Kinetic analysis of acid-catalyzed reaction of 1,4-cyclohexadiene

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Abstract

By analyzing the acid-catalyzed reaction of 1,4-cyclohexadiene in 96% sulfuric acid using UV-vis spectrophotometry, allylic and dienylic carbocations can be studied. This is possible because the lifetime of carbocations are extended when they are formed in acid solution. Reactions at temperatures of 11 °C, 15 °C, 20 °C , 30 °C, and 45 °C exhibited λ_{max} at around 257 nm, 321 nm, and 385 nm on UV-vis spectrophotometry. Furthermore, allylic cation intermediates exhibit maximum absorbances at 300 nm, dienylic carbocations at 380 nm, and 1,3-cyclohexadienes at 300 nm. Analysis of 1,4-cyclohexadiene in 96% sulfuric acid with UV-vis spectrophotometry shows maximum absorbances around each of these wavelengths. This reaction exhibits first-order reaction characteristics. Because of this, the Guggenheim method can be applied. Using the Guggenheim treatment on the spectral data at 385 nm gives observed rate constants of 0.1690 min^{-1} (0.9205), 0.2175 min^{-1} (0.9689), 0.3103 min^{-1} (0.9590), 0.4142 min^{-1} (0.8952), and 0.4682 min^{-1} (0.9832) for 11 °C, 15 °C, 20 °C , 30 °C, and 45 °C, and these rate constants can be used to calculate activation energy. From the temperature range, the reaction of 1,4-cyclohexadiene with 96% sulfuric acid to form a dienylic cation has an activation energy of 22 kJ/mol.

Introduction

An allylic cation has a maximum absorbance (λ_{max}) at 300 nm, a molar absorptivity around 10^4, and a strong symmetric band at the maximum.[1] Typically, allylic cations are short-lived, but when formed in sulfuric acid, the lifetime of the cation is extended and the cation is more stable.[2] A dienylic cation has very similar properties to an allylic cation; however, dienylic cations have a maximum absorbance at 380 nm.[3]

Figure 1 below is a proposed mechanism of the reaction. In step 1, one of the double bonds on the cyclohexadiene attacks the hydrogen ion to form a carbocation cyclohexene. This is most likely the rate determining step because the resulting carbocation is relatively unstable. In step 2a, a hydrogen shifts from the carbon adjacent to the double bond and the carbocation. This creates a more stable allylic carbocation due to resonance. In step 2b, a hydride transfer occurs from a hydrogen on the carbon between the two double bonds of the cyclohexadiene to the carbocation on the allylic cyclohexene, forming an allylic cyclodihexenyl carbocation and a cyclohexene.[4] In step 2b, a hydride transfer would occur from a hydrogen on the carbon between the two double bonds of the cyclohexadiene to the unstable carbocation on the cyclohexene.[4] If step 2a is favored, a larger absorbance would occur at 300 nm, while a larger absorbance would occur at 380 nm if step 2b or 2c are favored. In steps 3 and 4, an elimination reaction occurs on either the allylic carbocation cyclohexene from step 2a or the carbocation cyclohexene from step 1. This yields a 1,3-cyclohexadiene, which shows absorbance around 250 nm.

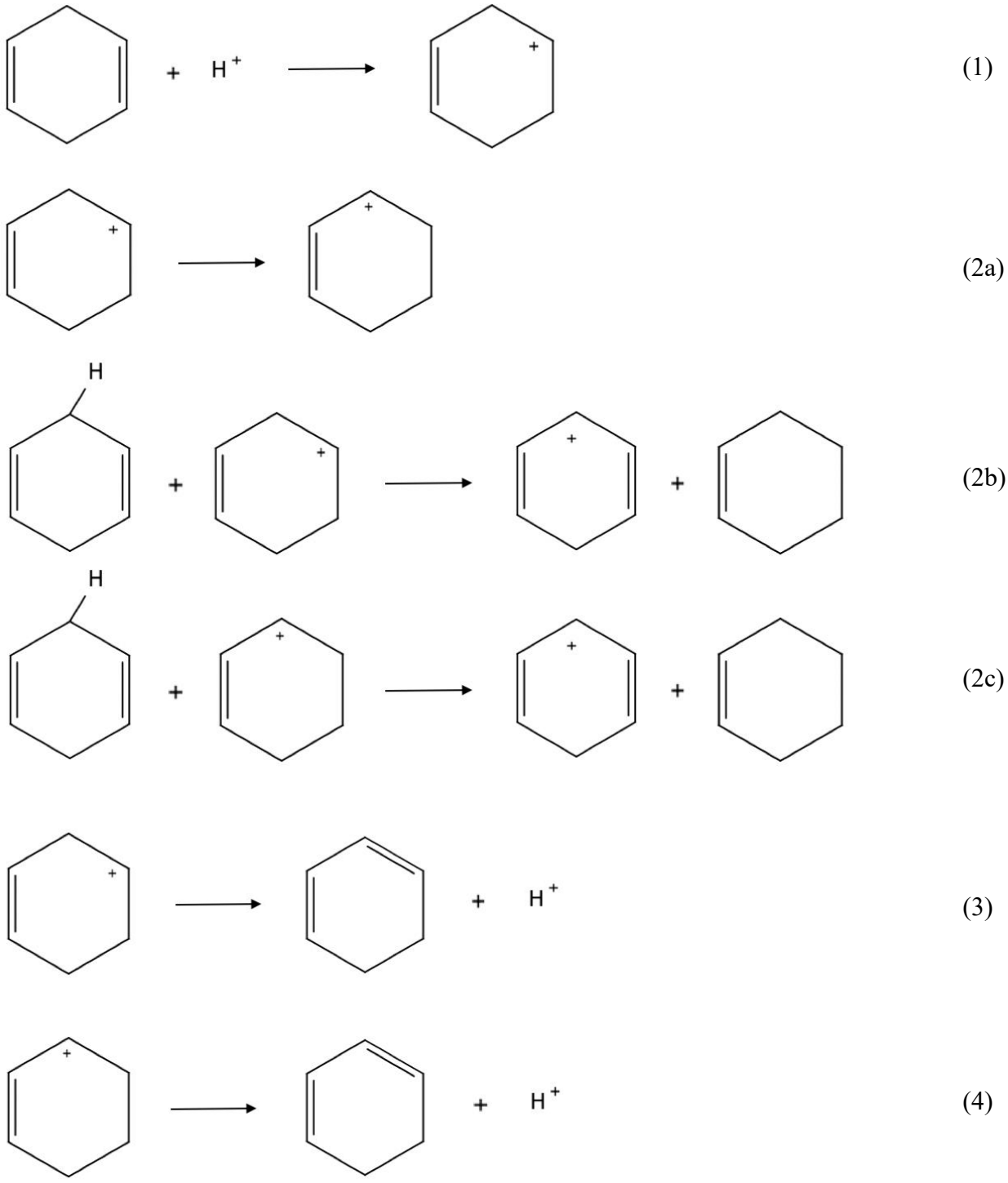

Figure 1. Proposed mechanism for the reaction of 1,4-cyclohexadiene is converted to either cyclohexenyl carbocation or cyclodihexenyl carbocation. Step 1 is the rate-determining step.

In this experiment, the goal is to see the effect of varying acidity and temperature on the spectra observed. In other words, what molecule is favored when the reaction is performed in various acidities and temperatures, and under which conditions is one favored over the other? Furthermore, the experiment will also show if either of these proposed mechanisms occur at all.

Experimental Method

Concentrations of H_2SO_4 in the range of 76-96% w/w were prepared from 96.00% w/w H_2SO_4 (Fischer Scientific, A300-212-2.5L) mixed with distilled water. 0.010 M 1,4-cyclohexadiene was prepared by diluting 97% w/w 1,4-cyclohexadiene (Aldrich 125415-5ML) in methanol (Aldrich, 176840025). A small amount of the diluted H_2SO_4 was added to each of two Starna 1-cm path quartz cuvettes (Starna Spectrosil, 1-Q-10-GL14C) using a pipet. A temperature control unit (NESLAB, EX-111) and a UV-visible spectrophotometer (Shimadzu, UV 2450) using UV probe software (UVProbe, v. 2.31) were used to record the absorbance spectra. The capped cuvettes were placed in the spectrophotometer. The reactions were initiated by injection of the studied species into a cuvette using a 0.500 mL GC syringe (Hamilton, 780). The cuvette was then removed, quickly inverted twice, then placed back into the instrument. The software recorded data until the end of the trial.

Results

Figure 2 shows a time-series absorbance spectra measured at 45 °C using 96.00% w/w H_2SO_4 as the catalyst. The absorbance values were recorded between 590 nm to 190 nm, with 120 seconds in between scans. In Figure 2, it is shown that there are maxima at around 300 nm and 380 nm, and shoulders around 200 nm and 250 nm.

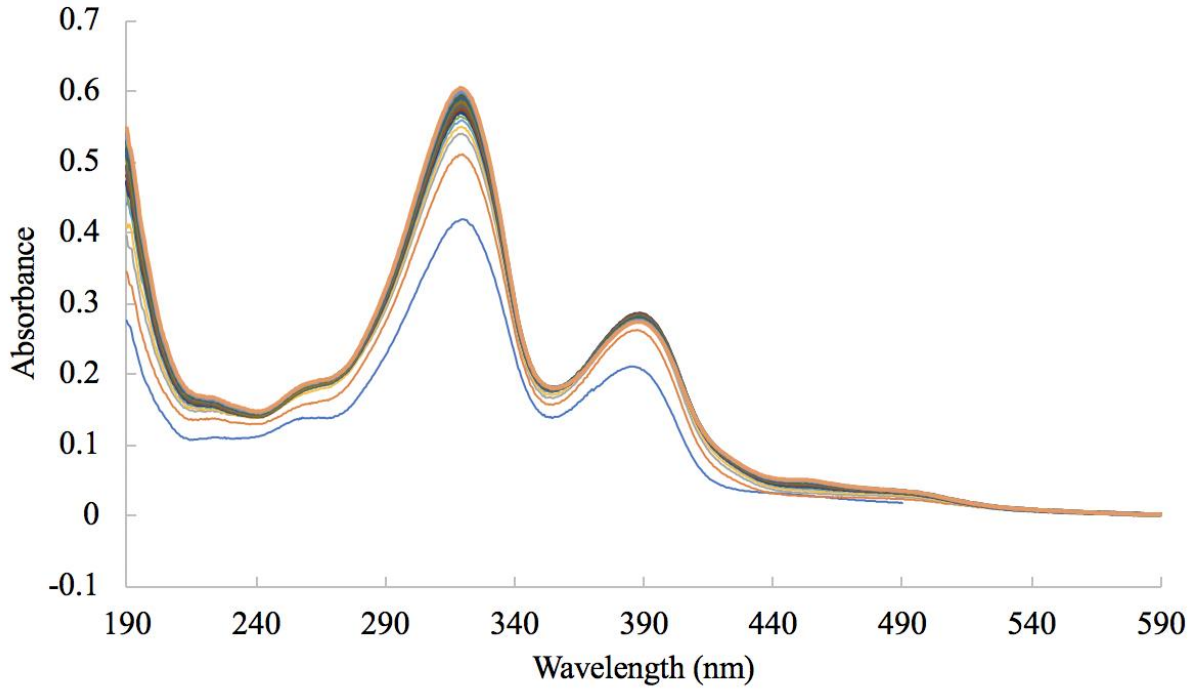

Figure 2. Absorbance spectra series of absorbance versus wavelength at 45 °C for the reaction of 1,4-cyclohexadiene and 96% sulfuric acid. Maximum absorbances are displayed at around 380 nm and 300 nm. There are also shoulders around 200 nm and 250 nm.

Figure 3 shows a time-series absorbance spectra measured at 11°C using 96.00% w/w H_2SO_4. The absorbance values were recorded between 590 nm to 190 nm, with 120 seconds in between scans. In Figure 3, it is shown that there is a maximum in absorbance at around 295 nm, a maximum at around 380 nm, a maximum around 250 nm, as well as a shoulder around 200 nm.

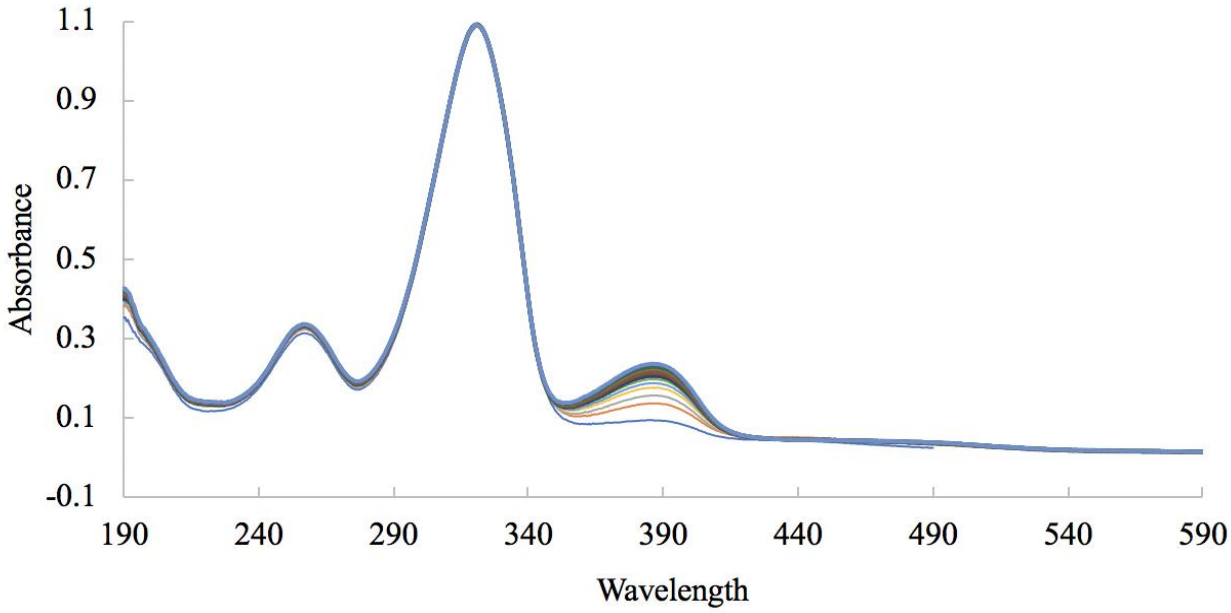

Figure 2. Absorbance spectra series of absorbance versus wavelength at 11 °C for the reaction of 1,4-cyclohexadiene and 96% sulfuric acid. Maximum absorbances are displayed at around 380 nm, 300 nm, and 250 nm. There is also a shoulder around 200 nm.

The maxima of interest lie at 257 nm, 321 nm, and 385 nm. Figures 4-6 are absorbance versus time plots using the absorbances at each wavelength over time. Five trials were taken at 11 °C, 20 °C, 15 °C, 30 °C, and 45 °C at 385 nm, and two trials were taken at 35 °C and 45 °C at 321 nm and 257 nm.

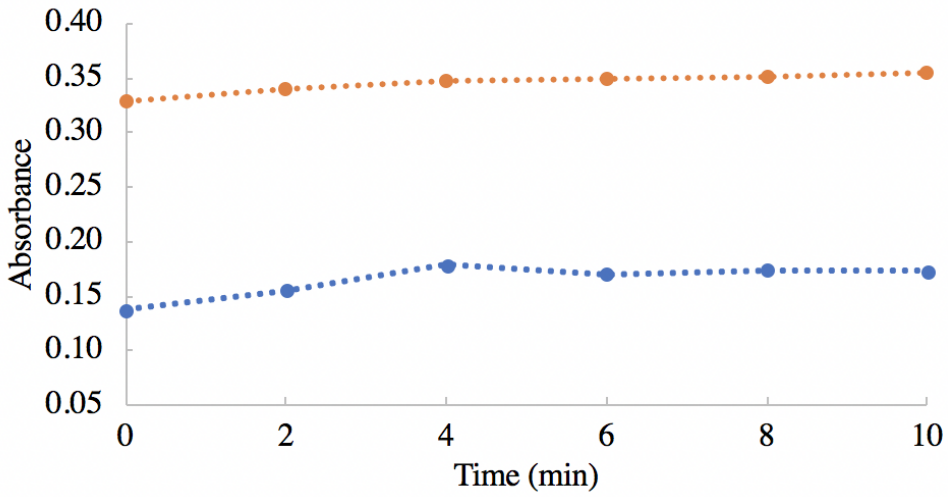

Figure 4. Absorbance versus time plot taken at 257 nm. The and blue dots correspond to trials at 30 °C and 45 °C respectively.

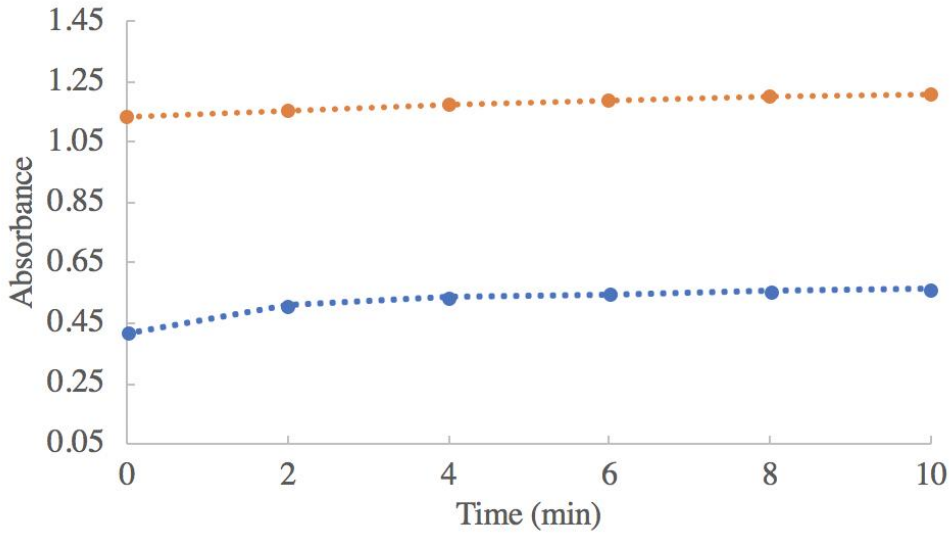

Figure 5. Absorbance versus time plot taken at 321 nm. The and blue dots correspond to trials at 30 °C and 45 °C respectively.

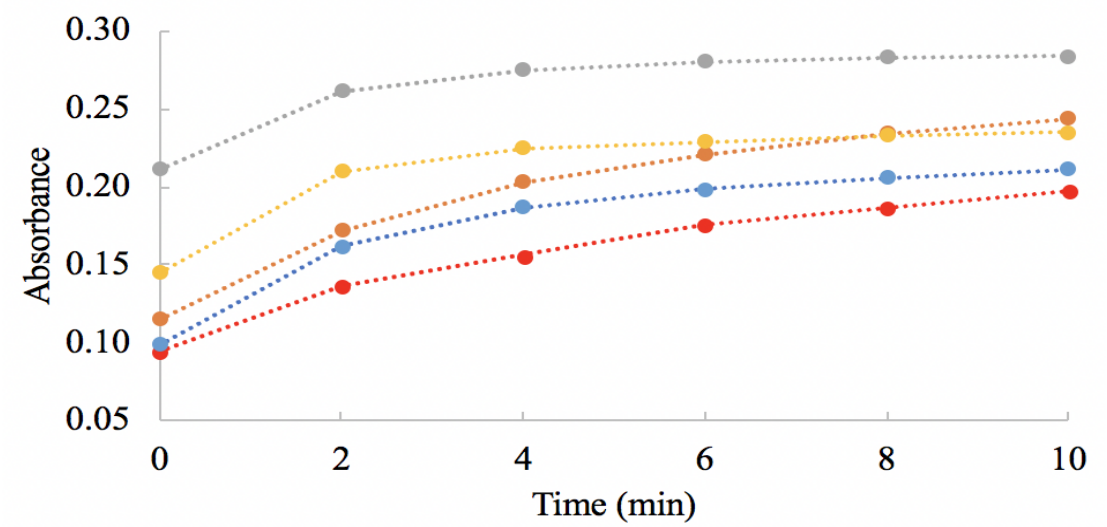

Figure 6. Absorbance versus time plot taken at 385 nm. The red, orange, blue, yellow, and gray dots correspond to trials at 11 °C, 15 °C, 20 °C, 30 °C, and 45 °C respectively.

Figures 7-9 are plots of ln(Abs) versus time using the Guggenheim method on the data from Figures 4-6. This is appropriate to apply since the reactions are first order.

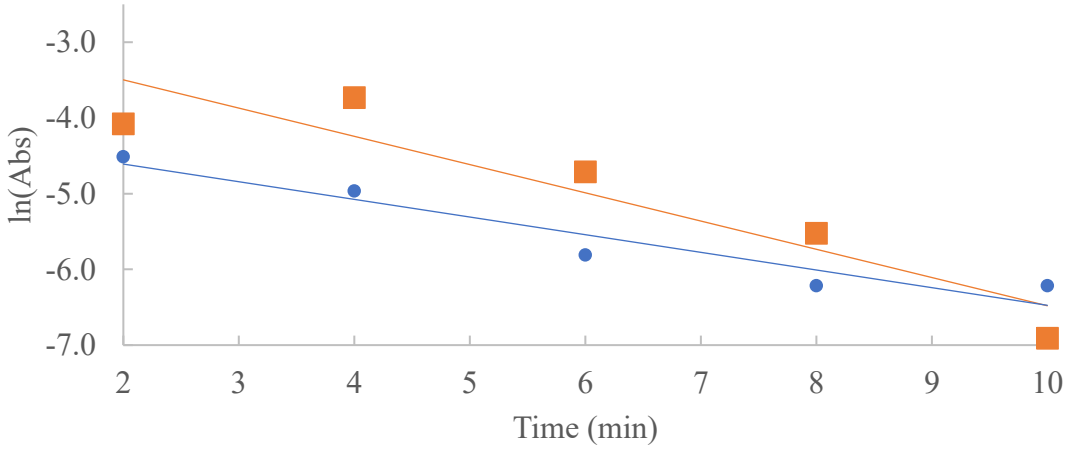

Figure 7. ln(Abs) versus time plot at 257 nm. The blue and orange dots correspond to trials at 30 °C and 45 °C respectively. Slopes and R^2 values were 0.3729 (0.8604) and 0.2331 (0.9140) for the orange and blue dots respectively.

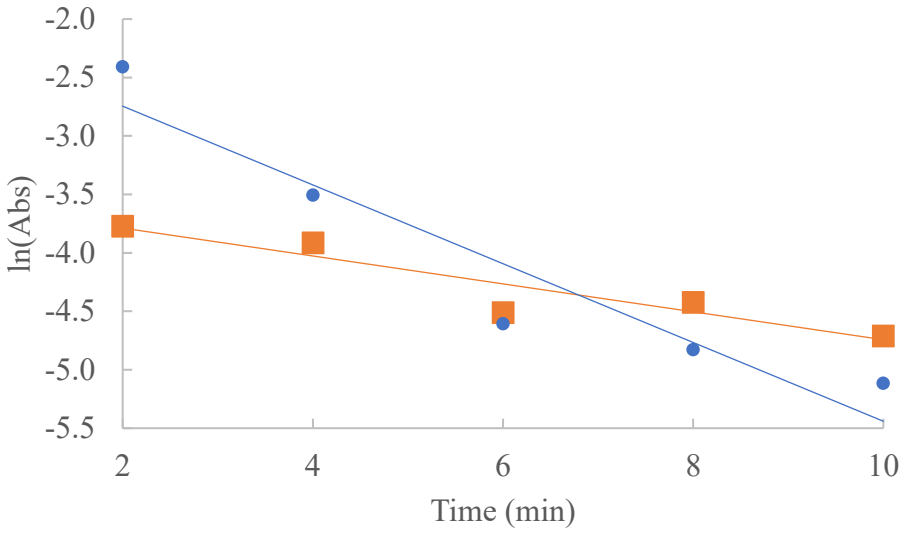

Figure 8. ln(Abs) versus time plot at 321 nm. The orange and blue dots correspond to trials at 30 °C and 45 °C respectively. Slopes and R^2 values were 0.1194 (0.8758) and 0.3369 (0.9020) for the orange and blue dots respectively.

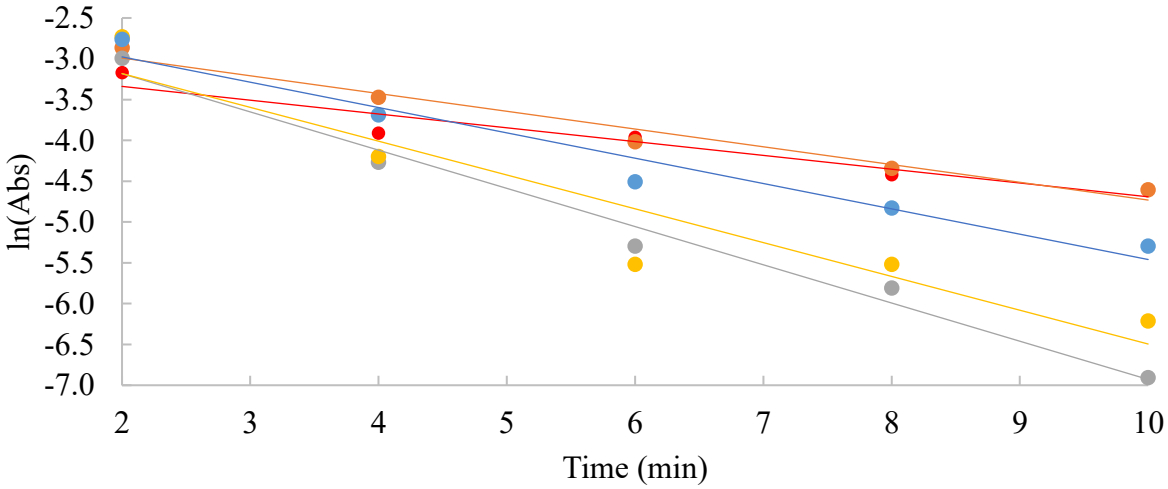

Figure 9. ln(Abs) versus time plot at 385 nm. The red, orange, blue, yellow, and gray dots correspond to trials at 11 °C, 15 °C, 20 °C, 30 °C, and 45 °C respectively. Slopes and R^2 values were 0.1690 (0.9205), 0.2175 (0.9689), 0.3103 (0.9590), 0.4142 (0.8952), and 0.4682 (0.9832) for the red, orange, blue, yellow, and gray dots respectively.

The absolute value of the slope from a line from the Guggenheim plot corresponds to the observed rate constant (k_{obs}) for that temperature. The rate constants for each line from Figures 7-9 were tabulated in Table 1.

Table 1. Observed rate constants for the reaction of 1,4-cyclohexadiene in 96% sulfuric acid at different temperatures and λ_{max} values.

temp (ºC)	257 nm k_{obs} (min^{-1})	321 nm k_{obs} (min^{-1})	385 nm k_{obs} (min^{-1})
11	-	-	0.1690
15	-	-	0.2175
20	-	-	0.3103
30	0.2331	0.1194	0.4142
45	0.3729	0.3369	0.4682

Figure 10 is a graphical representation of the data in Table 1. The observed rate constants at each λ_{max} were plotted versus temperature.

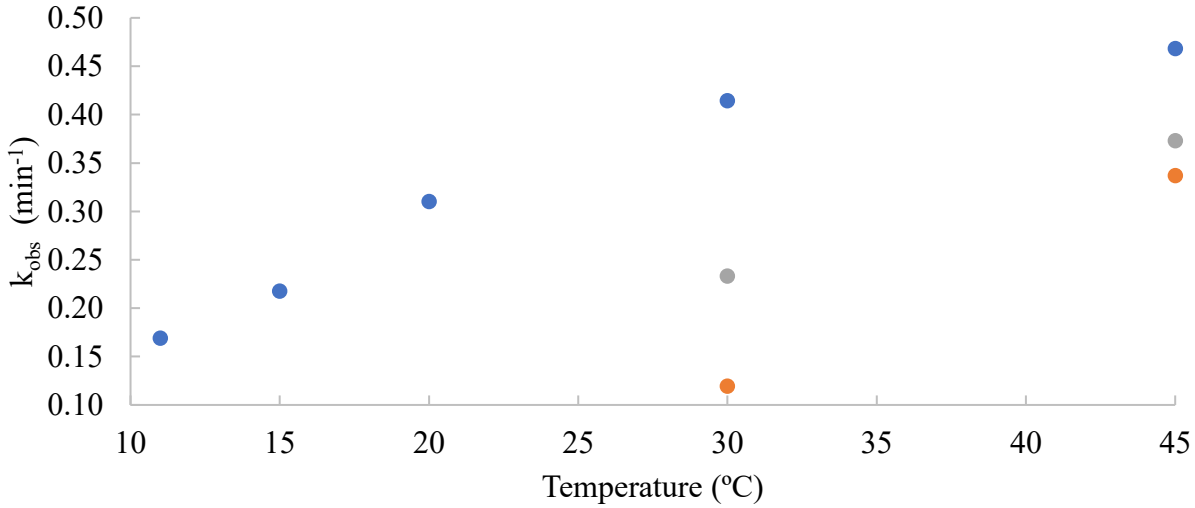

Figure 10. A plot of the observed rate constants versus temperature. The blue, gray, and orange dots correspond to λ_{max} values of 385 nm, 257 nm, and 321 nm respectively.

The $\ln(k_{obs})$ for each of the temperatures at 385 nm can be plotted against the inverse of the temperature in Kelvin. Table 2 tabulates these values.

Table 2. $\ln(k_{obs})$ values for 385 nm at each inverse of temperatures in Kelvin.

$Kelvin^{-1}$	385 nm $\ln(k_{obs})$
0.00352	-1.78
0.00347	-1.53
0.00341	-1.17
0.00330	-0.88
0.00314	-0.76

Figure 11 graphically represents the data in Table 2. A line of best fit can be applied, and the slope of the line can be used to calculate the activation energy of the reaction. This is also known as an Arrhenius plot. The activation energy for the formation of the dienylic cation at 385 nm can be calculated by multiplying the negative slope by R. E_A is 22 kJ/mol.

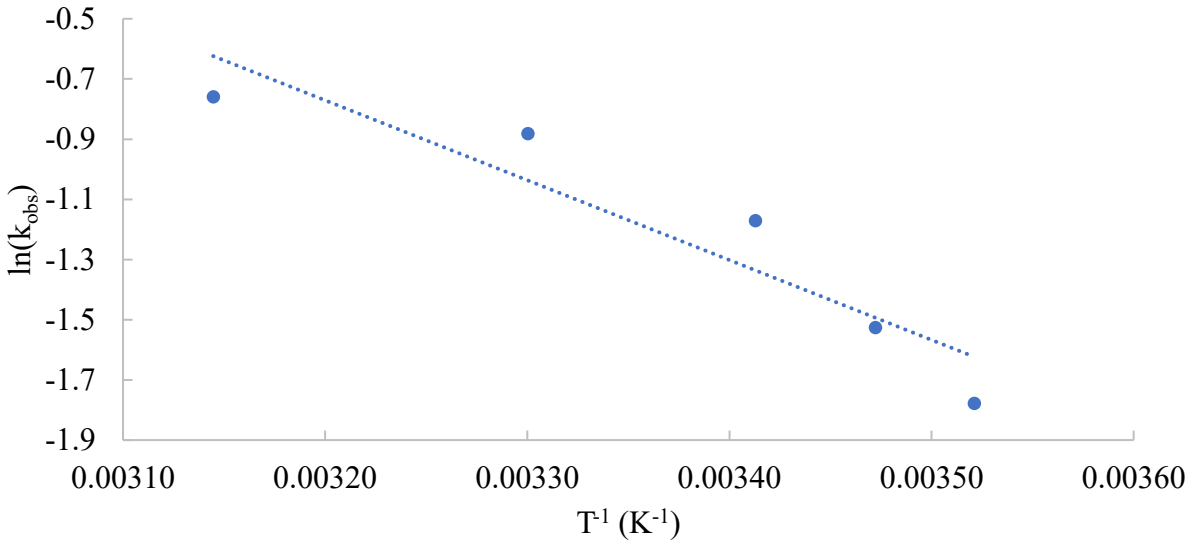

Figure 11. Arrhenius plot of the $\ln(k_{obs})$ versus the inverse of temperature in $Kelvin^{-1}$. The equation of the line of best fit is $\ln(k_{obs}) = -2654\ (T^{-1}) + 7.22$. R^2 for this plot is 0.8707. The activation energy is 22 kJ/mol for the formation of the dienylic cation at 385 nm.

Discussion and Conclusion

Strong symmetric maxima are found in both Figure 1 and Figure 2 around 300 nm, which is supported by the mechanism. This maximum is predicted by an allylic carbocation at 300 nm in the mechanism of Figure 1. The mechanism also predicts maxima around 380 nm and 250 nm for dienylic cations and 1,3-cyclohexadienes respectively, which are also present in Figure 2. As such, the mechanism predicted is supported by the observed spectra.

From the equation in Figure 11, the activation energy for the reaction of 1,4-cyclohexadiene and 96% sulfuric acid to form a dienylic cation is calculated to be 22 kJ/mol. This activation energy is within the range of activation energies of similar reactions.[5]

Experimental data collected by Chung is able to be compared to this data.[5] Chung investigated the reaction of 1-methyl-1,4-cyclohexadiene and 96% sulfuric acid at 45 °C. Due to the similarity in the starting reagent, Chung's results can be compared to Figure 2. Both spectra exhibit λ_{max} around 250 nm, 300 nm, and 380 nm. However, Chung's λ_{max} around 250 nm is shifted to the right compared to mine. This could be due to the methylation of his 1,3-cyclohexadiene products. Another difference is found in his λ_{max} at 300 nm. My maximum is very symmetrical compared to Chung's. This could be due to methylation. My mechanism only predicts one allylic carbocation species, while Chung's mechanism predicts four different allylic carbocation species due to methylation. Each of these allylic carbocations will absorb at slightly different wavelengths, causing Chung's maximum to be broader and less symmetrical. A final difference occurs at our λ_{max} around 300 nm. His absorbance at that wavelength decreases over time, while my spectra's absorbance increases over time. This could be due to Chung's allylic carbocation being consumed over time faster and in a larger quantity than my allylic carbocation species. Further research could be done to compare the effects of methylation on this reaction.

References

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