Kinetics of acid-catalyzed formation of cyclohexenyl cation from 1-methylcyclopentanol

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Abstract:

Methylated cyclopentanols are suspected to undergo an acid-catalyzed ring expansion, though it was unclear whether this expansion occurred from a tertiary carbocation. In order to confirm this reaction, a dehydration reaction of 1-methylcyclopentanol was carried out, while monitoring the progress using ultraviolet spectroscopy. The cyclohexenyl carbocation intermediates produced were catalyzed by 88% w/w sulfuric acid at temperatures at one degree intervals within the range of 45-50°C. Results suggested a ring expansion of 1-methylcyclopentanol, resulting in the formation of a cyclohexenyl carbocation and cyclohexane. The mechanism for the ring-expansion remains unclear, though perhaps it is driven by the stabilization provided through the relief of ring strain. The kinetic treatments of the data suggest a first order reaction. The activation calculated through a linearization of the Arrhenius relation is 52 kJ/mol.

Introduction:

Previous research comparing the time-series spectra for the acid catalyzed dehydration of 2-methylcyclopentanol and cyclohexanol at millimolar concentration suggested that a common product formed, since both products showed similar absorption band around 295 nm. Additional research discovered that, according to the GCMS data collected, cyclohexane predominated as a primary product of the reaction involving 2-methylcyclopentanol. This suggested that a ring expansion of 2-methylcyclopentanol occurred. The researchers proposed that the ring expansion relieves ring strain, and that this effect supersedes the inductive stabilization of a tertiary carbocation compared to a secondary carbocation.[1] While this research used 2-methylcyclopentanol as the reactant, 92% w/w H_2SO_4 as the catalyst, and a temperature range from 47°C to 55°C, performing a reaction using 1-methylcyclopentanol and 88 % w/w H_2SO_4 should produce some interesting insight specifically into the origin of this ring expansion. If the ring expansion occurs from the reaction involving 1-methylcyclopentanol, then the expansion likely occurs from the tertiary carbocation form, since this is the only form expected to occur from the dehydration of this molecule.

Figure 1 displays the mechanism for the proposed reaction. In step 1 of the mechanism, the 1-methylcyclopentanol is first protonated in acidic medium.[3] This protonation converts the hydroxyl into water, and subsequently water leaves. Because the resulting carbocation is somewhat unstable, this is proposed as the reaction's rate determining step.[4]

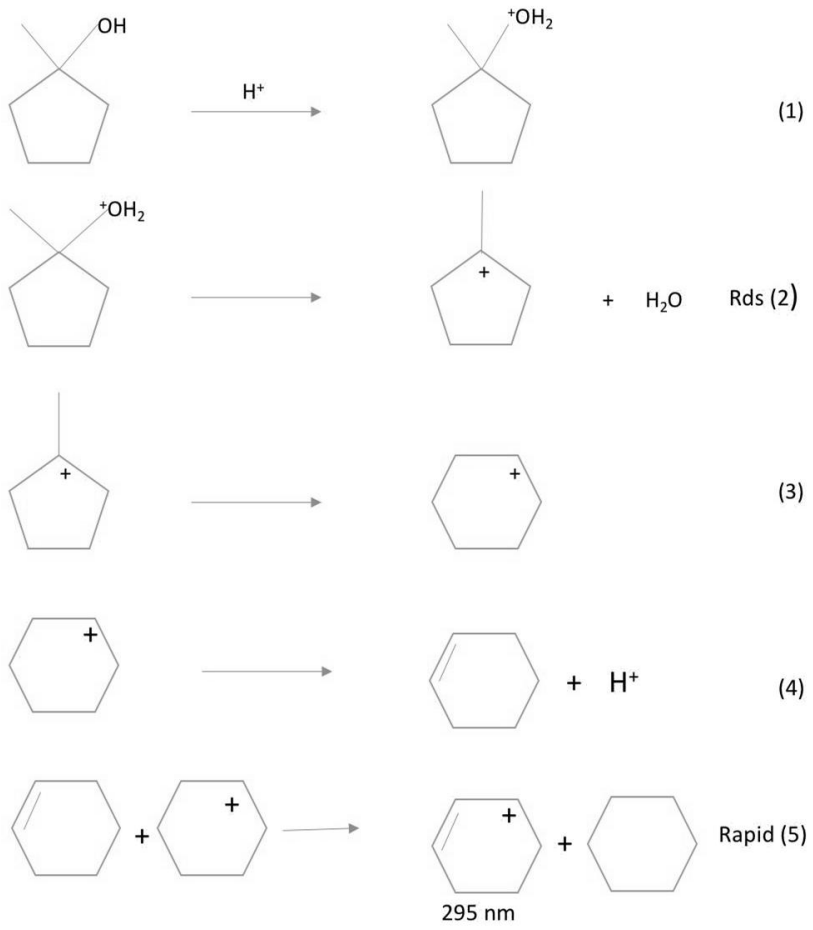

Figure 1. Proposed mechanism for the reaction in which 1-methylcyclopentanol is converted to cyclohexenyl carbocation and cyclohexane, where step 2 is the rate determining step.

It is unclear if or how the tertiary carbocation of the methylcyclopentanyl is converted into the cyclohexanyl cation in step 3 of the proposed mechanism. However, in step 4, it is clear that the unstable secondary carbocation loses a proton and converts to cyclohexene. Lingering cyclohexanyl cation and the cyclohexene react to form cyclohexane and cyclohexenyl cation by means of a hydride transfer.[5] The created cyclohexenyl cation, with its λ_{max} of 295nm and molar absorptivity of 10^4, would be relatively stable because of resonance.[2]

Definite evidence indicating whether the ring expansion occurs from the secondary or tertiary carbocation of the methylated cyclopentane is not readily available. Under acidic conditions, 2-methylcyclopentanol is also expected to be protonated and dehydrated, though it initially forms a secondary carbocation. The majority of the secondary carbocations formed then are expected to rearrange to the more stable tertiary carbocation. While this seems to be the most logical course, perhaps the ring expansion of the secondary 2-methylcyclopentanyl cation occurs rapidly following dehydration, before the cation rearranges to the more stable tertiary form. This work will attempt to clarify this question of the ring expansion's origin. The following possibility is under consideration, namely that following the protonation and dehydration of the 1-methylcyclopentanol, the tertiary cation is favored and that it is from this tertiary carbocation that the ring expansion progresses.

A kinetic study of 1-methylcyclopentanol with electronic spectroscopy is expected to reveal whether the same product will form when 1-methylcyclopentanol is used as the starting material as compared to when 2-methylcyclopentanol is used. If this reaction leads to a strong peak at 295 nm, then the ring expansion of a methylated cyclopentanol most likely proceeds directly from the tertiary, rather than the secondary carbocation of this molecule. Further experimentation under similar conditions of temperature and acidity should also be performed using a methylated cyclopentanol which favors formation of a secondary carbocation.

Once the change of absorbance with time at 295 nm for the reacting mixture is obtained, first and second-order kinetic treatments of the data provide the information necessary for determining several things: the order of the formation of the cyclohexenyl cation, and the observed rate constants. Systematically varying the temperature at which the reaction is carried out clarifies the dependence of the observed rate constant on temperature. When the experiment

is performed at fixed acidity and varying temperatures, the activation energy for the formation of the cyclohexenyl cation can be calculated by applying the data to the Arrhenius equation.

Alternatively, the tertiary carbocation may undergo a type-one elimination reaction under these acidic conditions, as can be seen in step 1 of Figure 2. In step 2, surplus tertiary carbocation and the 1-methylcyclopentene react under acidic conditions to form various resonance structures of the 1-methylcyclopentenyl cation. Based on the literature, the intermediate is expected to have an absorbance maximum of approximately 280 nm.[2] 1-methylcyclopentanol will form the tertiary carbocation, so if a peak at 280 nm is observed from a reaction with this molecule, then this will support the mechanism seen in Figure 2. Furthermore, this result would also suggest that the ring expansion from the less stable secondary carbocation is more energetically favorable than the relative stabilization achieved through the rearrangement to the tertiary carbocation.

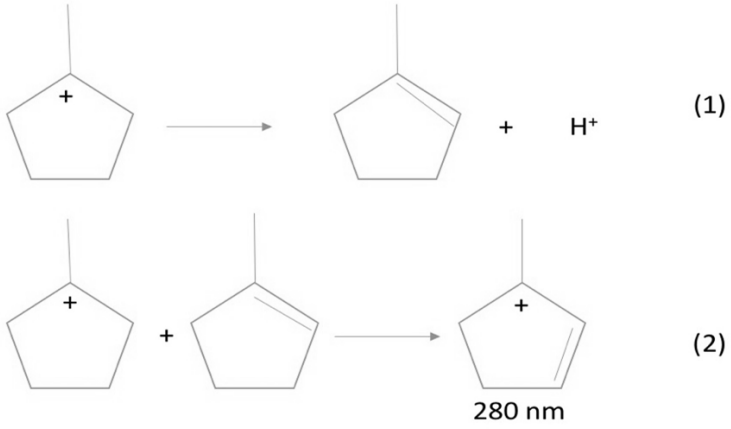

Figure 2. Alternate fate of the tertiary 1-methylcyclopentenyl cation. The literature maximum absorbance of the 3-methylcyclopentenyl cation is 280 nm[2].

Method:

Reactions were carried out in 92% w/w H_2SO_4 in distilled water. A solution of 1-methylcyclopentanol in methanol was created and used. The concentrated solutions of H_2SO_4 were prepared from stock solution H_2SO_4 (Sigma-Aldrich, 95.0-98.0%, 320501). The reactions were carried out in screw cap cells (Starna Spectrosil 1-Q-10-GL14C, close-capped) and a spectrophotometer (Shimadzu, model UV 2600) followed the reaction progress. A constant temperature for the system during a reaction run was maintained through the use of a water bath (Fisher Scientific Isotemp model no. 3016), while software (UVProbe v. 2.1) recorded the time-series absorbance data while the reactions took place.

A small aliquot of H_2SO_4 was added to both cuvettes using a graduated pipette. The prepared cuvettes were inserted into the instrument and the 1-methylcyclopentanol solution (35 μL) was added employing a 50 μL syringe (Hamilton 705 model GC syringe). The beginning reaction was marked by the point of injection. The cuvettes were removed from the instrument, inverted twice, then placed back in the instrument. The computer was set to take data readings at automated intervals from 185-400 nm. The same procedure was carried out for reactions at the other chosen temperatures.

From the measured absorbance, the rate constant for the reaction was determined. The data needed to plot the natural log of the rate constant versus 1/temperature (K) was obtained by carrying out the reaction at several temperatures. The plot was made using a linearization of the Arrhenius equation, $\ln(k)= -6226(1/T) + 17.442$. The activation energy of the rate determining step was determined using the slope of this plot.

Results:

Figure 3 relates absorbance at 295 nm to time. An equilibrium absorbance value is needed before further kinetic treatment of the data and can be obtained from this figure. Ideally, first or second order dependence may be determined as a result of this treatment. In order to make kinetic treatments suitable for this data, the curves are modified mathematically into decay curves. This is because the absorbance increases with time in this reaction, though absorbance eventually reaches an equilibrium value.

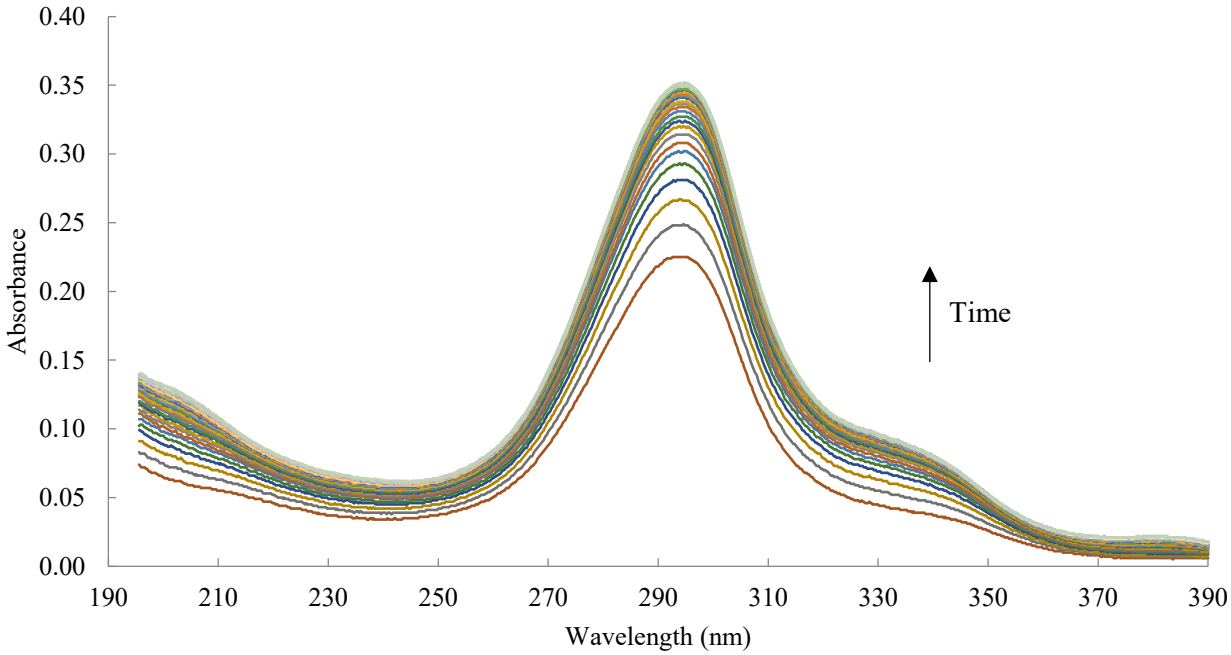

Figure 3. Time-series set of absorbance spectra at 47°C for .00010 M 1-methylcyclopentanol reacted with 88% w/w H_2SO_4. The observed maximum absorbance appears to be at approximately 295 nm.

Absorbance′, or the adjusted absorbance, is found through careful evaluation of the curve plateau of Figure 4, and then by estimating the average absorbance value of this plateau. This region of the curve with very little variation in absorbance over time is considered to represent

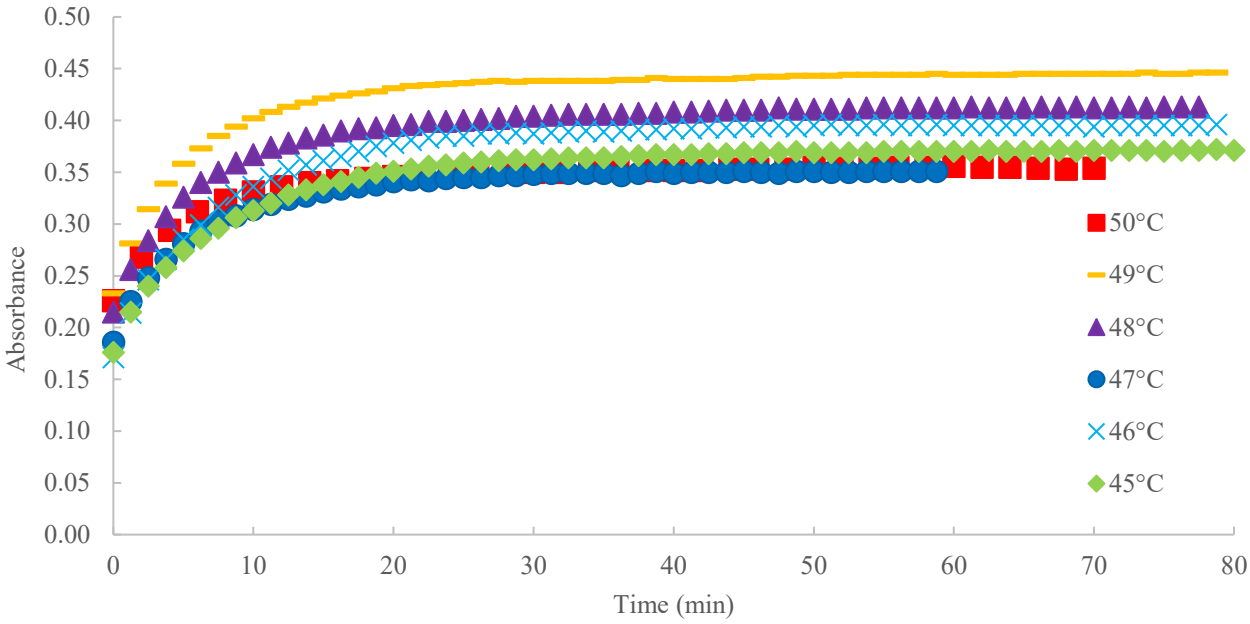

Figure 4. Absorbance at 295 nm vs time plots at 50°C, 49°C, 48°C, 47°C, 46°C and 45°C corresponding to the shapes squares, dashes, triangles, circles, crosses, and diamonds, respectively. The equilibrium absorbance for each temperature was estimated using the maximum absorbance at 295 nm.

equilibrium of the reaction. The equilibrium absorbance for the reaction at that temperature is equivalent to this unfluctuating absorbance value. In a crucial step of data manipulation, the absorbance at 295 nm is then subtracted from these equilibrium absorbance values. This adjustment produces the adjusted absorbance, absorbance′.

Figure 5 is the result of the first-order kinetic treatment, in which the natural log of absorbance' is related to time in minutes. The linear dependence with time indicates a first-order

reaction. The second-order kinetic showed exponential increase, and therefore, the reaction is not likely to be second order.

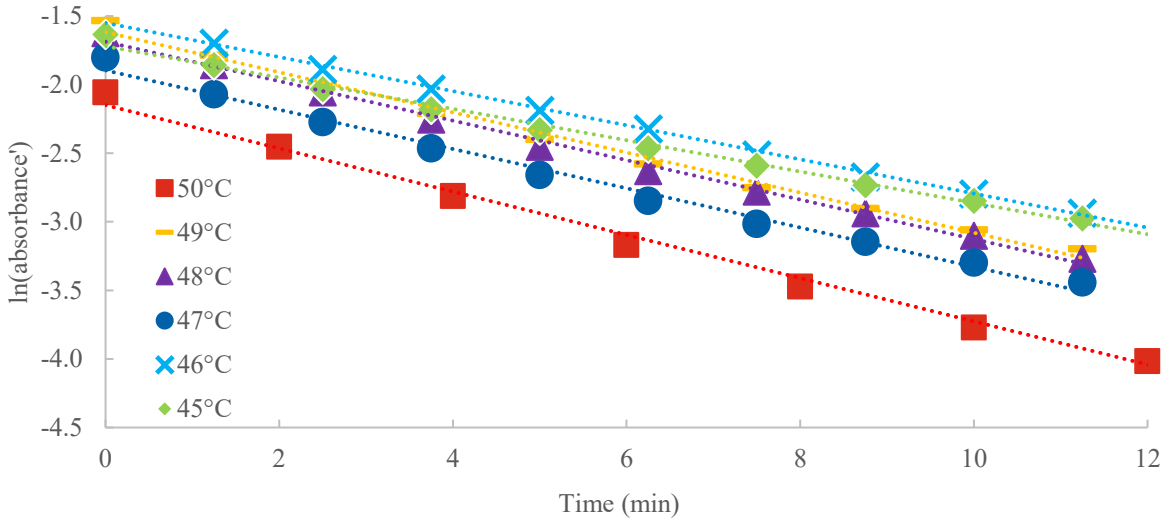

Figure 5. Natural log of absorbance' versus time. The slopes of the best fit line derived from the data were 0.158 min^{-1}, 0.146 min^{-1}, 0.144 min^{-1}, 0.143 min^{-1}, 0.124 min^{-1} and 0.114 min^{-1} corresponding to reactions at 50°C, 49°C, 48°C, 47°C, 46°C and 45°C respectively.

The slopes from the first order kinetic treatment seen in Figure 5 indicate the values of the reaction's rate constants. With these values, the activation energy of the reaction may be estimated, as seen in Figure 6. Table 1 associates the temperatures (given in both °C and K) with the appropriate rate constants.

Table 1. Calculated rate constants and their associated temperatures

T(K)	T(°C)	k/min
323	50	0.158
322	49	0.146
321	48	0.144
320	47	0.143
319	46	0.124
318	45	0.114

According to Equation 1, the slope of the best fitted line plotted in Figure 6 represents – activation energy/R. With knowledge of the value of the slope, the activation energy of the reaction can be solved for, resulting in a value of 52 kJ/mol.

$$\ln k = -\frac{E_a}{RT} + \ln A \qquad (1)$$

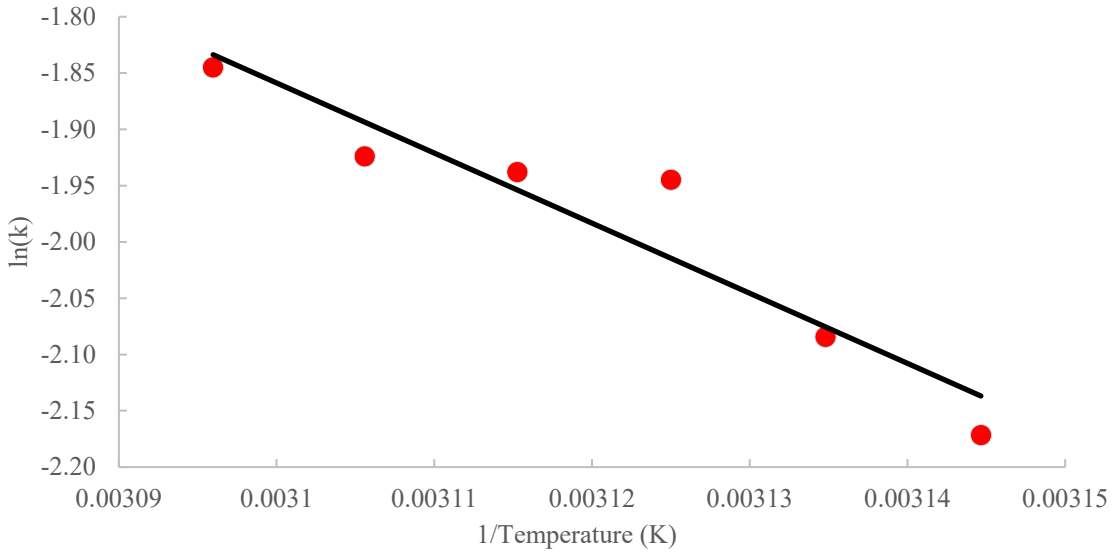

Figure 6. Plot of the natural log of the observed rate constants versus the inverse of the temperature in kelvins. Equation of the best fit line is equivalent to ln(k)= -6226(1/T) + 17.442. Using the slope of this line, the activation energy is calculated to be 52 kJ/mol.

Discussion and Conclusion:

Comparison of the time-series spectra for 1-methylcyclopentanol and cyclohexanol showed similar absorption around 295 nm, suggesting that a common product formed. Because the intermediate indicated on the absorbance spectra has a λ_{max} of 295 nm rather than 280 nm, the reaction proposed in Figure 2 did not occur under these conditions. It appears that the ring strain relieved from the ring expansion supersedes the inductive stabilization of a tertiary carbocation relative to a secondary. Based on the linear nature of the first order kinetic treatment seen in Figure 5, the reaction appears to be first order, while calculations based on Figure 6 indicate an activation energy of 52 kJ/mol. Student research performed in 2017 by Nishino found that the activation energy for the acid catalyzed reaction in which 1-methylcyclohexanol converts into the cyclohexenyl carbocation is approximately 50 kJ/mol.[7] The similarity between

these two discussed activation energies suggests that this ring expansion, which likely originates from the tertiary carbocation, is not the reaction's rate determining step.

References:

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