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# Acid-catalyzed Disproportionation of 3 and 4-Methylcyclohexene in Various Sulfuric Acid Concentrations

## **Cover Page Footnote**

I would like to extend my thanks to Dr. Menzmer for his assistance and guidance throughout the project, my fellow research colleagues for the assistance in preparing the various concentrations of sulfuric acid and Southern Adventist University's Department of Chemistry for providing me with such a privileged opportunity to conduct research to further expand my knowledge and understanding in the field of chemistry.

# Acid-catalyzed Disproportionation of 3 and 4-Methylcyclohexene in Various Sulfuric Acid Concentrations

*Daniel A. Salazar*

**Abstract:** Experiments were conducted to verify a mechanism for the formation of cyclohexenyl cations from 3 and 4-methylcyclohexenes. Three concentrations of sulfuric acid were subjected to various concentrations of sulfuric acid: 80, 89 and 96% (w/w). For 3-methylcyclohexene, at the 89 and 96% concentrations, the reaction did not occur. The results showed that the region for experimentation is between 78 and 83% (w/w) sulfuric acid. For 4-methylcyclohexene, all but the highest concentration was successful in evaluating the spectra for possible cation formations. These small-scale experiments along with the data collected will hopefully lead to future research to gain a better understanding of the mechanism of cyclohexenyl cations.

Considerable research has been done in order to gain a better understanding of the mechanism for formation of cycloalkenyl cations from the protonation of cycloalkenes, specifically focusing on the intermediates formed throughout the reaction as shown in Figure 1. Previous work done by Cummings and Menzmer indicate that cycloalkenyl cations can be formed through the protonation of alkylated cycloalkenes.<sup>1</sup>

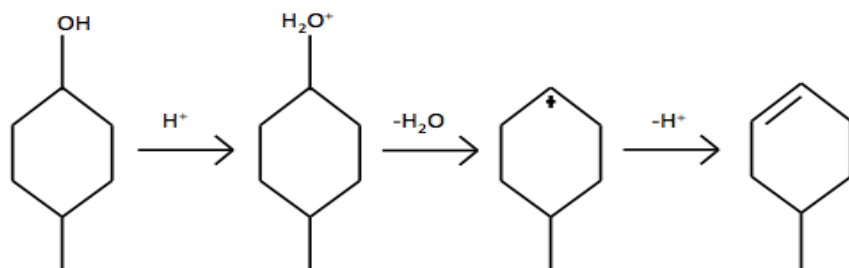


Figure 1: The formation of 4-methylcyclohexene from the protonation and hydride abstraction from the 4-methylcyclohexanol.

When the alcohol is placed in an acidic environment, it will take a proton from the acid. The alcohol now has formed water, which leaves, forming a cyclohexanyl cation. This cation can undergo various rearrangements and after an elimination step, yield three possible cyclohexenes: 1, 3 and 4-methylcyclohexene as seen in Figure 2, reaction 1.

Two methylcyclohexene compounds were evaluated in this project: 3 and 4-methylcyclohexene. The basic understanding of the mechanism is that when 3-methylcyclohexene accepts a proton from an acid, the double bond between carbons 1 and 2 is broken, yielding a cyclohexenyl cation. The carbocation can either a) undergo rearrangements, as

seen in reaction 1 in Figure 2, or b) abstract a hydride adjacent to an  $sp^2$  carbon in a cycloalkene forming a cyclohexenyl cation, as reaction 2 from Figure 2 illustrates.

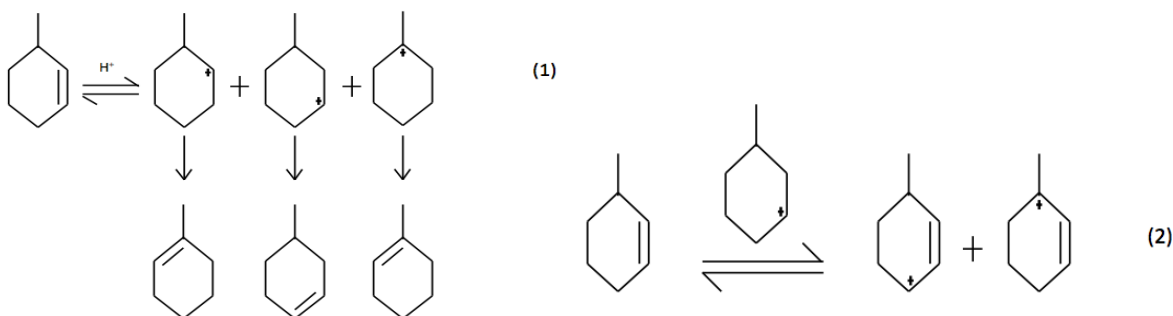


Figure 2: A simplified mechanism for 3-methylcyclohexene, showing the various cyclohexenyl cations formed.

A similar mechanism occurs for a 4-methylcyclohexene compound. Once again, just like with the 3-methylcyclohexene, the cycloalkene reacts with a cyclohexenyl cation, formed by a protonation of an alkene, forming one or more cyclohexenyl cation, as seen in equation 4 from Figure 3.

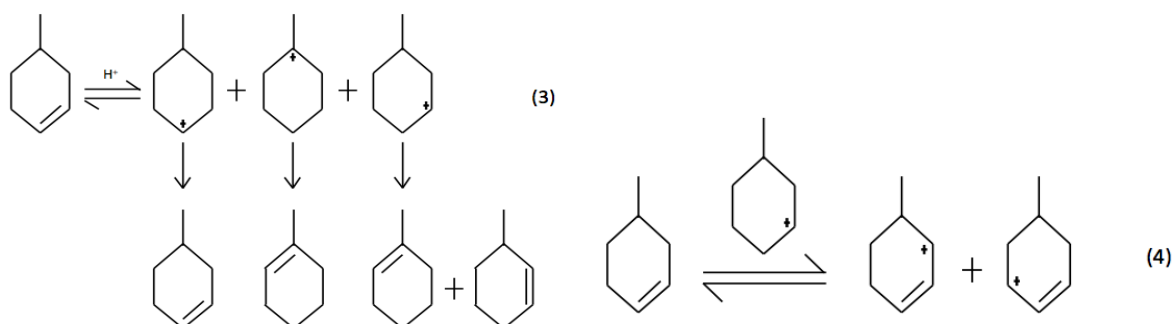


Figure 3: A basic mechanism for 4-methylcyclohexene.

Previous research done by Deno *et al.* on various alkenyl carbocations demonstrated that the wavelengths of the cyclohexenyl cations are found at approximately 300 nm, thus allowing for UV-vis detection. This is observed because cycloalkenes absorb photons in this region, exhibiting  $\pi \rightarrow \pi^*$  and thus can be detected.<sup>2</sup> Further work conducted by Deno *et al.* show similar results with cycloalkenyl cations. When compared to cyclopentenyl cations, cyclohexenyl cations have a great rate of exchange of protons (including deuterium). This means that carbocation stability is affected by the position of the methyl group(s) and is inversely proportional to proton abstraction.<sup>3</sup> Both of Deno *et al.*'s research concur with the results collected in this investigation and will be discussed in more detail in the Results and Discussion sections.

The purpose of this research is to determine for what range of acidity the methylated cycloalkenes generate a cycloalkenyl cation. Both of the compounds were reacted with three

different sulfuric acid concentrations and were analyzed, via UV-vis spectrophotometry, for confirmation of the maximum wavelength ( $\lambda_{\text{max}}$ ) of the various cycloalkenyl cations formed.

### Experimental Design

Various sulfuric acid concentrations were prepared by dilution with water, using a 96% (w/w) sulfuric acid from Sigma-Aldrich (#320501-2.5L). For this research, 80, 89 and 96% (w/w)  $\text{H}_2\text{SO}_4$  was selected. The methycycloalkene solutions (0.010 M) were each prepared by weighing and dilution in methanol (Aldrich #322415-2L) into a 100ml volumetric flask. Using a *Shimadzu UV-2450* UV-Vis Spectrophotometer, two quartz cells were placed inside the spectrophotometer: one was a reference and the other the experimental. The temperature was kept constant for all experimental runs at  $57.0^\circ\text{C}$  via a *Neslab EX-111* Circulating Temperature Control Water Bath in order to achieve the results quicker.

The spectrophotometer was connected to the computer and the UVProbe software was used for the analysis of the compounds. The spectrophotometer parameters were set to 200-600 nm wavelength range with fast acquisition, wide slit and repeat scans with 120 second intervals between scans. After the settings were completed and instrument warmed-up, a baseline correct process was done with both cuvette holders empty and cell compartment closed.

After the baseline correct, approximately 3.5 mL of the  $\text{H}_2\text{SO}_4$  (using a graduated Mohr type pipet) was added to both cells, capped and placed in their designated cuvette holders in the spectrophotometer and allowed to reach thermal equilibrium ( $\sim 10$  min). Then an autozero process was conducted with both cells in the spectrophotometer and at thermal equilibrium. The cycloalkene substrate was injected only into the experimental cell using a 50  $\mu\text{L}$  Hamilton syringe and then the data was collected.

### Results

The 3-methylcyclohexene substrate at the lowest concentration of  $\text{H}_2\text{SO}_4$  (80% w/w) showed significant evidence in the spectrum that a cyclohexenyl intermediate was present. Yet in the spectra, shown in Figure 4, there was a large noticeable gap about mid-way through the total experimental run. This gap is most likely due to a temporary increase in the rate of the reaction. Also notice how there are additional peaks near the 400 and 500 nm region. This research did not focus specifically on these areas and they are not discussed in further detail.

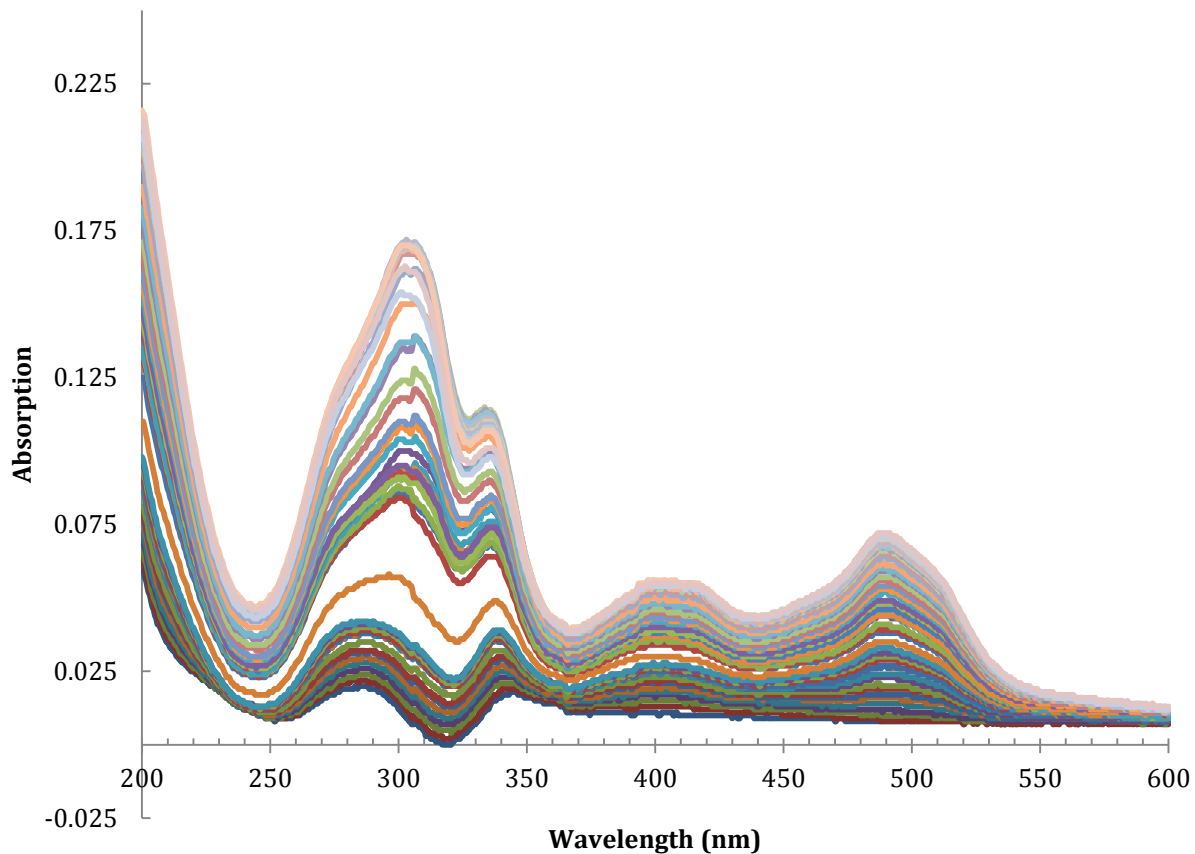


Figure 4: The UV-vis spectra of the 3-methylcyclohexene compound in 80% (w/w) H<sub>2</sub>SO<sub>4</sub>.

However, once the 3-methylcyclohexene was tested at the 89% and 96% (w/w) sulfuric acid concentration, the spectra produced no evidence of a reaction, as seen in Figure 5.

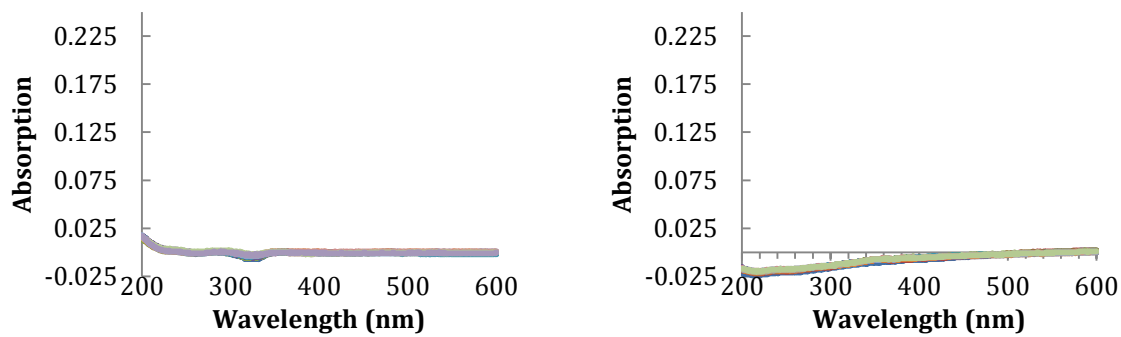


Figure 5: The Spectra for the 3-methylcyclohexene compound in 89%, on the left, and 96%, on the right, (w/w) H<sub>2</sub>SO<sub>4</sub>.

An experiment using an 83% (w/w) sulfuric acid concentration was conducted and found to show slight evidence for a reaction, but the reaction was essentially complete after about 10 runs, as seen in Figure 6.

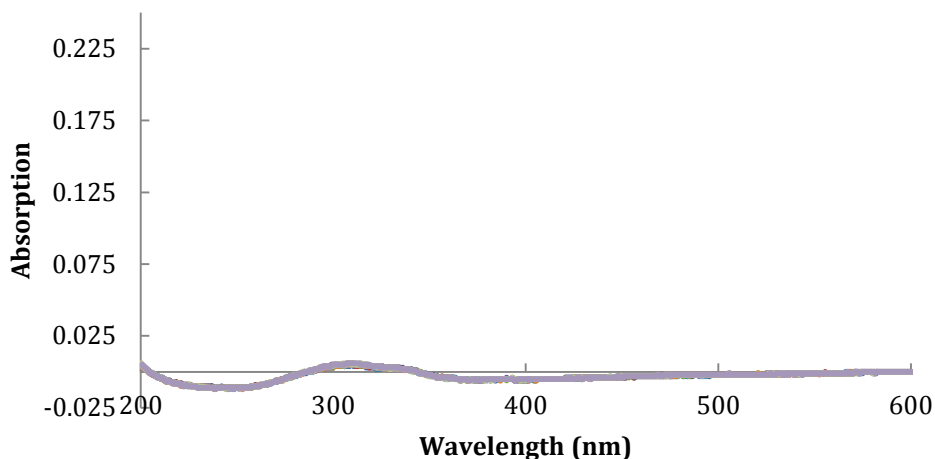


Figure 6: The spectrum for the 3-methylcyclohexene compound at 83% (w/w) H<sub>2</sub>SO<sub>4</sub>.

Two additional UV-vis spectrophotometry tests were run using 72% and 78% (w/w) H<sub>2</sub>SO<sub>4</sub>. At the 72% (w/w) concentration, the spectrum showed no reaction as seen in Figure 7.

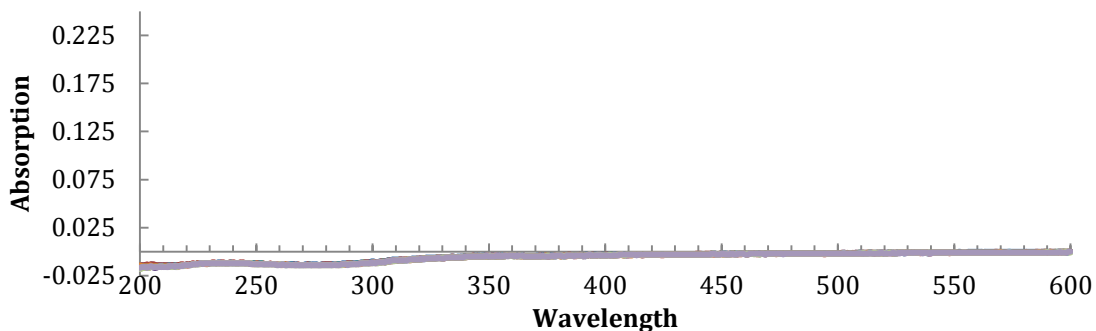


Figure 7: The spectrum for the 3-methylcyclohexene compound at 72% (w/w) H<sub>2</sub>SO<sub>4</sub>, which shows that no reaction occurred.

The 78% sulfuric acid showed a more similar result obtained from the 80% as seen in Figure 8.

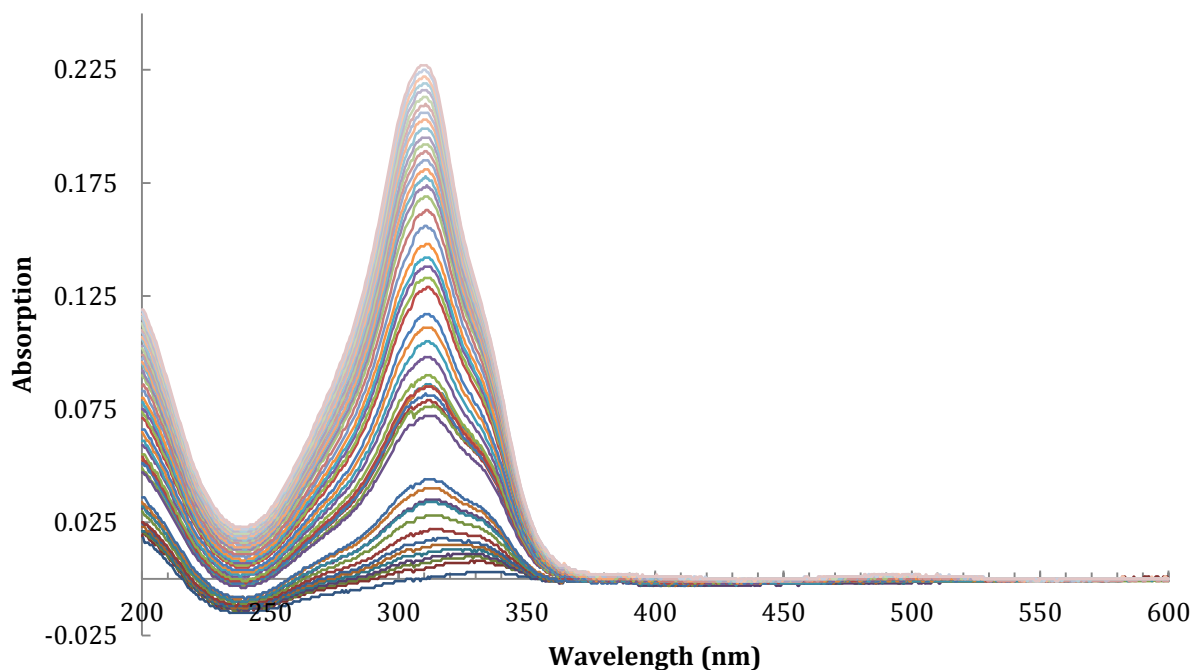


Figure 8: A spectra for the 78% sulfuric acid, which looks similar to the 80%.

On the other hand, the 4-methylcyclohexene has also presented some very interesting results. At the lowest concentration of sulfuric acid (80%), seen on Figure 9, the reaction was essentially complete after the first run.

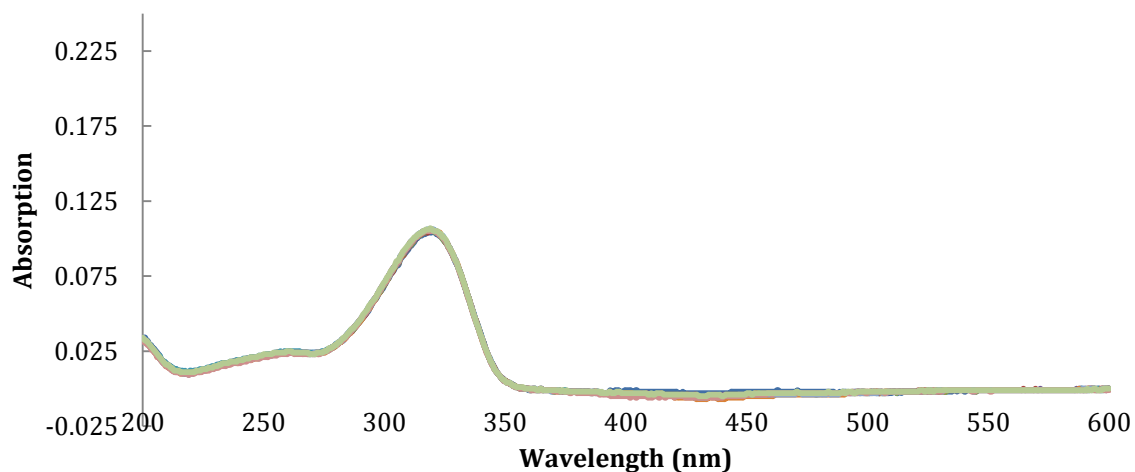


Figure 9: The spectrum for a 4-methylcyclohexene compound in 80% (w/w)  $\text{H}_2\text{SO}_4$

A small peak did appear around the 300 nm range, which confirms that the substrate had formed a cyclohexenyl cation. It was apparent that the reaction had already reached equilibrium and did not show much variance in the spectra over a 20 min. interval.

The second concentration, 89% (w/w) sulfuric acid, was conducted and displayed an increase overtime (seen in Figure 10). This was an unexpected result, considering that the 3-



methylcyclohexene compound did not absorb above 83% (w/w) sulfuric acid. This spectrum indicates that for a 4-methylcyclohexene compound, an acidity below 83% is not effective in analyzing a reaction.

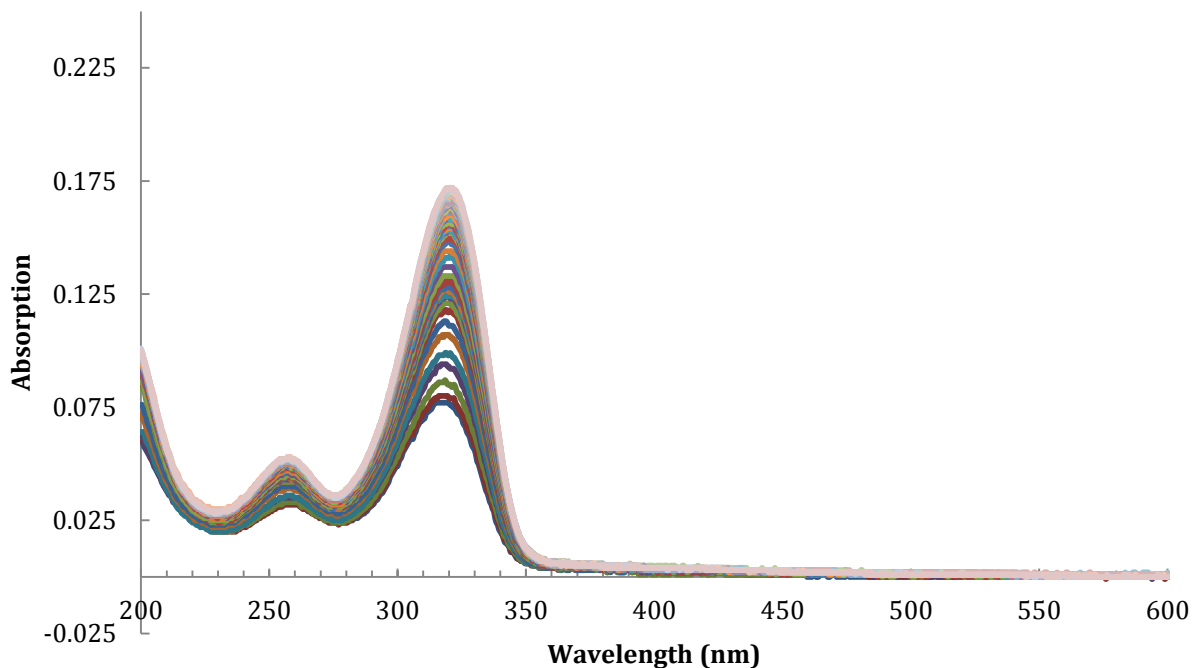


Figure 10: The spectrum for a 4-methylcyclohexene at 89% (w/w)  $\text{H}_2\text{SO}_4$ .

The final test for the 4-methylcyclohexene compound was conducted with the 96% (w/w) sulfuric acid concentration. As shown in Figure 11, this spectrum shows some similarities to the 96% sulfuric acid for the 3-methylcyclohexene compound in that once again, there was no evidence of an observed reaction. The results show that between 80% and 96% (w/w) sulfuric acid, the 4-methylcyclohexene can be observed. Further analyses can help determine which cyclohexenyl cation is formed.

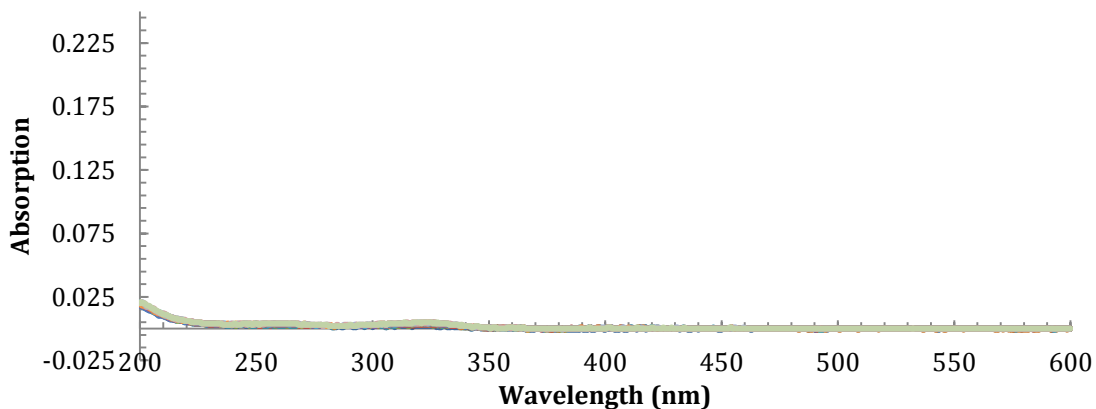


Figure 11: The spectrum for 4-methylcyclohexene at 96% (w/w)  $\text{H}_2\text{SO}_4$ .

## Discussion & Conclusion

Through the analysis of both compounds, one can see several general trends. The first is that for both cyclohexene compounds, there was a “flat line” displayed with the 96% (w/w) sulfuric acid concentration, as shown in Figure 12. This indicates that there is no reaction occurring and there is not much else that can be said at this point. More research would have to be conducted to determine why both of these compounds simply won't react at the highest concentration of sulfuric acid used.

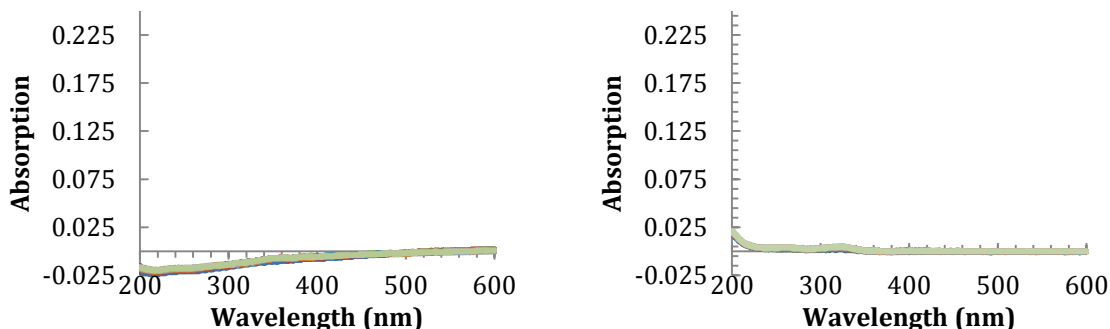


Figure 12: The spectra for 3 and 4-methylcyclohexene at 96% (w/w)  $\text{H}_2\text{SO}_4$ .

Another trend that might be noticeable is that the graphs of both compounds point to an inverse relationship with the acid. For the 3-methylcyclohexene, its region of acidity is between 78 and 83% (w/w) sulfuric acid, while the 4-methylcyclohexene is higher at the 89% range. Note the two graphs below in Figure 13.

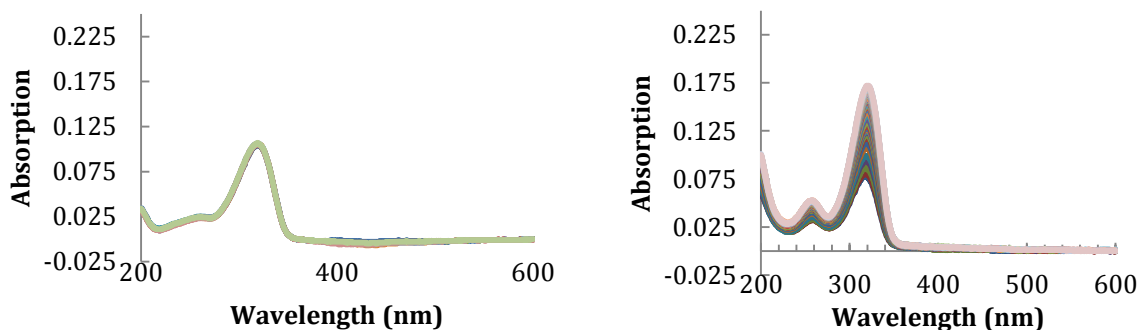


Figure 13: Comparing the spectra between 80 and 89% (w/w)  $\text{H}_2\text{SO}_4$  for 4-methylcyclohexene.

The spectrum at 80% sulfuric acid was essentially completed after the first run and there was no continual growth in the rate of the reaction. One can still identify the broad peak around 300 nm, which does indicate a cyclohexenyl cation intermediate. However, it is not the same on the spectrum at 89% sulfuric acid. Here, the reaction increases with every run, making it clear that a cyclohexenyl cation intermediate is detected. Also, a second smaller peak emerges at

around the 260 nm region. This is attributed to a cyclohexadiene, which is known to absorb in this region.

For the 3-methylcyclohexene, the concentration must be between 78% and 83% (w/w) sulfuric acid. Any concentration above or below this range does not allow for a complete analysis of the compound through UV-vis spectrophotometry. Yet, notice the gaps in between the runs in the 78 and 80% spectra shown in Figure 14.

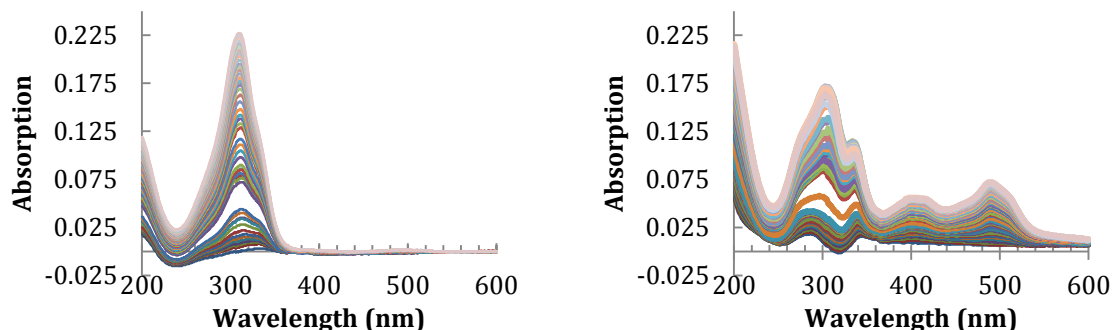


Figure 14: The gaps shown in the 78 and 80% sulfuric acid spectra could indicate a temporary increase in the reaction speed.

This was truly a remarkable find because it was something that had not been observed before. No literature cited in this paper mentioned anything on a gap in the spectra. A speculation could be that the acid formed a cyclohexenyl cation that allows the reaction to occur at a faster rate for a brief period of time before slowing down again. This observation indicates the need for further research, including testing greater variety of acid concentrations, both lower and in-between those used in this project. It may also be advantageous to include analyzing the 1-methylcyclohexene compound and comparing its results to the other two compounds.

## References

1. Cummings, C; Menzmer, M. *CHEM 497*. "Cyclohexenyl carbocation synthesis via the acid-catalyzed dehydration of cyclohexanol and the protonation of cyclohexene mechanisms." SAU, 2013.
2. Deno, N.C.; Bollinger, J.; Friedman, N.; Hafer, K.; Hodge, J.D.; Houser, J.J. "Carbonium Ions XIII: Ultraviolet Spectra and Thermodynamic Stabilities of Cycloalkenyl and Linear Alkenyl Cations." *JACS* 85. 1963.
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