Development of a method for evaluating absorption spectra irregularities: 3-methylcyclopentanol and 4-methylcyclohexanol

Development of a method for evaluating absorption spectra irregularities: 3-methylcyclopentanol and 4-methylcyclohexanol

Charlotte Ishikawa

Abstract: Accurate rate constant values are critical for understanding chemical reaction pathways involving cyclopentenyl and cyclohexenyl cation intermediates. One approach for determining this essential kinetic information follows the time rate of change of such cations using UV-visible spectrophotometry. However, the obtained absorption spectra often show asymmetric irregularities such as shoulders due to interfering side reactions. The aim of this exploratory study was to develop a method of interpreting UV-visible spectra that provides accurate rate constant values in addition to clarifying the cause of signal abnormalities. In this investigation, changes in spectra of the cation intermediates were followed over the course of time using UV-visible spectrophotometry for acid-catalyzed reactions for 3-methylcyclopentanol and 4-methylcyclohexanol. Guggenheim treatment of spectral data were then applied to obtain rate constant values at intervals of wavelength across the range of the spectra. From analysis of 3-methylcyclopentanol, the observed rate constants were highly accurate over a range of wavelengths (wavelengths 285 nm to 300 nm): the actual rate constant values remained constant at around 0.099 s^{-1}, associated with coefficients of determination that were consistently high at 0.99. Hence, consistent and quality observed rate constants were obtained in the region of the absorbance spectra farthest away from asymmetric anomaly, not just at the maximum wavelength. The data from analysis of 4-methylcyclohexanol supports the aforementioned conclusion but goes beyond 3-methylcyclopentanol's analysis by providing support for the nature of the mechanism and relationship between two intermediates. It is anticipated that the developed method has potential for resolving more complex cases of time-series absorbance spectra showing deviations stemming from reactions involving cyclopentenyl and cyclohexenyl intermediates.

Introduction

In understanding the kinetics of acid-catalyzed reactions of cyclic alcohols and alkenes, a process of interest is the formation of aliphatic alkenyl cation intermediates in the presence of concentrated sulfuric acid. The mechanism described in Figure 1 describes the formation of such cation intermediates:
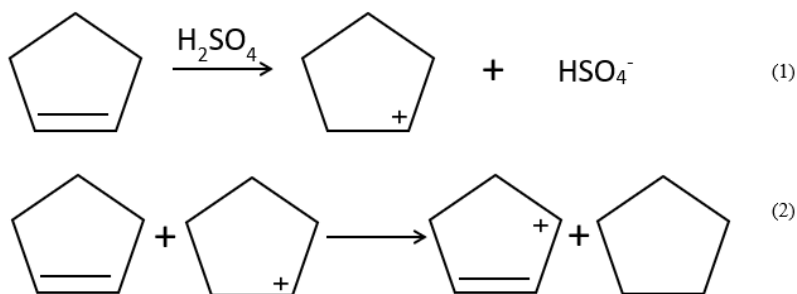
Figure 1. Mechanism for formation of aliphatic alkenyl cation from cyclopentene in the presence of concentrated sulfuric acid.

In the first step, the cyclopentene gives a cyclic alkanyl carbocation after protonation. This cyclic alkanyl carbocation then reacts with the original cyclic structure in mixture, performing a hydride transfer to produce an alkenylyl carbocation and cycloalkane.[1] This disproportion step yields two stoichiometrically equal products of alkenyl carbocation and cycloalkane.[1] While carbocation species are known to have lifetimes on the order of microseconds,[2] alkenyl carbocations in sulfuric acid exist in species for at least an hour,[3] making alkenyl carbocations useful in analysis with UV-VIS scanning spectrophotometer.

Alkenyl carbocations show absorbance spectra characterized by a single, relatively symmetric peak: a slow formation signal at the 300 nm region and a monotonic increase from 240 to 220 nm.[4] Their maximum wavelength ranges from 275 to 320 nm and the molar absorption coefficient averages about 10 to the fourth power.[4]

In practice, the presence of shoulders, additional peaks, or asymmetry is a persistent issue faced in kinetic analysis of the cyclic absorbing species. One idea behind these unexpected deviations is that the overlap of the absorbance bands has kinetic influence because the signals are not resolved. Hence, the absorbance band interference potentially contributes to irregularities in absorbance-time plots. To address this problem, kinetic analysis is typically aided by programs such as the COPASI software package utilizing the Levenberg-Marquardt algorithm, which obtains rate constants from nonlinear time-course data with minimal errors.[5] However, this procedure is not compatible with the available lab software,[6,7] and in general, the influence of overlapping absorbance bands remains mainly unaddressed across previous studies. Looking at the methods by prior students,[6,7] a novel approach proposed is to develop a method based on kinetic analysis at multiple wavelengths across the absorption spectra. By plotting absorbance vs time curves at several different wavelengths associated with the same absorbance band, kinetic treatments of this data could obtain observed rate constants. If this method resolves the irregularities in absorbance vs time plots by approaching a constant value, then observed rate constant vs wavelength plots derived from the absorbance vs time plots would clarify whether there is influence of overlapping bands on the rate constant and whether the overlapping interference or some other variable is the cause of the signal abnormalities.

For this investigation, the reagent chosen to develop the method is

3-methylcyclopentanol after considering the low complexity of the typical absorption spectra, the little deviation from the ideal graphical representation, and the speed of reaction.[6] The mechanism in Figure 2 illustrates the reaction progression:
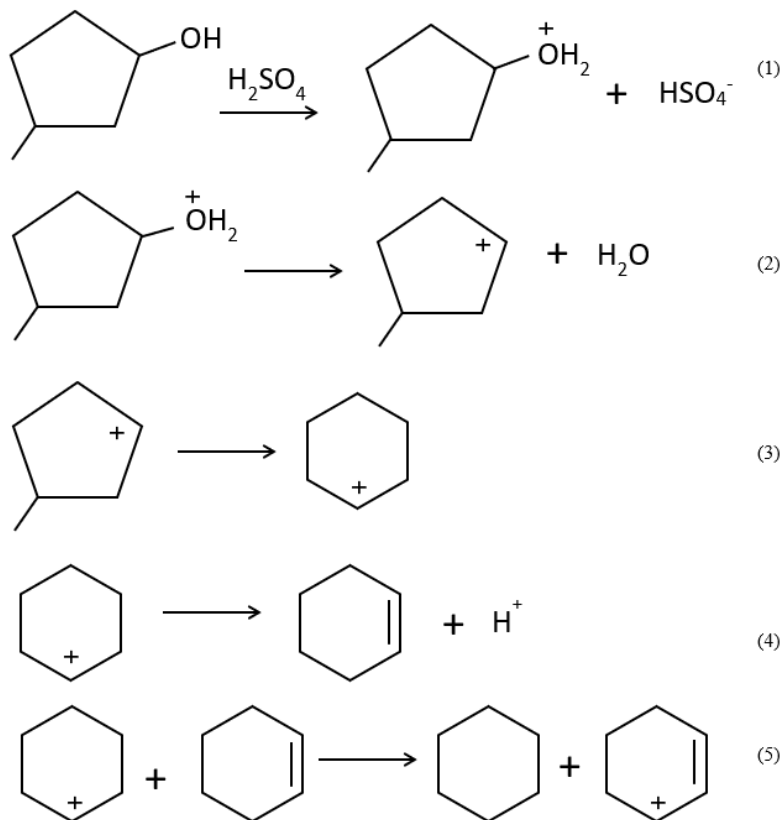

Figure 2. Mechanism for formation of aliphatic alkenyl cation from 3-methylcyclopentanol in the presence of 88% concentrated sulfuric acid.

In the first step, 3-methylcyclopentanol produces a cyclopentanyl carbocation after protonation by sulfuric acid. This cyclopentanyl carbocation then shifts into a cyclohexanyl carbocation intermediate before producing a cyclohexene. The cyclohexanyl carbocation and cyclohexene in mixture perform a hydride transfer to produce a cyclohexenylyl carbocation and cyclohexane.[6] Reactions of 0.00010 M 3-methylcyclopentanol in methanol introduced into nominally 88% sulfuric acid at 45.0°C are used for method development.

To assess the developed method, the same kinetic treatment is applied to a more complex absorption spectra of the reaction of 4-methylcyclohexanol with nominally 96% sulfuric acid at 60.0°C, obtained from prior research,[7] whose proposed mechanism
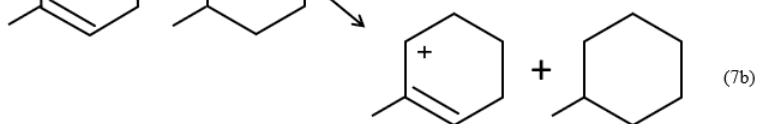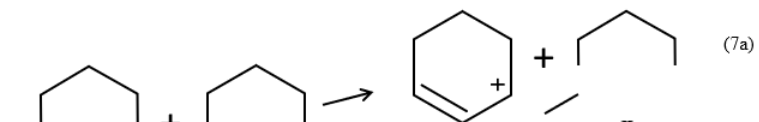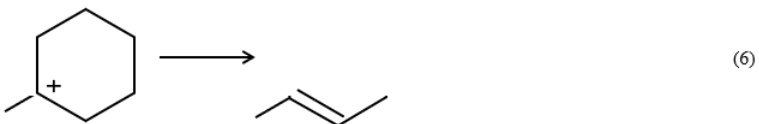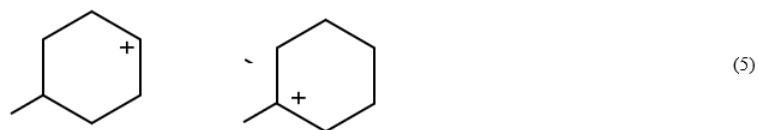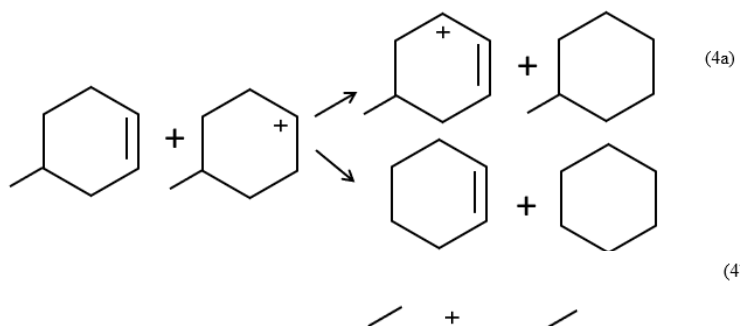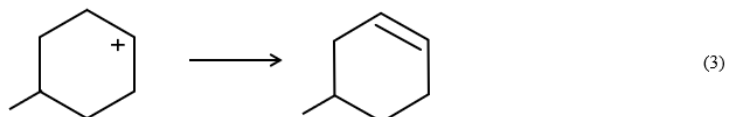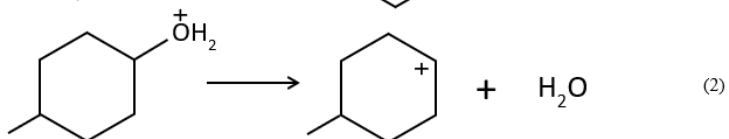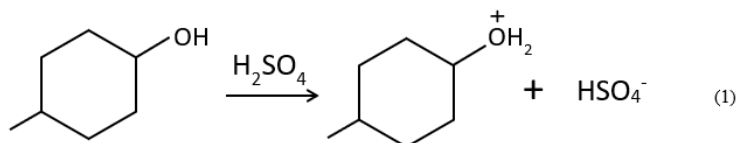
is shown in the figure below:

Figure 3. Mechanism for formation of aliphatic alkenyl cation from 4-methylcyclohexanol in the presence of 96% concentrated sulfuric acid. There are four potential cyclohexenyl cation intermediates formed, found in steps 4a, 4b, 7a, and 7b.

The above proposed mechanism is a much more lengthy and complicated process, revealing four potential cyclohexenyl cation intermediates that may be detected by the UV-visible spectrophotometer in steps 4a, 4b, 7a, and 7b. As these four intermediates are isomeric, their signals in the UV-visible spectra could potentially have overlapping bands, which could lead to interferences in the form of shoulders. Consequently, a successful method would be especially valuable for this mechanism.

Experimental design

To obtain the absorption spectra, a syringe method as described below has typically been performed.[6,7] Solutions of 0.011 M 3-methylcyclopentanol (Aldrich, 99%, 196169-5G) in methanol (Aldrich, 176840025) and acid catalyst of 87.96% w/w H_2SO_4 from 96.00% w/w H_2SO_4 (Fisher Scientific, A300-212-2.5L) were prepared. Starna 1-cm path quartz cuvettes (Starna Spectrosil® 1-Q-10-GL14C, close-capped) containing control and experimental solutions were placed into the spectrophotometer (Shimadzu UV-visible spectrophotometer, UV-2600) that was controlled by the software (LabSolutions UV-VIS, v. 1.11) and temperature control unit (Fischer Scientific, Isotemp 3016) set to 45.0° C. After running calibration and baseline, absorbance-time data of the reaction was obtained through instrument readings at 60-second intervals in the 390 to 190 nm wavelength range. For the experimental solution, a syringe (Hamilton 780 model GC syringe 50 µL capacity) was used to add the 3-methylcyclopentanol solution. Once data on absorbance vs wavelength over a length of time was measured, various kinetic treatments were performed to obtain the observed rate constant.

Using the Guggenheim method, natural log in the differences of absorbance was plotted against time in minutes to obtain the slope (magnitude equal to observed rate constant) and coefficient of determination. The observed rate constant and coefficient of determination were each plotted separately against wavelength in nm to evaluate kinetic behavior across the absorption spectra.

To further evaluate this method, more complex absorbance spectra of acid-catalyzed reaction of 4-methylcyclohexanol obtained by a previous student[7] was treated by the same kinetic treatment as described above. The previous student had used a similar method to obtain this absorption spectra as the process described prior to obtain absorbance spectra of acid-catalyzed reaction of 3-methylcyclopentanol.

Results

The UV spectrophotometer provided a representation of the 3-methylcyclopentanol reaction using an absorbance vs wavelength graph. As shown in the graphed lines of Figures 4 and 5, there is a shoulder revealed within the 305 nm to 320 nm range. Analysis of the absorbance vs wavelength graphical representation in context of scanning rate provides sufficient time indicators to plot an accurate absorbance vs time of various wavelengths from 285 nm to 330 nm. For the kinetic treatment, the Guggenheim method is used to obtain linear first-order plots. This Guggenheim method for kinetic analysis allows for obtaining the observed rate constant from the

magnitude of the slope of such graphs. To observe trends around the shoulder from the absorbance vs wavelength graph, Figures 4 and 5 plot (in points) the observed rate constant vs wavelength and the coefficient of determination against wavelength, respectively.
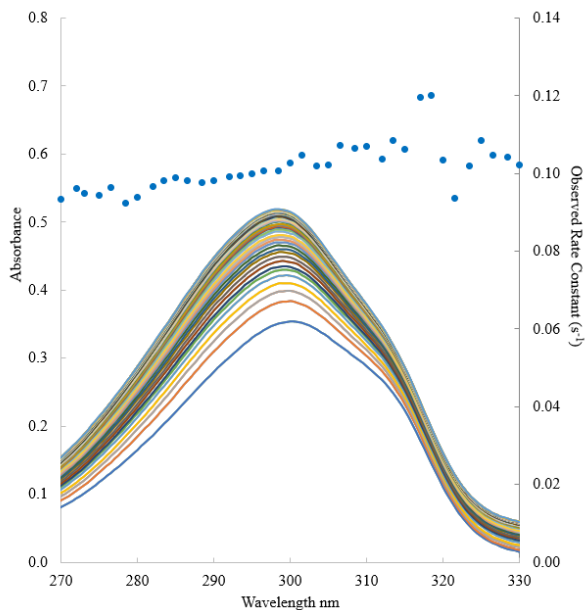

Figure 4. Plot of observed rate constant (calculated from Guggenheim plot trendlines by linear regression function in Excel) against wavelength (in nm) compared with the time-series absorption spectra of 3-methylcyclopentanol reaction with 87.96% sulfuric acid catalyst.
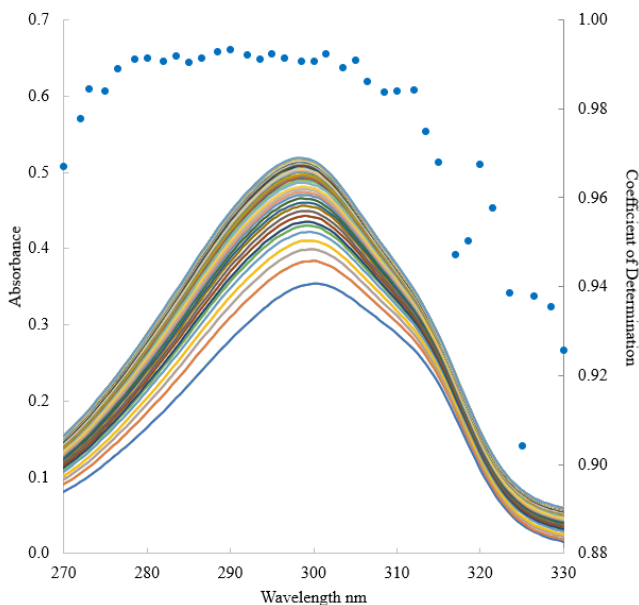
Figure 5. Plot of coefficient of determination (calculated from Guggenheim plot trendlines by linear regression function in Excel) against wavelength (in nm) compared with the time-series absorption spectra.

For the 4-methylcyclohexanol data from a previous study, the graphed lines of Figures 6 and 7 show the absorbance spectra for this molecule's reaction with concentrated sulfuric acid.[7] To aid in understanding the absorbance spectra, absorbance is plot against time (in minutes) in Figure 6 below:
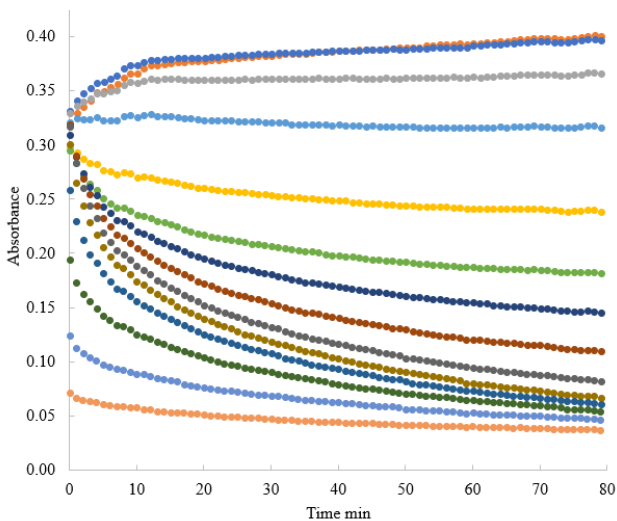
Figure 6. Plot of absorbance vs time (in minutes) of 4-methylcyclohexanol reaction with 96% sulfuric acid catalyst at 60°C in UV spectrophotometer. Data obtained at wavelengths from 285 nm to 350 nm every 5 nm increments. Absorbance vs time (in minutes) of wavelength 300 nm is the blue dataset that remains constant around absorbance of 0.32.

At wavelengths shorter than 300 nm, the absorbance-time graphs reveal a more logarithmic curve while absorbance-time graphs at wavelengths longer than 300 nm reveal an exponential decay behavior.

Using the same Guggenheim kinetic treatment process as the earlier analysis of 3-methylcyclopentanol, observed rate constants are obtained from the magnitude of the slope of such graphs. To observe trends around the shoulder from the absorbance vs wavelength graph, Figures 7 and 8 plot (in points) the observed rate constant vs wavelength and the coefficient of determination against wavelength, respectively.

Figure 7. Plot of observed rate constant (calculated from Guggenheim plot trendlines by linear regression function in Excel) against wavelength (in nm) compared with the time-series absorption spectra of 4-methylcyclohexanol reaction with 96% sulfuric acid catalyst.
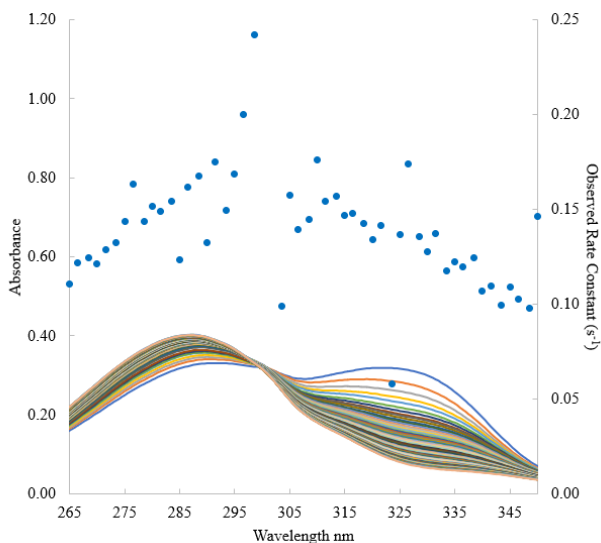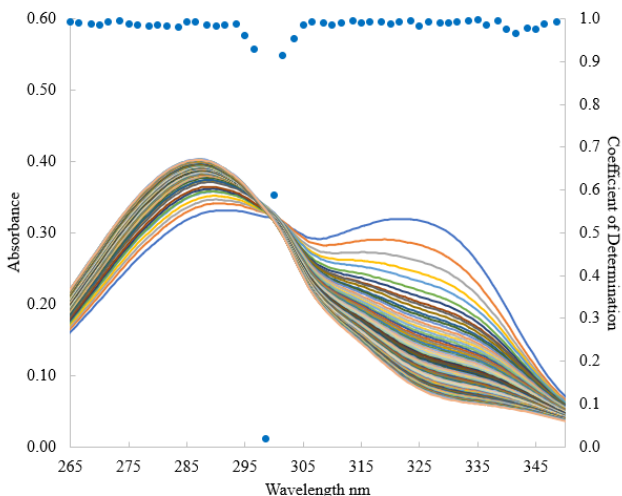
Figure 8. Plot of coefficient of determination (calculated from Guggenheim plot trendlines by linear regression function in Excel) against wavelength (in nm) compared with the time-series absorption spectra.

Discussion and Conclusion

In both graphical analyses of observed rate constant and coefficient of determination for 3-methylcyclopentanol (Figures 4 and 5, respectively), there is a deterioration within the 305 nm to 320 nm wavelength region corresponding to the estimated shoulder of the absorbance vs wavelength graph. For the observed rate constant, there is a much more random scattering around this shoulder region while the wavelengths apart from the shoulder obtain relatively constant observed rate constant values. This indicates the plot of the observed rate constant against wavelength to be a good indicator of the shoulder in the absorbance vs wavelength graph. For the coefficient of determination, there is a steep negative downward trend in the shoulder region, but there is also a steep downward trend from 270 nm to 280 nm. Therefore, the coefficient of determination against wavelength is not a good indicator of the shoulder. However, the coefficient of determination does indicate the most accurate observed rate constant in the wavelength range of 280 nm to 300 nm.

The scattering in the observed rate constant graph (Figure 4) implies that the data of the side reaction could be influencing data from the main peak in instrument readings. At this moment, it is unclear whether the kinetics of the shoulder is affecting the kinetics of the main signal. Using the coefficient of determination graph (Figure 5), the observed rate constants are determined to be highly accurate and consistent over wavelengths 285 nm to 300 nm. The actual rate constant values remain constant at around 0.099 s^{-1}, and the associated coefficients of determination values with the rate constants in this wavelength region are consistently high at 0.99. In conclusion, the data supports that consistent and quality observed rate constants are obtained in the region of the absorbance spectra farthest away from asymmetric anomaly, not just at the maximum wavelength.

In applying the method to test validity of analyzing absorption spectra of reactions similar to acid-catalyzed reaction of 3-methylcyclopentanol, the absorbance-time graph of 4-methylcyclohexanol reacting with sulfuric acid (Figure 6) supports the findings concerning the data of the side reaction affecting the data of the main peak. For instance, very close to the peak at 295 nm (the grey dataset, third line from the top in Figure 6), the data in the equilibrium portion of the graph remains relatively stable at a steady-state value while the data at 280 nm and 290 nm appear to creep upwards in the equilibrium portion. Hence, there is influence at wavelengths closer to the asymmetric portion of the absorbance-wavelength graph that pull the data points downward, while there is little influence at wavelengths farther away, resulting in a non-steady state value in the equilibrium region. In this way, the method helps in identifying the range of influence that the overlapping bands cause deviations.

As for the observed rate constants and coefficient of determination graphs (Figures 7 and 8, respectively), the data matches well with time-series absorption spectra and absorbance-time plots (Figure 6). Based on Figure 8, the observed rate constants are generally of quality. In Figure 7, the rate constants also reveal relative consistency at wavelengths outside the influence of overlapping bands, remaining in the range of 0.10 s^{-1} to 0.15 s^{-1} at wavelengths where there is minimal scattering. There are anomalies in behavior for both Figures 7 and 8 at 300 nm where the absorbances merge in the time-series absorption spectra.

There are noteworthy findings regarding rate constants at wavelengths with minimal influence by overlapping bands. At 265 nm, the rate constant associated with the absorbance band with lambda max of 285 nm has minimal influence from the absorbing band at 325 nm. Likewise, at around 347 nm, the rate constant associated with the absorbance band with lambda max of 325 nm has minimal influence from the absorbing band at 285 nm. The fact that the rate constants for both bands are nearly equivalent provides evidence that the intermediates may be directly related. Since the main peak is centered around 285 nm, the first signal is likely associated with the allylic cation while the second signal is associated with a different intermediate. In the proposed mechanism for acid-catalyzed reaction of 4-methylcyclohexanol, there are four potential intermediates detected by the UV-visible spectrophotometer, so the spectra revealing the detection of two intermediates is plausible. In conclusion, the observed rate constant is not only able to be evaluated for accuracy but can also provide support for the mechanism of the reaction.

Overall, the developed method holds promising results for understanding the kinetics and determining the most accurate observed rate constants for intermediates involved in acid-catalyzed dehydration of 3-methylcyclopentanol and 4-methylcyclohexanol. The method appears to support both low and medium complexity of absorption spectra analysis.

Limitations and Future Research

Due to the nature of the Guggenheim method selecting varying intervals for difference in absorbance, it is difficult to standardize the newly developed method for replicability. To combat this issue, other research groups should continue to apply the developed method to 3-methylcyclopentanol and 4-methylcyclohexanol in order to confirm the consistency in results. Moving forward to evaluate generalizability, other

reactions involving cyclic carbocation intermediates should also be investigated, testing whether this method will aid in their general kinetic analysis.

Acknowledgements

References

1. Deno, N. C.; Pittman, C. U. *J. Am. Chem. Soc.* **1963**, 86, 1744-1745.

2. Jagannadham, V. Osmania University, India, Personal communication, 2007.

3. Deno, N. C.; Richey, H. G. R.; Hodge, J. D.; Wisotsky, M. J. *J. Am. Chem. Soc.* **1962**, 84, 1498-1499.

4. Deno, N. C.; Bollinger, J.; Friedman, N.; Hafer, K.; Hodge, J. D.; Houser, J. J. *J. Am. Chem. Soc.* **1963**, 85, 2998-3000.

5. Bockisch, C.; Lorance, E. D.; Hartnett, H. E.; Shock, E. L.; Gould, I. R. *ACS Earth Space Chem.* **2018**, 2 (8), 821-832. American Chemical Society Database. https://doi.org/ 10.1021/acsearthspacechem.8b00030

6. Mulder, P.; Menzmer, M. Southern Adventist University, United States of America, Personal communication, 2018.

7. Drab, E.; Menzmer, M. Southern Adventist University, United States of America, Personal communication, 2018.

Charlotte Ishikawa