
Project supervisor: Mitch Menzmer, Chemistry
Student: Dequina Nicholas

Project report title: “Activation Energy of the Formation of the Allylic Carboxylation in the Acid Catalyzed Dehydration of 4-Methylcyclohexanol”

“A” quality work for the following reasons:

1. Enthusiasm for the project: consistently very high
2. Performance on the project: excellent, capable of working through challenging problems independently, reaching valid solutions – never “dropped the ball”
3. Faithfulness in making appointments: superb, never missed a (weekly) scheduled meeting; occasional reschedule always made ahead of time.
4. Time spent on the project: well beyond the minimum required, in lab, with data analysis, and writing the report.
5. Results of Dequina’s research are significant, and worthy of peer-reviewed publication.

My qualifications for evaluating this work are as follows: I hold the PhD in Chemistry from Clarkson University, earned under the supervision of Petr Zuman. My background is in analytical and physical chemistry, in particular in application of kinetic analysis to reaction of organic and biological molecules in strongly acidic media. I also have considerable experience in software applications in this area. I have given two presentations at professional meetings and published two papers in this area and my work has been cited in other works. Dequina’s project stems from some of my earlier work.
Activation Energy of the Formation of the Allylic Carbocation in the Acid Catalyzed Dehydration of 4-Methylcyclohexanol

Dequina Nicholas

Department of Chemistry, Southern Adventist University

In partial fulfillment of Senior Project under the supervision of Dr. Mitch Menzmer
Abstract

The existence of a persisting allylic compound at equilibrium of the dehydration of 4-methyl cyclohexanol in 80% w/w sulfuric acid is supported by absorbance vs. time plots from UV-vis analysis. The peak seen at 305 nm is an indication of the formation of an allylic carbocation over time and therefore can support a proposed mechanism for this reaction. Kinetic analysis of the compound at 35.0°C, 48.5°C, 60.0°C, and 66.8°C shows that the dehydration reaction is first order with rate constants of 1.83 x 10^{-5}s^{-1}, 1.27 x 10^{-4}s^{-1}, 9.28x10^{-4}s^{-1}, and 9.55x10^{-4}s^{-1} respectively for each temperature and an activation energy of 116 kJ mol^{-1}.

Introduction

In the study of Chemistry, acid catalyzed dehydration reactions of cyclic alcohols can be observed. Because the mechanism of this reaction is not totally understood, deriving proposed mechanisms and constants such as activation energy can contribute to an overall understanding of what happens throughout the course of the reaction.

Using UV-vis spectrophotometry to study mixtures of cyclic alcohols and strong acids, it is possible to follow changes in concentration of carbocation intermediates within the course of a dehydration reaction because any peaks in absorbance observed from UV-vis analysis represent a conjugated system. Changes in concentration of the carbocation intermediates are directly related to the change in absorbance over time at a given maximum wavelength. Kinetic analysis of such reactions can provide supportive data for and increase the knowledge of mechanisms of dehydration reactions in strongly acidic media.

It is already known that the alcohol groups of sterols "[are] protonated in strongly acidic media and form carbocations." In the case of 4-methylcyclohexanol, the kinetics of the formation of an allylic carbocation can be examined due to the presence of a persistent intermediate at equilibrium as observed by UV-vis analysis. In particular, the activation energy
for the formation of the allylic carbocation intermediate resulting from the sulfuric acid
catalyzed dehydration of 4-methylcyclohexanol has not been published.

By obtaining the activation energy for the formation of the allylic carbocation, one more
piece to the puzzle of understanding basic acid catalyzed dehydration mechanisms can be
solved. Once this is done, further research can determine the entire mechanism of the reaction.
This will contribute to a general understanding of reaction mechanisms and can be used in
further applications such as organic synthesis.

The method used to obtain the activation energy for the dehydration of
4-methylcyclohexanol in concentrated sulfuric acid was derived from a method used to obtain
the activation energy of the decarboxylation of o-benzoylbenzoic acid in strongly acidic media
The treatment of data consisted of producing time-series absorbance spectra, identifying \( \lambda_{\text{max}} \)
for the intermediate of interest from the time-series spectra absorbance spectra, constructing
an absorbance time plot for the band at \( \lambda_{\text{max}} \), and finally carrying out standard kinetic analysis,
described below, to verify reaction order and calculate the rate constant (k). By repeating this
procedure at several temperatures, the activation energy was calculated.

Once an absorbance time plot has been made at each temperature, three methods of
kinetic analysis can be used to determine the rate constant. The first standard procedure
involves converting absorbance vs. time plots at the four specified temperatures to \( \ln(A_{\text{eq}}-A) \) vs.
time plots where \( A_{\text{eq}} \) is the absorbance at equilibrium and A is the absorbance at time t. The rate
constant is determined using the slope of the \( \ln(A_{\text{eq}}-A) \) vs. time plot as described in Chemistry:
Principles and Reactions\(^3\). The second method, the Guggenheim method\(^4\), is of use when an
equilibrium value, in this case \( A_{\text{eq}} \), is unknown. By plotting the \( \ln(A_{t+\Delta}-A_t) \) vs time, where \( A_t \) is the
absorbance at time t and \( A_{t+\Delta} \) is the absorbance at time t plus \( \Delta \), a constant time interval, a line
representing a \( \ln(A_{\text{eq}}-A) \) vs. time plot is derived. From this plot, the rate constant is determined
using the slope just as in the first method. The third method involves using the slope at the inflection point of the absorbance vs. time plots. The slope at the inflection point is equal to the rate at the time of inflection. The result of dividing this value by the absorbance at the time of inflection was proposed as an estimate of the rate constant. From rate constants at different temperatures, the activation energy is calculated from a plot of \( \ln k \) vs \( 1/T \) where \( k \) represents the rate constant at temperature \( T \) in Kelvin. Absorbance data obtained from the dehydration of 4-methylcyclohexanol in concentrated acid, are obtained at a constant acid concentration due to the variance of activation energy with acid concentration as shown by the dehydration of o-3,4-dimethylbenzoylbenzoic acid in strongly acidic media.

**Experimental Details**

Four dehydration reactions of 4-methylcyclohexanol in concentrated sulfuric acid were done at 35.0°C, 48.5°C, 60.0°C, and 66.8°C. All the independent variables of each reaction were kept constant with an exception to temperature. The solutions for the reaction mixtures were prepared as follows:

Approximately 150 mL of an 80.94 % w/w solution of \( \text{H}_2\text{SO}_4 \) was prepared. The solution was prepared directly from 97% weight \( \text{H}_2\text{SO}_4 \) stock solution (from Fischer Scientific) with a density of 1.84 g/mL. Reverse osmosis deionized water was used as the solvent. A 50 mL solution of 0.020 M 4-methylcyclohexanol in ethanol is prepared. The 98% pure cis/trans 4-methylcyclohexanol used had a density of 0.914 g/mL and was manufactured by SigmaAldrich.

The apparatus involved in the use of the UV-vis spectrophotometer included a temperature regulator, a water jacketed beaker as the reaction vessel, magnetic stirrer, a spectrophotometer and UV-vis software. The temperature regulator used was the NESLAB XE-111. The apparatus regulated temperature by a circulating water bath and insulated piping to
transfer the heated or cooled water through the water-jacketed reaction initiation chamber and
the water-jacketed spectrophotometer cell holder. Ocean Optics USB2000 UV-vis
spectrophotometer and accompanying software (OOiBase-32) was used for the experiment.

The procedure was determined as outlined by a similar kinetic experiment of sterols in
concentrated sulfuric acid\(^6\). Once the water bath was equilibrated at the desired temperature
and the UV-vis software was set to run, the reaction mixture was prepared. To prepare the
reaction mixture, 0.10 of 0.020 M 4-methylcyclohexanol was added to 10 mL of 80% w/w H\(_2\)SO\(_4\)
in the water-jacketed reaction initiation chamber with a magnetic stir bar for a final molarity of
0.0002. After a few seconds of stirring, a small aliquot of the reaction mixture was then
transferred into a quartz cuvette for analysis in the UV-vis spectrometer. The time between
initiation of reaction and first spectra taken was then recorded. Frequency of spectra taken was
as follows: for 0.0002 M 4-methylcyclohexanol reacting at or above 60.0°C, spectra was taken
every two minutes for forty minutes, then every five minutes for an hour, then every hour for
two hours. At lower temperatures, spectra were taken every 10 to 20 minutes over an extended
period of time until the reaction reaches equilibrium. Data were recorded during the course of
the reaction as absorbance in the wavelength range between 200nm and 500nm until
equilibrium was reached or sufficient time had lapsed. Data obtained were then imported into
Microsoft Excel for further treatment.

Results and Discussion

Time series data (such as Figure 1) or a graph containing a picture of recorded
absorbencies at a given time in the reaction offers much information. Each separate line on a
time series graph represents a different time. Time series data obtained from the UV-vis
absorbance spectra for the reaction of 4-methylcyclohexanol in concentrated sulfuric acid
reveals a prominent band at 305 nm (Figure 1) caused by an increase in absorbance with time.
This band is attributed to the presence of an allylic carbocation\(^7\). One can reason that the allylic carbocation intermediate is formed via the protonation of the alcohol, and consequent leaving of water (equation 1), producing a secondary carbocation. Following the formation of a double bond (equation 2), a hydride transfer produces an allylic carbocation absorbing at 305 nm (equation 3). This intermediate then reacts to make further rearrangements (equation 4).

\[
1) \quad \text{Methylcyclohexane} + \text{H}_2\text{SO}_4 \rightleftharpoons \text{allylic carbocation} + \text{H}_2\text{O} \quad (1)
\]

\[
2) \quad \text{allylic carbocation} \quad (2)
\]

\[
3) \quad \text{Methylcyclohexane} + \text{allylic carbocation} \quad \text{hydride transfer} \quad \text{methylcyclohexane} + \text{allylic carbocations} \quad 305 \text{ nm} \quad (3)
\]

\[
4) \quad \text{Further rearrangements} \quad (4)
\]

For this reason, a \(\lambda_{\text{max}}\) of 305 nm was selected for subsequent kinetic treatment. From the absorbance vs. time plot at 305nm (Figure 2), it can be deduced that the carbocation is at least a second step intermediate. An induction period in the earliest stages of reaction of the allylic carbocation indicates that it is preceded by the reaction of at least one other intermediate.

**Kinetic Analysis**

In the kinetic analysis of 4-methylcyclohexanol, absorbance vs time plots at four specified temperatures were first converted to \(\ln(A_{eq}^{-A})\) vs. time plots to determine a rate constant for the reaction. A second method involved using the Guggenheim method\(^4\). A third method used to determine the rate constant requires using the slope inflection point on an
absorbance vs. time plot relative to the absorbance value at the time of inflection. The average activation energy for the reaction was calculated from all methods except the inflection point method. Why this method is omitted in activation energy calculations is later discussed.

The major product of the reaction absorbs at 305 nm as can be seen in the time series absorbance spectra at 60.0°C (Figure 1). Time series absorbance spectra at different temperatures showed the same pattern. At each temperature, an absorbance vs. time plot with 305 nm as the $\lambda_{\text{max}}$ was made (Figure 2). From the figure it can be seen that both the reaction at 60.0°C and 66.8°C reached equilibrium within an hour. The reaction at 48.5°C neared equilibrium after 19 hours. The reaction at 35.0°C did not reach equilibrium even after 62 hours.

Figure 1

UV-Vis Spectra of .0002 M 4-Methylcyclohexanol in 80% w/w H$_2$SO$_4$ at 60.0°C

Time Series Spectra of 4-Methylcyclohexanol at 60.0°C (305nm)
Absorbance vs time at various temperatures

The flat area of the 60.0°C and 66.8°C plots indicate that the system is at equilibrium. At 60.0°C and 66.8°C, the equilibrium absorbance value is approximately 1.1 and 1.2 respectively. The plots at 35.0°C and 48.5°C did not reach equilibrium and therefore do not show the same trend.

Determination of Reaction Order

Before determining rate constants at any temperature, the reaction was determined to be first order. Upon plotting the ln(A_{eq} - A) vs. time, the reaction at each temperature showed a linear trend (Figure 3), indicating first order. Plots of 1/ (A_{eq} - A) vs time eliminate the possibility of the reaction being second order (Figures 4a, 4b, & 4c). These plots show an exponential trend rather than a linear trend; therefore the reaction is not second order.
First order plots of dehydration of 4-methylcyclohexanol at various temperatures

The second order plot of the reaction at 35°C does not follow a linear trend, therefore eliminating the classification of the allylic carbocation formed via the dehydration of 4-methylcyclohexanol as a second order reaction.
Second order analysis of dehydration of 4-methylcyclohexanol at 48.5°C
The second order plot of the reaction at 48.5°C clearly indicates that the reaction is not second order due to not following a linear trend.

Second order analysis of dehydration of 4-methylcyclohexanol at 66.8°C and 60.0°C
The second order plots of the reaction at high temperature clearly indicate that the reaction is not second order due to not following a linear trend.
To make a first order plot for the reaction at 35.0°C, the absorbance value at equilibrium had to be estimated because the reaction never did reach equilibrium. The estimated value used was 0.50 based on the trend of decreasing $A_{eq}$ values with a decrease in temperature (Table 1). At 48.5°C, the equilibrium value used (0.685) was estimated from the absorbance vs. time graph at $t=19$ hours, a point near equilibrium. The slope of the first order plot is used to calculate the rate constant at each temperature. Table 2 shows the equation for the first order plots at each temperature and the rate constant derived from it. At 35.0°C the rate constant value is approximately $1.83 \times 10^{-5}$ s$^{-1}$. At 48.5°C the rate constant value is approximately $1.27 \times 10^{-4}$ s$^{-1}$. At 60.0°C and 66.8°C, the rate constants are $9.28 \times 10^{-4}$ s$^{-1}$ and $9.55 \times 10^{-4}$ s$^{-1}$ respectively.

### Table 1

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Equilibrium Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>66.7</td>
<td>1.21</td>
</tr>
<tr>
<td>60.0</td>
<td>1.14</td>
</tr>
<tr>
<td>48.5</td>
<td>0.69</td>
</tr>
<tr>
<td>35.0</td>
<td>0.50</td>
</tr>
</tbody>
</table>

**Temperature vs. equilibrium absorbance value**

The equilibrium absorbance value of the reaction run at the given temperatures shows a trend in which the $A_{eq}$ is directly related to temperature.

### Table 2

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Equation of line</th>
<th>$k$ value (min$^{-1}$)</th>
<th>$k$ value (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.0</td>
<td>$y=-0.0011x+0.1405$</td>
<td>0.0011</td>
<td>$9.55 \times 10^{-4}$</td>
</tr>
<tr>
<td>48.5</td>
<td>$y=-0.0076x-0.5604$</td>
<td>0.0076</td>
<td>$9.28 \times 10^{-4}$</td>
</tr>
<tr>
<td>60.0</td>
<td>$y=-0.0554x-0.1361$</td>
<td>0.0554</td>
<td>$1.27 \times 10^{-4}$</td>
</tr>
<tr>
<td>66.8</td>
<td>$y=-0.0573x-0.2300$</td>
<td>0.0573</td>
<td>$1.83 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

**Rate constants determined from ln($A_{eq}$-$A$) vs time**

From the equation of the best fit line, the slope can be determined. The slope in units of min$^{-1}$ can be converted into s$^{-1}$ to give the rate constant value. The equation of the plot at each temperature with their respective rate constant values can be seen in the above table.
Rate constants for the reaction at each temperature were also obtained using the Guggenheim method. The Guggenheim method of determining rate constants can be used for any reaction that is known to be simple first-order, for which equilibrium values are unknown, and for which initial measurements at constant time increments of a physical property are known. Figure 5 shows a Guggenheim plot for the formation of an allylic carbocation via dehydration of 4-methylcyclohexanol at each temperature. Table 3 shows the equation for the plots at each temperature and the rate constant derived from it. The Guggenheim rate constants at 35.0°C, 48.5°C, 60.0°C, and 66.8°C are $1.83 \times 10^{-5}$ s$^{-1}$, $9.28 \times 10^{-4}$ s$^{-1}$, $8.95 \times 10^{-4}$ s$^{-1}$, and $8.68 \times 10^{-4}$ s$^{-1}$, respectively. The Guggenheim values correlate very well with the rate constant value determined from the plots of $\ln(A_{eq} - A)$ vs. time.

Figure 5

Guggenheim Estimation of Rate Constant

Guggenheim estimation of rate constant
Rate constants derived from Guggenheim method
The rate constant value for a Guggenheim estimation is determined from the negative slope of the graph. Because the units are in min\(^{-1}\), they must be converted into s\(^{-1}\) to give the rate constant value. The equation of the plot at each temperature with their respective rate constant values can be seen in the above table.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>Equation of line</th>
<th>k value (min(^{-1}))</th>
<th>k value (s(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.0</td>
<td>y=-0.0011x-1.9411</td>
<td>0.0011</td>
<td>9.55 x 10(^{-4})</td>
</tr>
<tr>
<td>48.5</td>
<td>y=-0.0070x-1.1680</td>
<td>0.0070</td>
<td>9.28 x 10(^{-4})</td>
</tr>
<tr>
<td>60.0</td>
<td>y=-0.0537x-0.2489</td>
<td>0.0537</td>
<td>1.27 x 10(^{-4})</td>
</tr>
<tr>
<td>66.8</td>
<td>y=-0.0521x-0.3299</td>
<td>0.0521</td>
<td>1.83 x 10(^{-5})</td>
</tr>
</tbody>
</table>

A third method, using the inflection point of the absorbance vs. time plot (Figure 2), was used to obtain rate constants for the reaction at 60.0°C and 66.8°C. At 60.0°C, the rate constant value determined from the inflection point is 4.31x10\(^{-4}\)s\(^{-1}\), a value approximately half the other rate constant values at that temperature. At 66.8°C, the rate constant was determined to be 20.4x10\(^{-4}\)s\(^{-1}\), a value approximately twice that of the other rate constant calculated at that temperature. Due to the inconsistency of data obtained from this method, rate constants derived from the inflection point were not used to calculate activation energy. In addition to inconsistent data, rate constants derived from inflection points could not be obtained from reactions at lower temperature because of the difficulty in identifying the inflection point.

The activation energy of the dehydration of 4-methylcyclohexanol was calculated using the rate constants at the four specified temperatures derived from both the ln(Aeq-A) vs. time plots and the Guggenheim method. The activation energy determined from the rate constants determined from the ln(Aeq-A) vs. time plots is 116 kJ mol\(^{-1}\) (Figure 6). The activation energy determined from rate constants derived via the Guggenheim method is 114 kJ mol\(^{-1}\) (Figure 7). All values for the experiment are summarized in Table 4.
Figure 6

Activation Energy of the formation of an allylic carbocation via dehydration of 4-methylcyclohexanol in 80% w/w sulfuric acid

The rate constant values used to calculate the activation energy were derived from the first order plot at the four temperatures of 35.0°C, 48.5°C, 60.0°C, and 66.8°C Celsius.

Figure 7

Activation Energy of the formation of an allylic carbocation via dehydration of 4-methylcyclohexanol in 80% w/w sulfuric acid
The rate constant values used to calculate the activation energy were derived using the Guggenheim method with data obtained at the four temperatures of 35.0°C, 48.5°C, 60.0°C, and 66.8°C.

Table 4

<table>
<thead>
<tr>
<th>Temperature Celsius</th>
<th>Temperature Kelvin</th>
<th>Ln(Aeq-A) vs time</th>
<th>Guggenheim</th>
<th>Inflection point</th>
<th>Activation energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>66.8</td>
<td>340</td>
<td>0.0573 min⁻¹</td>
<td>0.0521/min⁻¹</td>
<td>0.122 min⁻¹</td>
<td>From ln(Aeq-A) values 116 kJ mol⁻¹</td>
</tr>
<tr>
<td>60.0</td>
<td>333</td>
<td>9.55 x 10⁻⁴ s⁻¹</td>
<td>8.68 x 10⁻⁴ s⁻¹</td>
<td>20.4 x 10⁻⁴ s⁻¹</td>
<td></td>
</tr>
<tr>
<td>48.5</td>
<td>322</td>
<td>0.0557 min⁻¹</td>
<td>0.0537 min⁻¹</td>
<td>0.0258 min⁻¹</td>
<td>From Guggenheim values 114 kJ mol⁻¹</td>
</tr>
<tr>
<td>35.0</td>
<td>308</td>
<td>9.28 x 10⁻⁴ s⁻¹</td>
<td>8.95 x 10⁻⁴ s⁻¹</td>
<td>4.31 x 10⁻⁴ s⁻¹</td>
<td></td>
</tr>
</tbody>
</table>

Summary Table of rate constant values and activation energy for the formation of allylic carbocation via acid catalyzed dehydration of 4-methylcyclohexanol.

Conclusions and Summary

Although the complete mechanism of the dehydration of 4-methylcyclohexanol has not yet been determined, the activation energy for the first step in the reaction forming the allylic carbocation intermediate has been obtained. The value for this activation energy is 116 kJ mol⁻¹ by the ln(Aeq-A) vs. time method and 114 kJ mol⁻¹ by the Guggenheim method. Further research is to be done in determining the mechanism of the entire reaction, all intermediates, and activation energies for the various steps of the reaction.
References