Determining activation energy in the acid catalyzed dehydration reaction of 2,6-dimethylcyclohexanol using ultraviolet-visible spectrophotometry

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Abstract

The reaction of 2,6-dimethylcyclohexanol in sulfuric acid produces a variety of alkenyl carbocations, which produce a single symmetric band on UV-Vis near λ_{max}=295 nm. The reaction mechanism is a multi-step, multi-pathway reaction. Reactants, 0.0010M 2,6-dimethylcyclohexanol and 86% w/w sulfuric acid, were placed in a cuvette in a UV-Vis instrument and were held at a constant temperature. Three trials were run for each of four temperatures, 50, 52, 57, and 60 degrees Celsius. Reaction progress was tracked by the UV-Vis instrument taking scans over 190-390nm. The linear plot suggests that the reaction is first order when plotted $\ln A = -kt + \ln A_o$. The rate constant is given by the negative of the slope of each line, k_{obs}. This can be plotted via the Arrhenius equation , $\ln k_{obs} = \frac{-E_a}{R}\frac{1}{T} + C$. The negative of this slope is multiplied by the gas constant, R, giving an activation energy of near 85.8 kJ/mol*K.

Introduction

The dehydration reaction of 2,6-dimethylcyclohexanol catalyzed by H_2SO_4, which is known to be a strong dehydrating agent, produces four possible relatively stable dimethylcyclohexene carbocations which are stabilized by H_2SO_4[1] [2]. These carbocations should produce a band on ultraviolet-visible spectrophotometry near λ_{max}=300 [3].

The proposed mechanism for the reaction, shown in figure 1, consists of a four step process. The second step gives an unstable secondary carbocation. Steps 4a and 4b are hydride transfers and occur quickly [4].

Step 1 starts the reaction with a protonation of the alcohol group leading to a positively charged OH_2 group, which is a decent leaving group that leaves in step 2. This leaving of OH_2 results in an unstable secondary carbocation that can proceed down one of two reactions shown in step 3a and step 3b. The more unstable the ion, the faster H^+ is lost in the next step [3]. In step 3a, a H^+ leaves and its electrons from a double bond. A hydride transfer occurs in step 3b to form a more stable tertiary carbocation, which also loses an H^+ to form two cyclohexene products. Both steps 3a & 3b result in the replenishing of free protons, which makes H_2SO_4 a catalyzer. Ignoring possible stereochemistry, one of the products in step 3b is the same as the product of step 3a. Therefore, the reaction will continue with two steps. Step 4a and 4b are practically identical. They both involve a hydride transfer from one molecule to the other, result in two possible products, and result in a common byproduct. Step 4b results in a tertiary carbocation, thus this will likely be the favoured product of step 4b. The products of step 4a are both secondary carbocations.

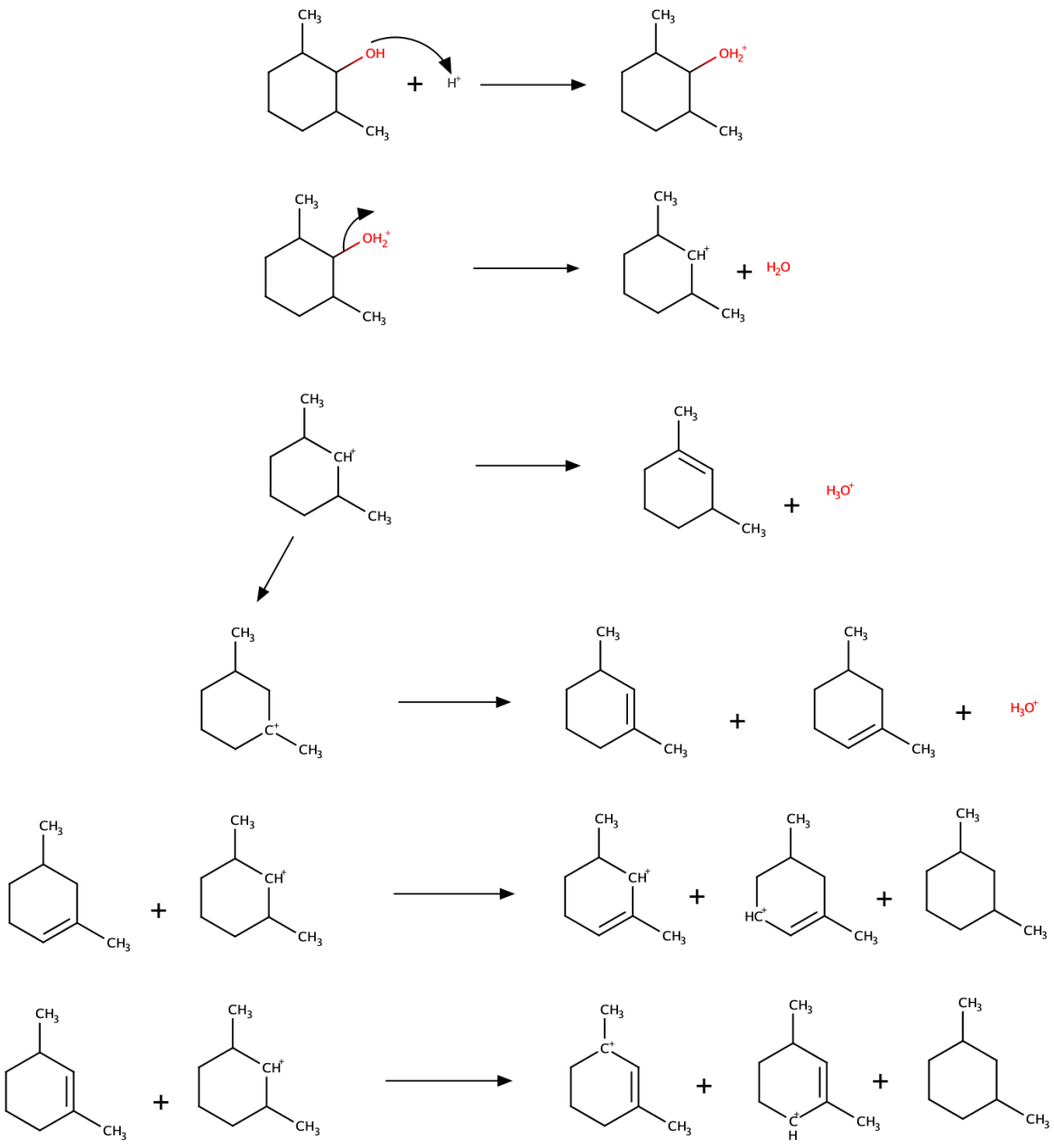

Figure 1 Shows the proposed mechanism for the reaction of 2,6-dimethylcyclohexanol with H_2SO_4.

The purpose of this study is to determine the energy of activation for the reaction by using the Arrhenius equation, $\ln k_{obs} = \frac{-E_a}{R}\frac{1}{T} + C$. The observed rate constant, k_{obs}, can be

found by plotting ln(Abs) versus time. Next, the data is plotted according to the Arrhenius equation, using ln k_{obs} as y and 1/T as x. The resulting slope of the line is $-E_a/R$, allowing for the easy calculation of activation energy.

Methods

Solutions were prepared by weighing the 2,6-dimethylcyclohexanol (Acros Organics, 99%, 149810500). The 2,6-dimethylcyclohexanol was dissolved in methanol (Acros Organics, 99.8%, 176840025) to make 0.010M 2,6-dimethylcyclohexanol in methanol. 86% w/w H_2SO_4 (Fisher Scientific, 96% w/w, A300-212) was used as the acid catalyst.

Then 3.50mL of 86% w/w H_2SO_4 was placed in two Starna Spectrosil 1-Q-10-GL14C, close-capped cuvettes. Approximately 3.5μL of 0.010M 2,6-dimethylcyclohexanol in MeOH was injected using a Hamilton 780 model GC syringe into the 3.5mL of 86% w/w H_2SO_4 catalyst to give approximately 0.00010M of 2,6-dimethylcyclohexanol and then both cuvettes (one with only catalyst and one with the 2,6-dimethylcyclohexanol solution) were placed in a Shimadzu UV-visible spectrophotometer model UV-2450. Scans were obtained from 190 nm to 390 nm at 120 second intervals as the temperature was maintained by a Fisher Scientific Isotemp model no. 3016. This reaction was repeated three times for each of the following temperatures in degrees Celsius: 50, 52, 57, 60.

Results

Scans were taken, which produced spectra for each of the trials, such as the one in fig. 2. Figure 2 shows the time series absorbance spectra for one of the reactions between 0.00010M cyclohexanol in 86% w/w H_2SO_4 at 50.0 degrees Celsius, showing increasing absorbance at about 295 nm.

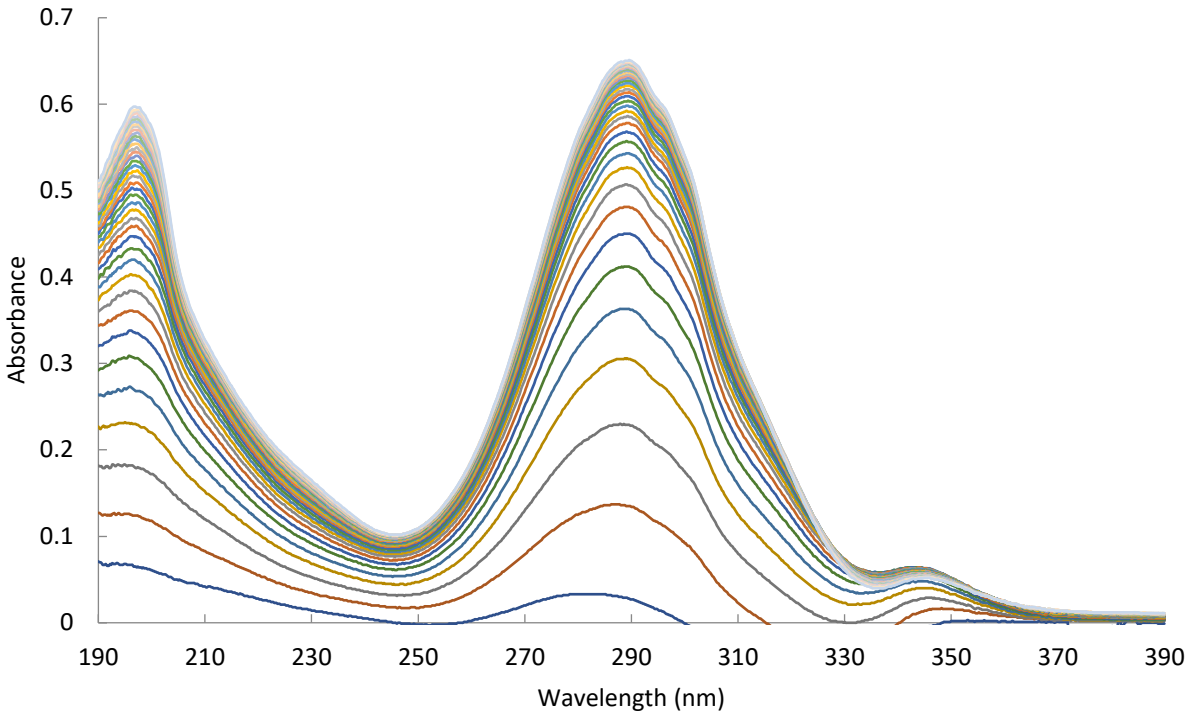

Figure 2. Time series absorbance spectra for a reaction between 0.00010M 2,6-dimethylcyclohexanol in 86% w/w H_2SO_4 at 50.0 degrees Celsius, showing increasing absorbance at about 295 nm.

Figure 3 shows the absorbance at 295 nm for one trial of each of the temperatures together.

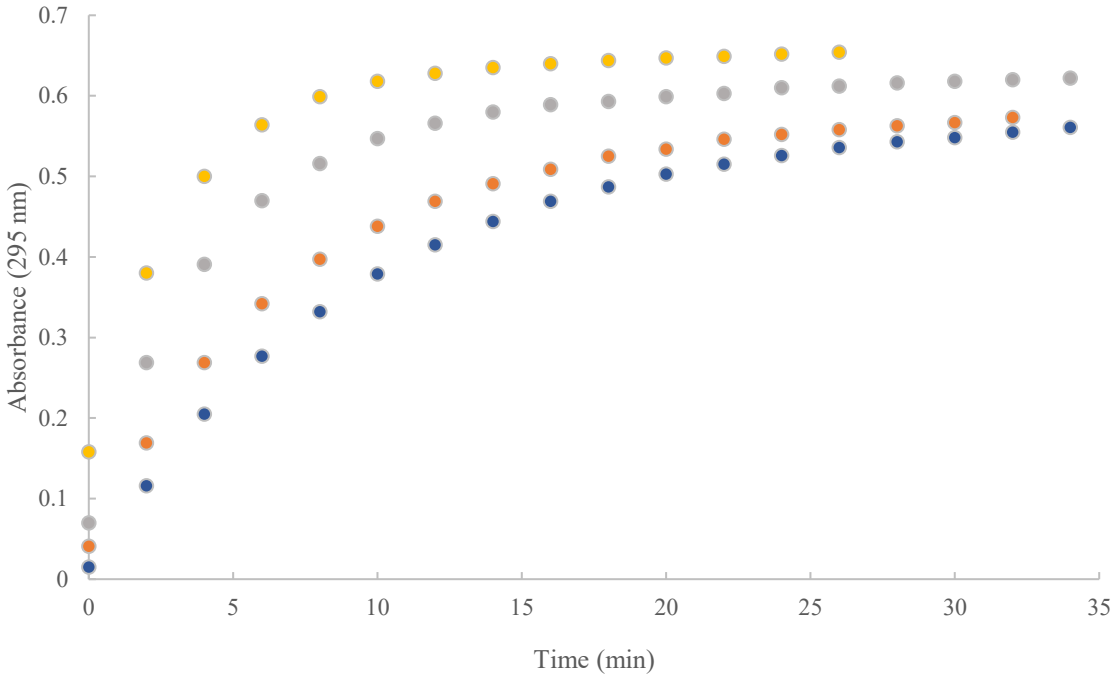

Figure 3. Absorbance at 295 nm versus time for one trial at each of the four temperatures, 50ºC shown in blue, 52ºC shown in orange, 57ºC shown in grey, and 60ºC shown in yellow.

Kinetic treatment plots were made testing for first order dependence, shown in figure 4. Since these plots require data in a decay style format and not increasing absorbance, the equilibrium absorbance was estimated and the absorbance was subtracted from that value for each data point. This new value is notated as Abs'.

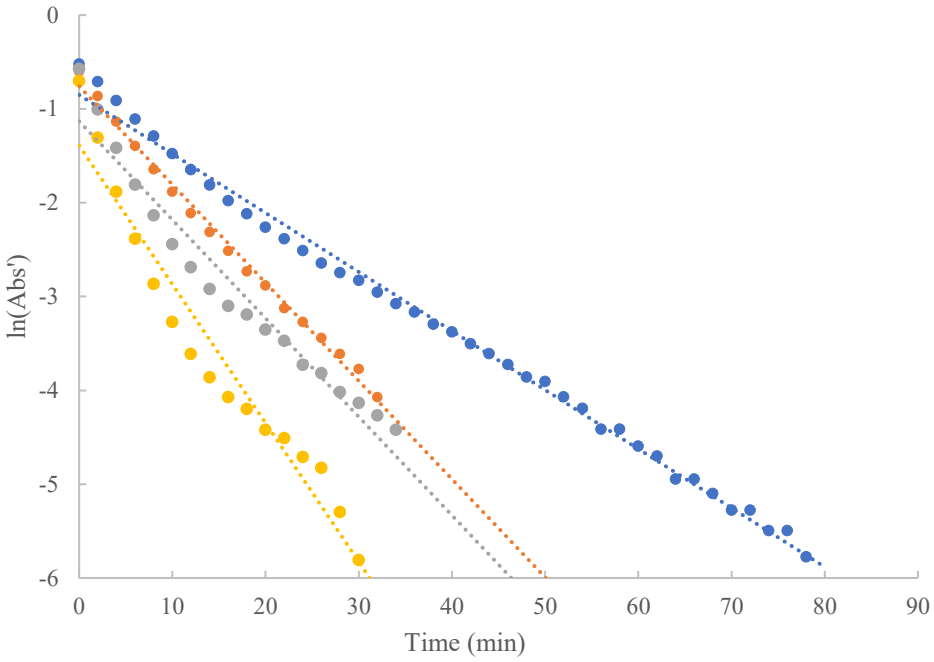

Figure 4. Natural logarithm of Abs' at 295 nm versus time in minutes for the four temperatures. 50ºC shown in blue, has an equation of lnAbs'= -0.0629t - 0.8507 with R^2=0.9943. 52ºC, shown in orange, has an equation of lnAbs'= -0.105t – 1.1317 and R^2= -0.9545. 57ºC, shown in grey, has an equation of lnAbs'= -0.1047t – 07587 and R^2=0.9940. 60ºC, shown in yellow, has an equation of lnAbs'= -01478t – 1.3913 and R^2= 0.9470.

Table 6 shows the temperatures in Celsius and Kelvin and their corresponding average observed rate constants, k_{obs}.

Temp/ºC	Temp/ K	K_{obs} (avg) /min^{-1}
50	323	0.0373
52	325	0.104
57	330	0.0842
60	333	0.142

Table 1. The temperatures in Celsius and Kelvin, with the average rate constants of the trials for each temperature.

Figure 5 shows the Arrhenius plot, $\ln k_{obs} = \frac{-E_a}{R}\frac{1}{T} + C$, whose slope will give $-E_a/R$, allowing for the easy calculation of activation energy. Each data point represents one temperature and was calculated by using the average rate constant of the trials. Moving left to right, the points are 60ºC, 57ºC, 52ºC, and 50ºC.

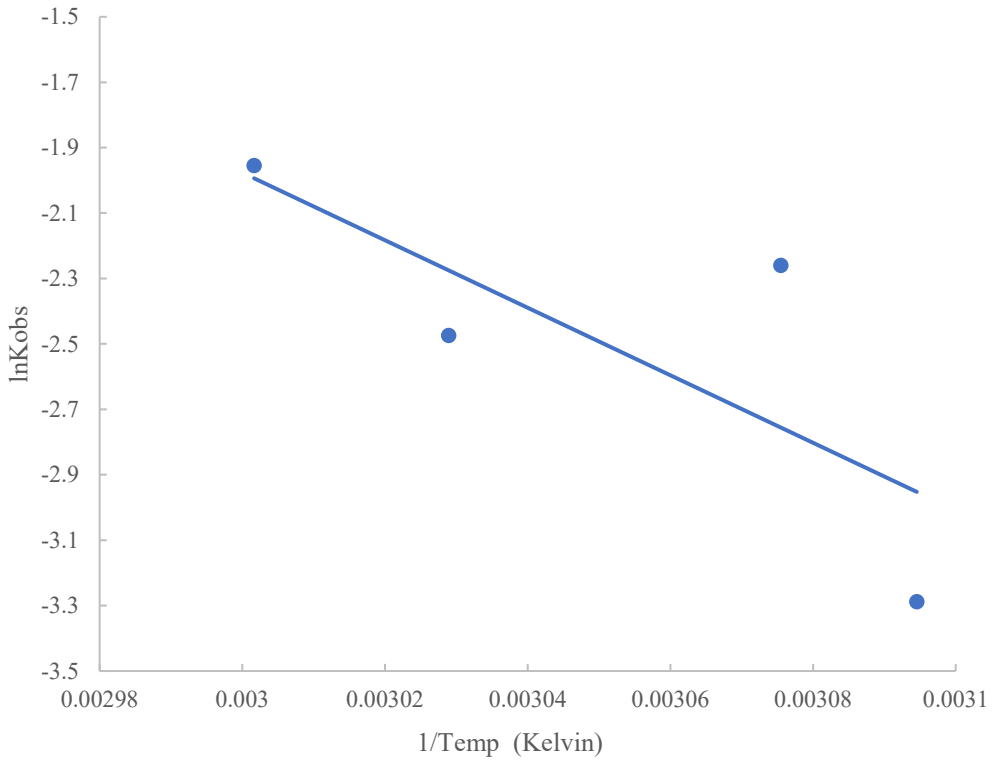

Figure 5. Shown is the Arrhenius plot using the average of the observed rate constants for each temperature. Moving left to right, the points are 60ºC, 57ºC, 52ºC, and 50ºC. The equation of the trendline is $ln k_{obs}$ = -10319 *1/T + 28.981.

Multiplying the slope of the line is -10319 by -8.314 $*10^{-3}$ kJ/mol, yielding an activation energy of 85.79 kJ/mol.

Discussion

Although a peak is clearly visible at 295 nm on the figure 2, a larger, more prominent peak is visible near 290 nm, suggesting that another product absorbs in this region. Furthermore, a large visible peak is seen at 190 nm, which could be the catalyst, other intermediates or one of the allylic carbocation products. Another small peak is visible near 345 nm, suggesting that it is one of the less favoured carbocation products. One of the products in step 4b of the proposed mechanism is a tertiary allylic carbocation, which may likely produce the largest peak at 290 nm.

The second product of step 4a is a secondary allylic carbocation, but has the least electron donating groups. This product is likely to be the least favoured of the products, possibly being responsible for the peak near 345 nm. The fourth product likely absorbs near 310, where a bit of a shoulder is seen.

Figures 3 and 4 both show trends. Figure 3 & 4 show that the higher the temperature, the quicker the reaction progresses and the higher the estimated equilibrium. The linear relationship shown in figure 4 suggests that the reaction is 1^{st} order.

Figure 5 shows the Arrhenius plot with a data point for each of the four temperatures. The trendline shows a clear trend with a negative slope, but the data point for 57ºC seems to be far away from that line.

Conclusions

The goal of this study was to find the activation energy of 2,6-dimethylcyclohexanol and this was accomplished. Further research on the sources of the peaks at 345 nm, 190 nm, and 290 nm should be considered. As well as repeating the trials at 57ºC, as the data from 57ºC does not line up with the trends seen in the rest of the trials.

References

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