CHM 2330:

Experiment N: Kinetics of the Depolymerization of Diacetone Alcohol via Basic Catalysis

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Objectives

The objective of this experiment is to understand the empirical rate equation of the depolymerization of diacetone alcohol via basic catalysis. In this experiment, the relationship between volume change and concentration of the catalyst will be observed using a dilatometer and thermostated bath. The data observed will be used to determine the hydroxy-dependent rate constant k_{obs}, the value of the exponent m, and the rate constant k.

Introduction

Depolymerization is the process of converting a polymer into a mixture of monomers without changing the percent composition. In this experiment a base catalyst was used to disassociate diacetone alcohol into propan-2-one molecules, as represented in the figure below.

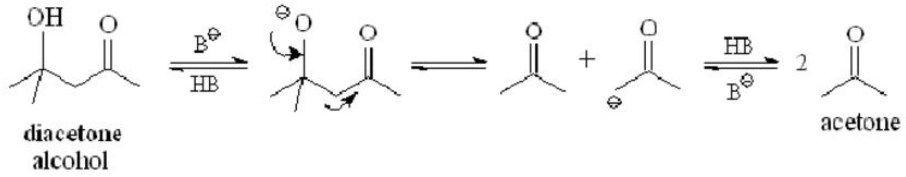


Figure 1.1 - Diacetone alcohol retroaldolization ((Pérez et al., 2009))

This reaction is reversible and would come to equilibrium if not pushed in a certain direction (Experiment 4). The sodium hydroxide acts as a catalyst by lowering the activation energy and accelerating the reaction thermodynamically. It does not undergo any permanent chemical changes during the reaction. The sodium hydroxide is used in excess to force the reaction to completion. The product of this reaction will have a smaller molecular weight than its

reactant but a larger volume density which causes the observable volume change in the dilatometer (Tafur). The unit of measurement for concentration is mol/L and the unit of time is minutes.

The rate equation of a reaction depends on initial concentrations of the reactants, refer to equation 1.

$$-\frac{\partial}{\partial x} = kx^{n}[OH]^{n} \quad (1)$$

Having the hydroxide ions in excess also eliminates the concentration of OH from the rate equation because the concentration will essentially remain the same throughout the entire reaction(Hewett). A hydroxy-dependent rate constant can then be measured to solve for a pseudo-first-order rate law, see equation 2(Reactions).

$$-\frac{d}{dx} = k_{obs}x \quad (2)$$

The observable rate constant is adjusted for the specific initial concentration of hydroxide ions and contains the actual rate constant, refer to equation 3.

$$k_{obs} = k[OH]^{m} \quad (3)$$

The volume change measured in the dilatometer is directly proportional to the concentration of the product because of the increase volume density as the reaction proceeds. By measuring the height of the meniscus in the dilatometer at certain time intervals, the observable rate constant will be the slope of the straightened curve. Because the reaction is first order, plotting the ln of volume change as a function of time will straighten the curve, refer to equation 4 (Tafur).

$$ln(V_{t} - V_{\infty}) = -k_{obs}t \quad (4)$$

Where V_t is the volume in the dilatometer and V_∞ relates to volume of starting material(Tafur).

Once an observed rate constant is found at each concentration of NaOH catalyst, a relation between the log of K_{obs} and the log of [OH] can be plotted to solve for the actual rate constant and the degree of [OH]. The slope of this line represents the exponent of [OH], see equation 1, and the point at x=0 represent log(k). The rate equation for the depolarization of diacetone alcohol in base catalyst is then complete.

Procedure

The NaOH came in a stock solution of 0.3M and 0.4M. It was a clear low viscosity liquid. The HCl came in 0.1M and was a low viscosity liquid. The phenolphthalein came in a 0.1% solution and was a low viscosity liquid. The diacetone alcohol is low viscosity clear liquid.

200 mL of 0.3 NaOH solution and 100 mL of distilled water was added to a 500 mL beaker to prepare a 0.2M NaOH solution. A titration was performed for a solution of 0.2M and 0.3M of NaOH with 0.1M HCl to verify that the correct concentration was prepared. The 0.4 M solution of NaOH was titrated by another group.

In Week 2, large ratios NaOH to diacetone alcohol such as 60 mL of base to 20 mL of alcohol were used. This led to very inaccurate results and so the following week, the ratio of 100 mL of NaOH to 1 mL of diacetone alcohol was used.

In week 3, 100 mL of NaOH was place into a reaction flask. The solution was placed in a $25 \circ C$ thermostated bath (manufactured by VWR Scientific and model 1122) and was left for 15 minutes. 1 mL of diacetone alcohol was added to the same flask and solution was stirred. When the two reagents were combined initially, a clear, yellow tinted solution appeared. Once the flask was secured with the universal clamps, the tint disappeared and the solution was colourless.

The change in volume was recorded in two minute intervals until the volume remained constant. The same procedure was repeated for the 0.2M and 0.3M NaOH solutions. The 0.4M solution was testing by another group. This procedure was created by using the guiding questions to determine the goal of the experiment. The *Kinetics Study of Base Catalysed Diacetone Alcohol Depolymerisation* by David Hewett was used a reference to create a better defined procedure.

Table 1.0 Uncertainty of Instruments

Instrument	**Uncertainty**
40 mL Beaker	± 5 %
400 ml Beaker	± 5 %
10 mL Graduated Cylinder	± 0.1mL
100 mL Graduated Cylinder	± 0.1mL
Burette	± 0.1mL

Results

The trials from week two are not included because no accurate data was obtained. The volume of diacetone alcohol added was too large causing the solution to spill out the top of the dilatometer in less than 6 minutes.

The concentration of th 0.3M NaOH was verified by titrating 10 mL of NaOH with 30.8 mL of 0.1M HCl, refer to Table 1.1. The results showed the concentration of NaOH used for the 0.3M trials to be 0.308 mol/L.

The following table displays the data for the titration for the concentration determination of 0.3M NaOH.

Table 1.1- 0.3M NaOH solution characteristics

Volume of 0.3M NaOH (mL) (titration)	10
Volume of 0.1M HCl (mL) (titration)	30.8
Concentration of HCl (mol/L)	0.1
Concentration of NaOH (mol/L)	0.308

The volume of solution in the dilatometer was recorded at 2 minute intervals until the reaction is complete, refer to Table 1.2. The total volume change was very different for each trial despite using the same amount of reactants. The reaction time varied slightly but was within a reasonable range for the accuracy of the procedure.

The following table displays the volume of the meniscus in the dilatometer at each time interval for 3 trials using 0.3M NaOH catalyst. A ratio of 1 mL of diacetone alcohol to 100 mL of NaOH was reacted at 25.2°C.

Table 1.2- Volume change over time in dilatometer for 0.3M NaOH catalyst

Trial 1		Trial 2		Trial 3	
Time (min)	Volume (mL)	Time (min)	Volume (mL)	Time (min)	Volume (mL)

0	0	0	0	0	0
2	2.8	2	5.4	2	8.4
4	3	4	8.8	4	13.9
6	3.7	6	11.3	6	18.6
8	4.4	8	13.2	8	22.1
10	4.8	10	14.2	10	24.3
12	5.2	11	15.4	12	26.6
14	5.5	13	16.2	14	28.1
16	5.7	15	16.8	16	29.5
18	5.8	17	17.2	18	30.5
20	5.8	19	17.6	20	30.9
22	5.9	21	17.7	22	31.7
24	6	23	17.7	24	31.8
26	6			26	32
				28	32
				30	32.1
				32	32.1
				34	32.1

The 0.2M NaOH stock solution was produced by diluting 200 mL of 0.3M NaOH stock solution with 100 mL of distilled water, its concentration was then verified by titrating 19 mL of 0.1M HCl with 10 mL of 0.2M NaOH solution, refer to Table 2.1. The resulting concentration of NaOH was 0.19 mol/L.

The following table displays the data from the dilution for 0.2M stock NaOH solution and the titration with HCl.

Table 2.1- 0.2M NaOH Characteristics

Volume of 0.3M NaOH solution (mL)	200
Volume of distilled water (mL)	100
Volume of 0.2M NaOH (mL) (titration)	10
Volume of 0.1M HCl (mL) (titration)	19
Concentration of NaOH (mol/L)	0.19

The volume change in the dilatometre were recorded every 2 minutes until the reaction is complete, refer to Table 2.2.

The following table displays the volume of the meniscus in the dilatometer at each 2 minute intervals for 2 trials. A ratio of 1 mL of diacetone alcohol to 100 mL of 0.2M NaOH catalyst was used to react at 25.1 °C.

Table 2.2- Volume change over time in dilatometer for 0.2M NaOH catalyst

Trial 1		Trial 2	
Time (min)	Volume	Time (min)	Volume
0	0	0	0

2	3	2	4.1
4	5.7	4	8
6	6.9	6	10.9
8	8.3	8	13.2
10	9.7	10	15.3
12	10.6	12	17
14	11.5	14	18.5
16	11.9	16	19.7
18	12.7	18	20.7
20	13.2	20	19.7
22	13.7		
24	14.1		
26	14.4		
28	14.6		
30	14.8		
32	14.9		
34	15		
36	15		

The concentration for the 0.4M NaOH solution was verified by titrating the 0.4M stock solution of NaOH with 0.1M HCl, refer to Table 3.1. He results show the NaOH concentration of 0.393 mol/L.

The following table displays the data collected from the titration of 0.4M NaOH and 0.1M HCl.

Table 3.1- 0.4M NaOH solution characteristics

Volume of NaOH (mL) (titration)	4.0
Volume of HCl (mL) (titration)	15.75
Concentration of HCl (mol/L)	0.1

Concentration of NaOH (mol/L)	0.39375

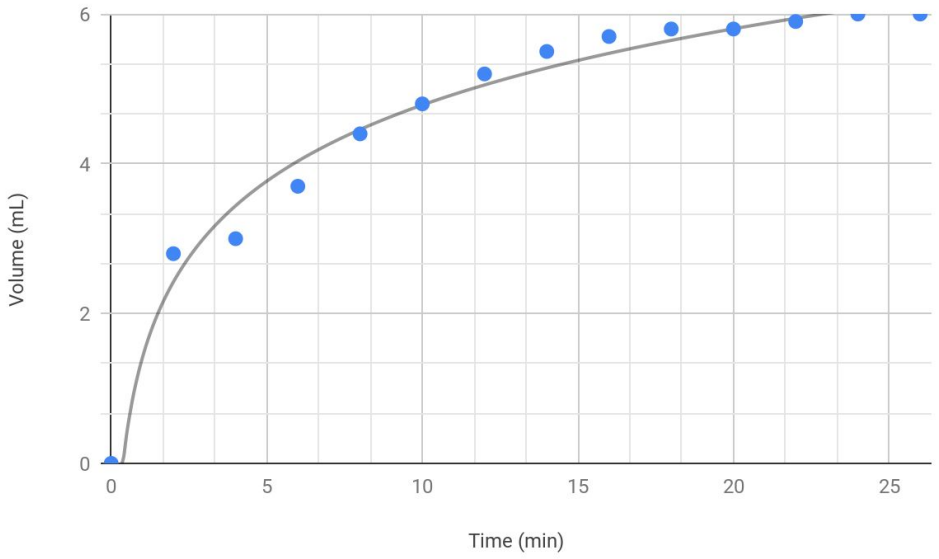
The volume change in the dilatometer were recorded every 2 minutes until the reaction with 0.4M NaOH and diacetone alcohol was complete, refer to Table 3.2.

The following table displays the data collection for the change in volume at the meniscus in the dilatometer at each time interval. A ratio of 0.98 mL of diacetone alcohol to 98.5 mL of 0.4M NaOH was used at 25.2°C. This experiment was performed by another group.

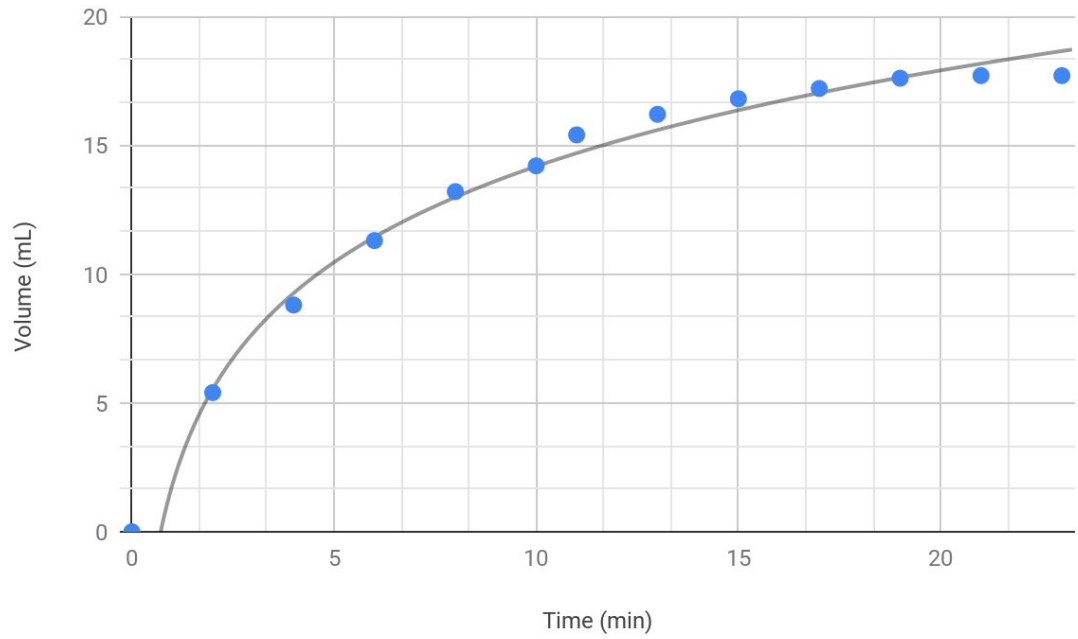
Table 3.2 - Trials of 0.4M NaOH Catalyst

Trial 1		Trial 2	
Time (min)	Volume (mL)	Time (min)	Volume (mL)
0	0	0	0
3	11	2	13
4	15.4	4	21.2
6	20.4	6	26.9
8	23.7	8	30.6
10.38	26.6	10	33.4
11.57	28	12	34.7
14	29.4	14.1	36.1
16	30.2	16	36.8
18	30.6	18	36.9
20	31	20	36.9
22	31.1		
24	31.1		
26	31.1		

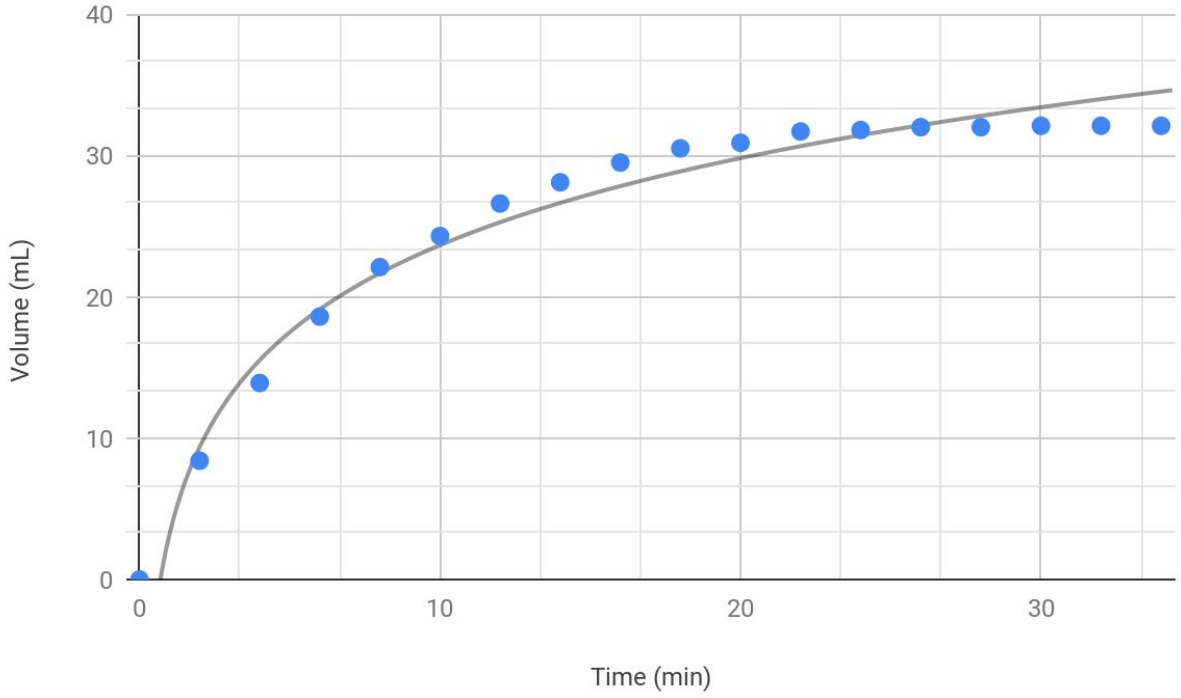
The following graphs, 1.1, 1.2, 1.3. 2.1, 2.2, 3.1, 3.2, display the graphical results for the change in volume over time, the results show a logarithmic trendline for each trial.



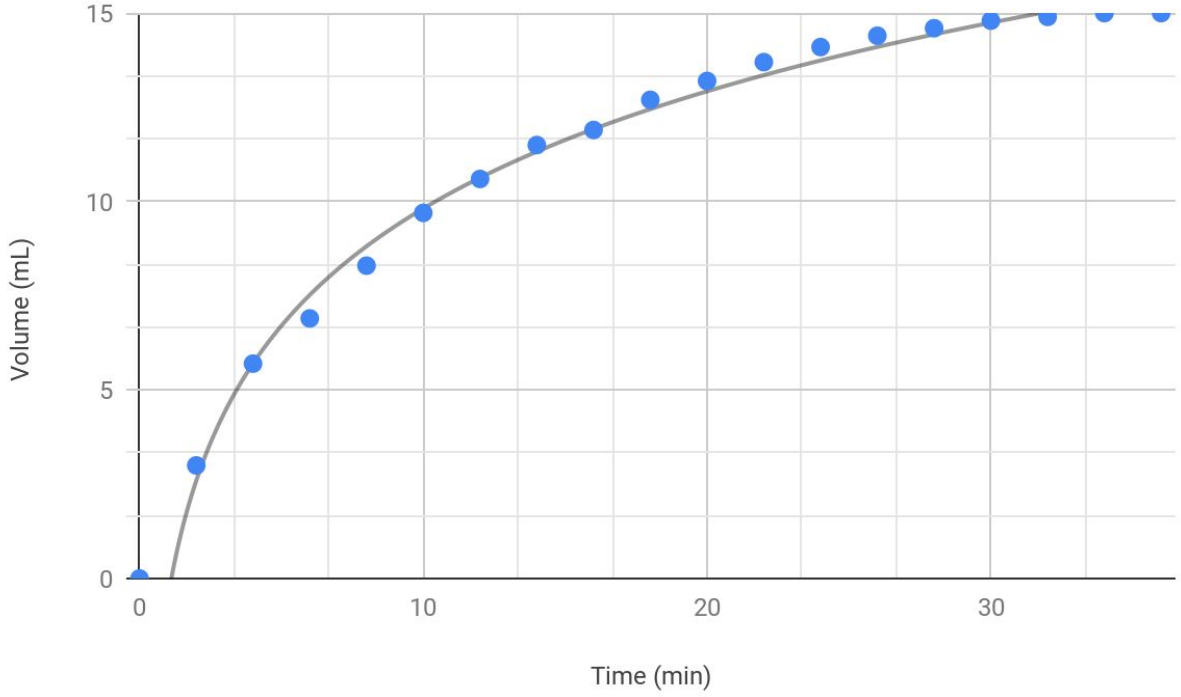
Graph 1.1- Trial 1, Volume change as function of time in dilatometer for 0.3M NaOH catalyst



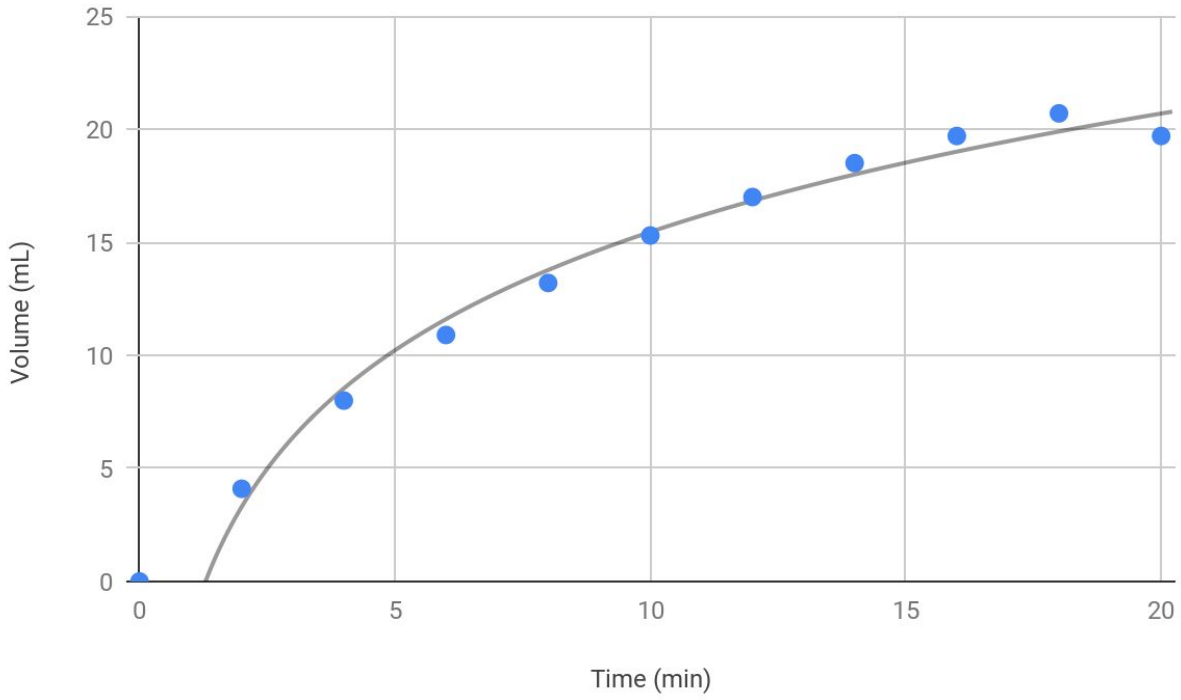
Graph 1.2- Trial 2, Volume change as function of time in dilatometer for 0.3M NaOH catalyst



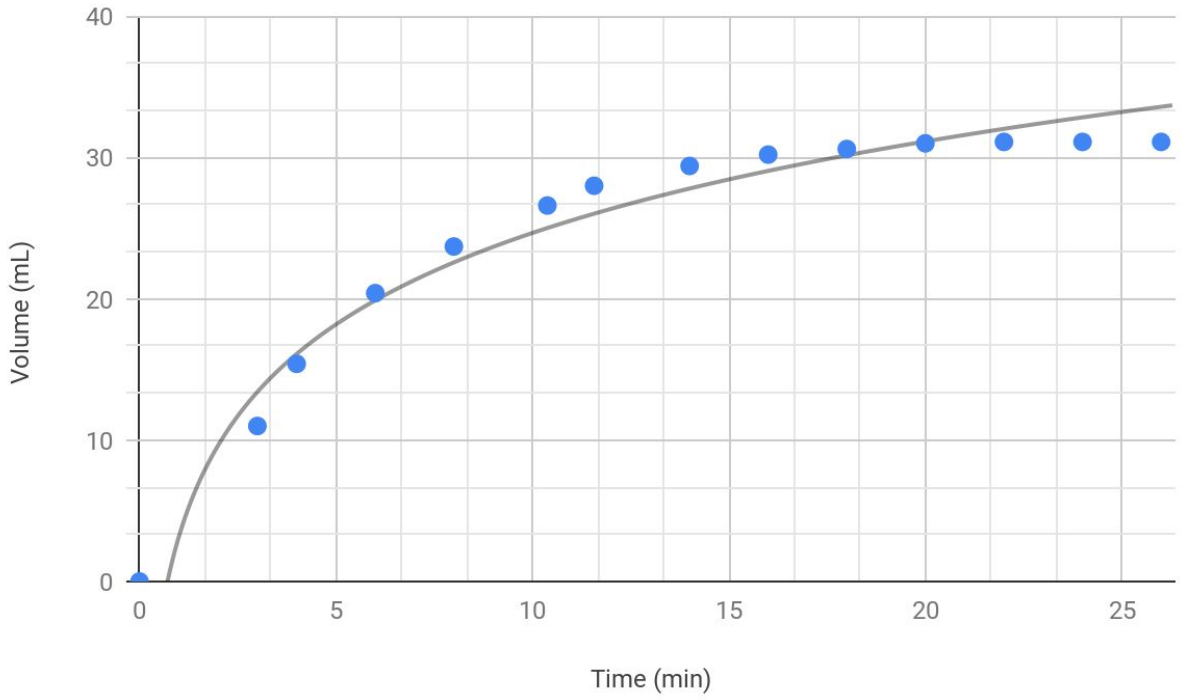
Graph 1.3- Trial 3, Volume change as function of time in dilatometer for 0.3M NaOH catalyst



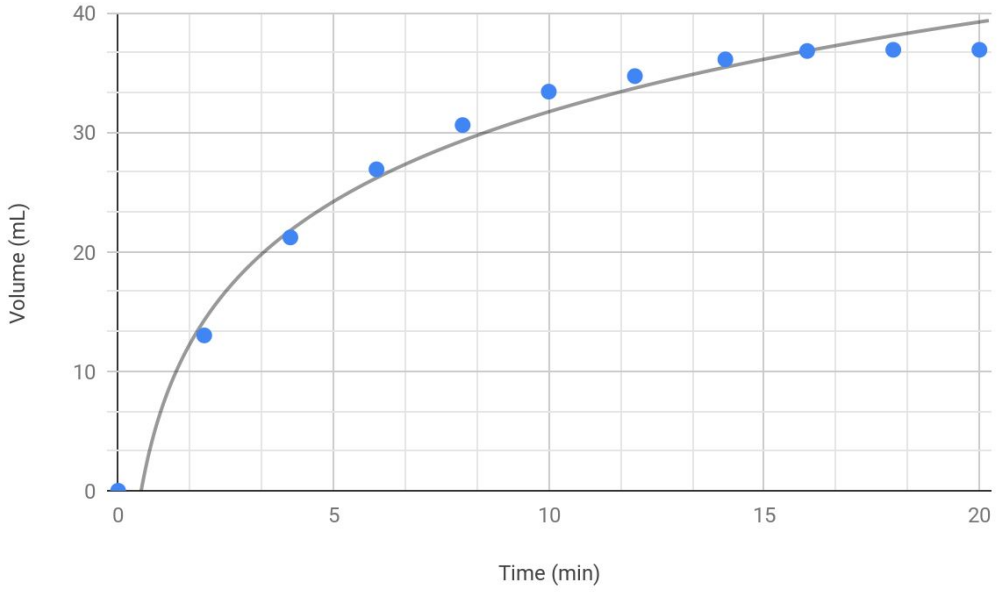
Graph 2.1- Trial 1, Volume change as function of time in dilatometer for 0.2M NaOH catalyst



Graph 2.2- Trial 2, Volume change as function of time in dilatometer for 0.2M NaOH catalyst

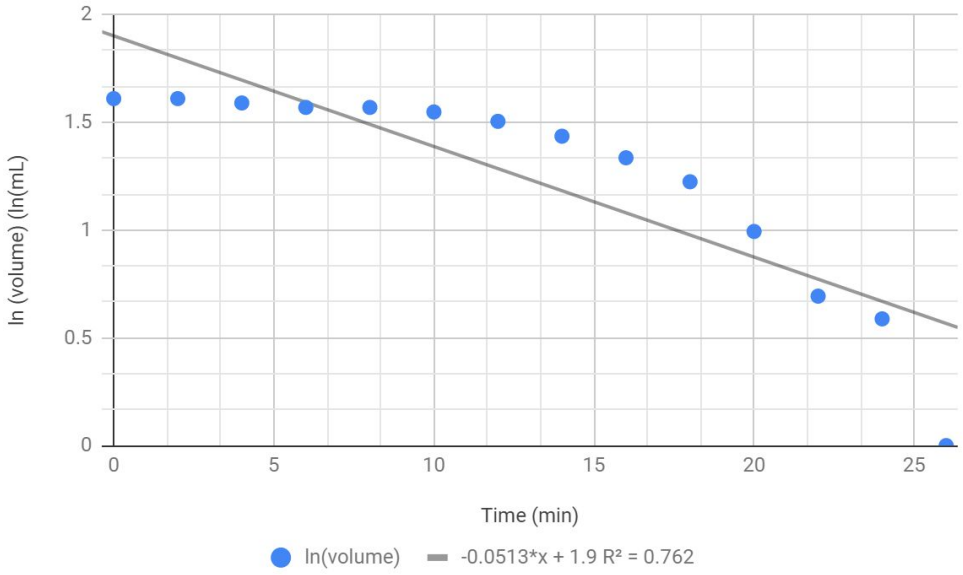


Graph 3.1- Trial 1, Volume change as function of time in dilatometer for 0.4M NaOH catalyst

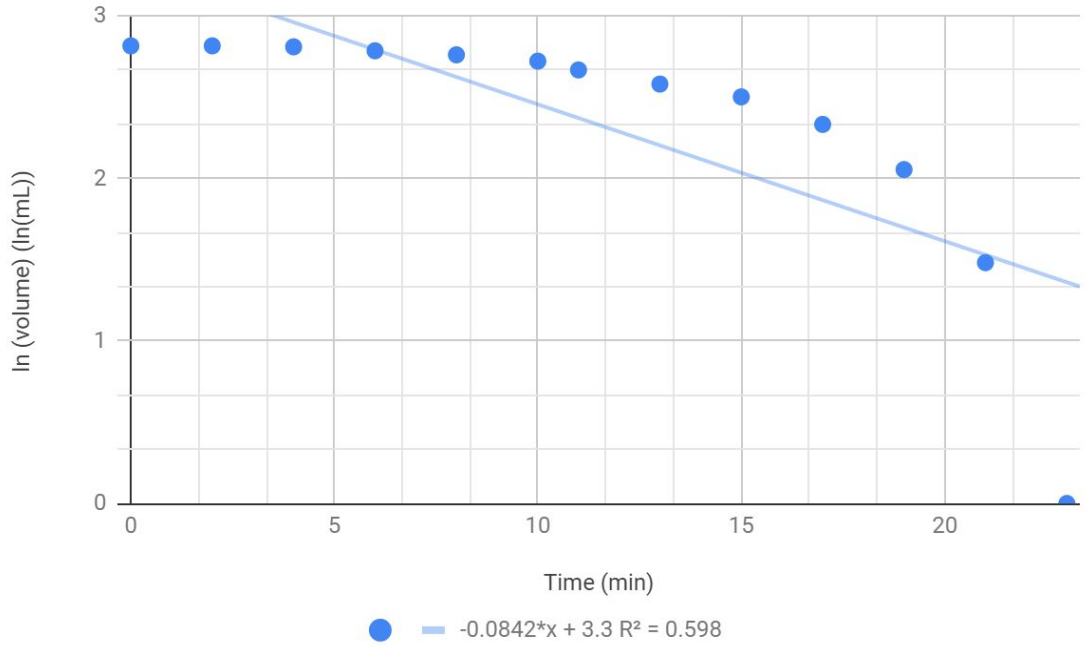


Graph 3.2- Trial 2, Volume change as function of time in dilatometer for 0.4M NaOH catalyst

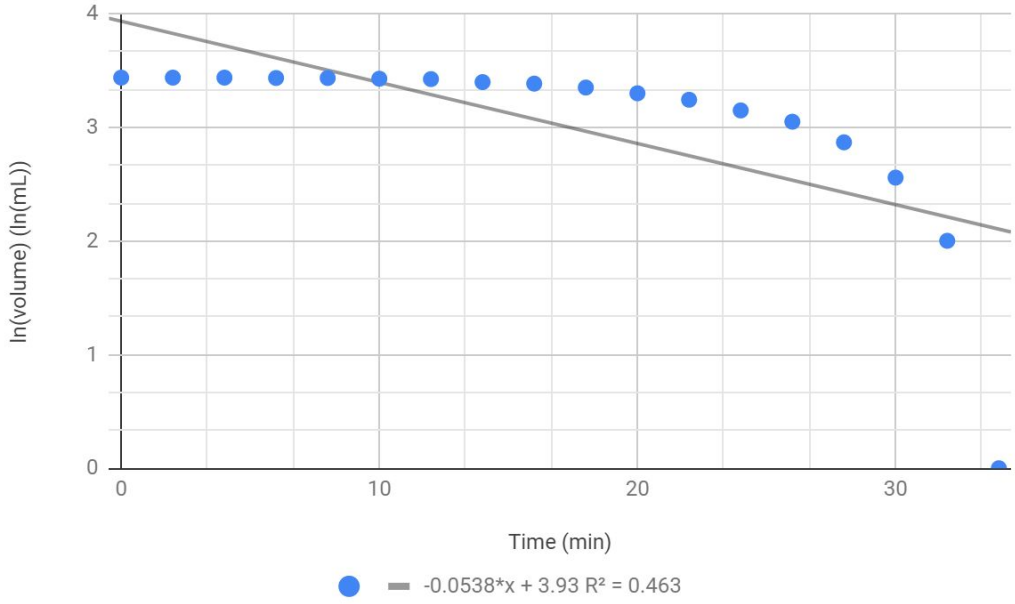
The following graphs, *1.4, 1.5, 1.6, 2.3, 2.4, 3.3, 3.4,* plot the ln of volume change over time to straighten the curves. The slope of the linear trendlines represent the K_{obs} for each of the NaOH catalyst concentrations.



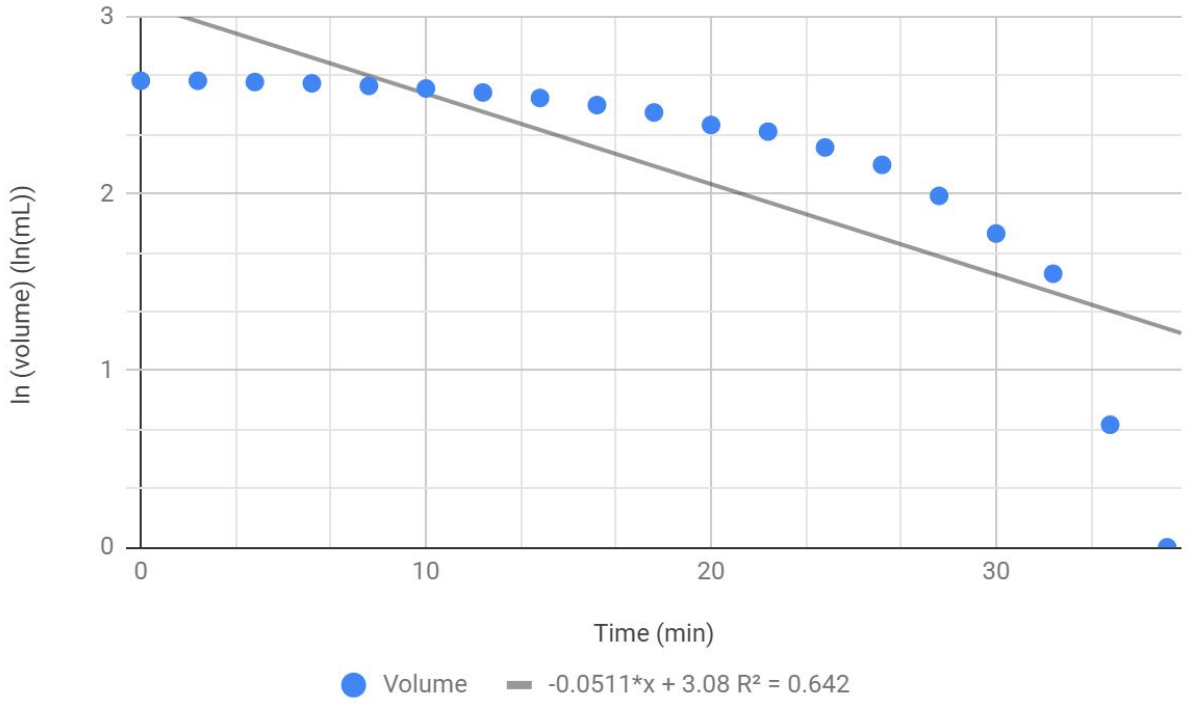
Graph 1.4- Straightened curve for trial 1 of 0.3M NaOH using the ln of volume change as a function of time to solve for Kobs



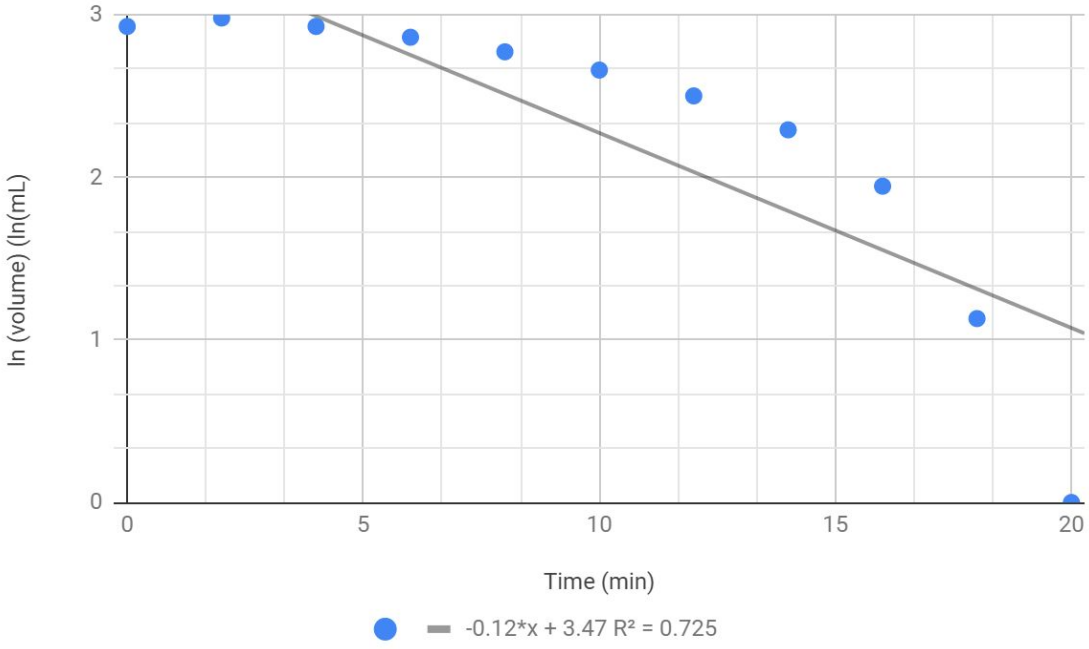
Graph 1.5- Straightened curve for trial 2 of 0.3M NaOH using the ln of volume as a function of time to solve for Kobs



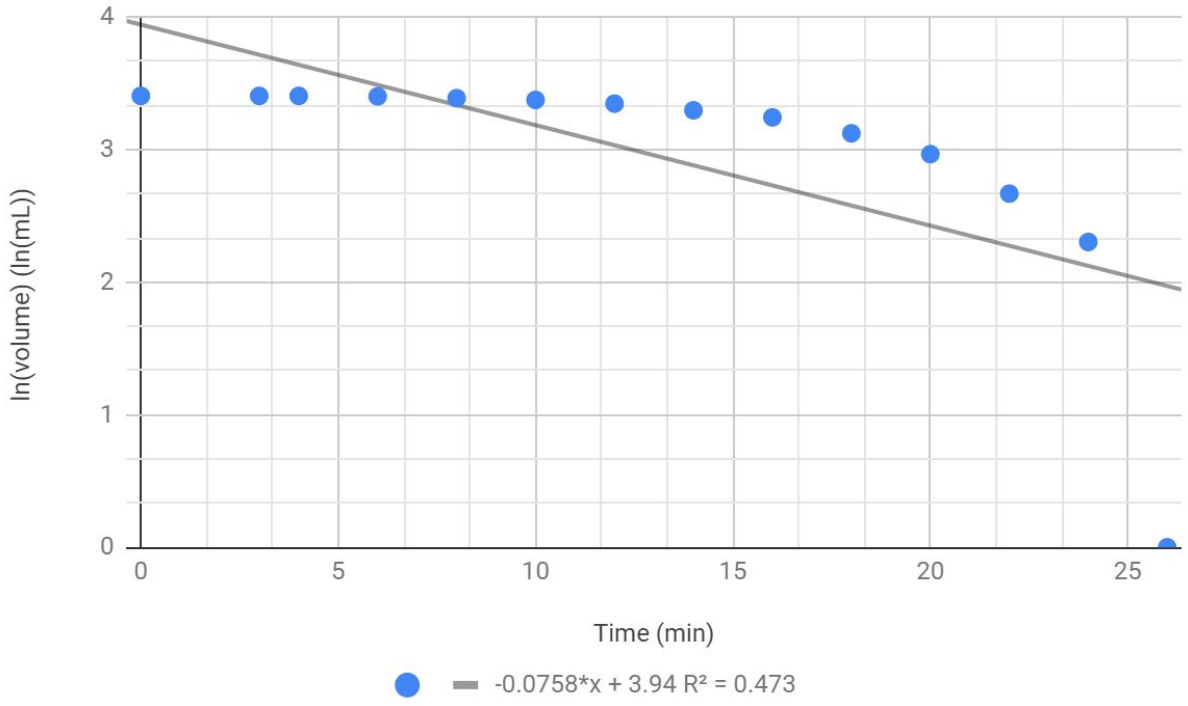
Graph 1.6- Straightened curve for trial 3 of 0.3M NaOH using the ln of volume as a function of time to solve for Kobs



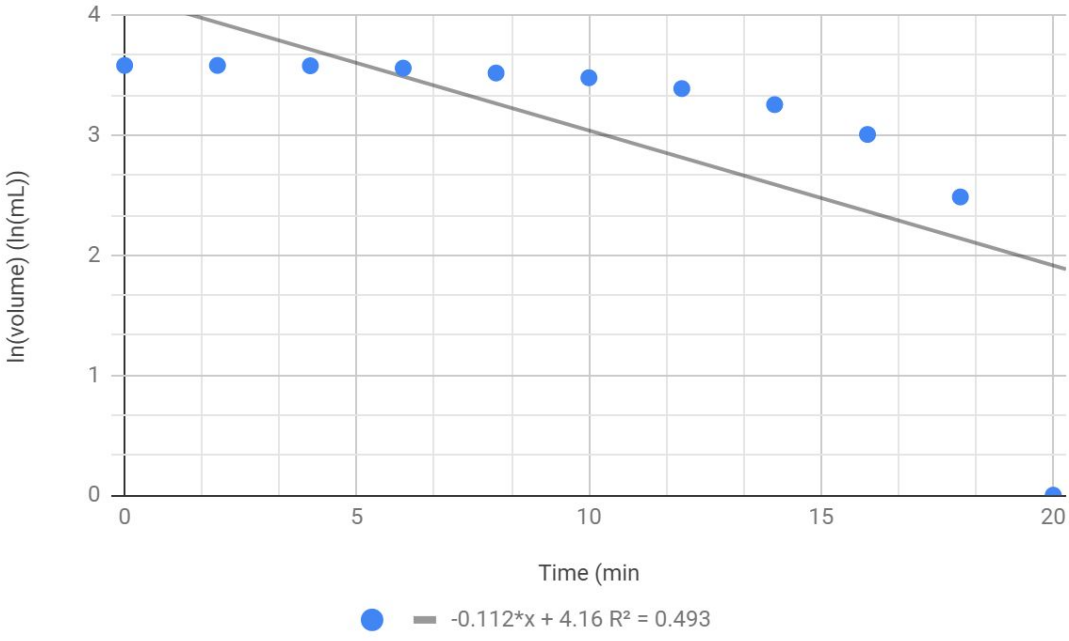
Graph 2.3- Straightened curve for trial 1 of 0.2M NaOH using ln of volume change as a function of time to solve for Kobs



Graph 2.4- Straightened curve for trial 2 of 0.2M NaOH using ln of volume change as a function of time to solve for Kobs



Graph 3.3- Straightened curve for trial 1 of 0.4M NaOH using ln of volume change as a function of time to solve for Kobs



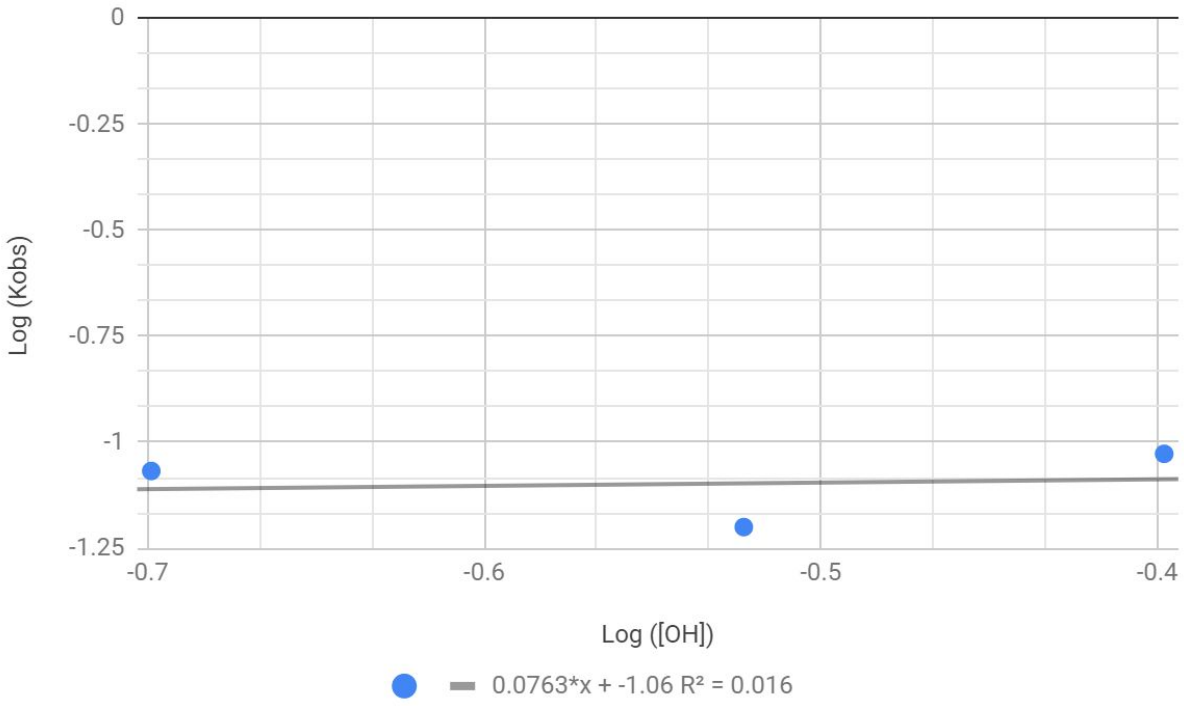
Graph 3.4- Straightened curve for trial 2 of 0.4M NaOH using ln of volume change as a function of time to solve for Kobs

The slopes of the trials for each NaOH concentration were averaged to plot the log of them against the log of [OH].

Table 4.1- Average Kobs values for each concentration based on the slope of straightened curves

[OH]	Average Kobs
0.2	0.08555
0.3	0.0631
0.4	0.0939

The following graph, 4.1, plots the log of the average K_{obs} for each concentration of NaOH catalyst used as a linear function of the log of the OH concentration. The slope of this graph represents the rate constant for the overall reaction.



Graph 4.1- The log of the Kobs for each concentration as a function of the log of the OH concentration to solve for the exponent m

The slope of this graph represent the exponent m for [OH] in the rate equation and is 0.0763. The y-intercept at -1.06 represent the log(k) of the rate equation.

Calculations

Calculation for k from y-intercept:

log(k)=0.0763 (0) -1.06

log(k)= -1.06

K = 0.0871

Calculation for average K_{obs}

Average K_{obs}=(0.112+0.0758)/2

= 0.08555

Discussion

The reaction that was observed was depolymerization. In this experiment, the aldol molecule dissociated into ketones. The hydroxide ion deprotonated the alcohol to form an acid. The to stabilize itself, the oxygen formed a double bond and expelled the the ketone. The acid stabilized the carbocation that was formed to create two acetone molecules. To see the full mechanism, please refer to f*igure 1.1* in the introduction. This reaction is typically reversible but due to the excess of the strong base catalyst, the reaction was shifted towards the production of the ketones. The purpose of this experiment was to observe the kinetics of the reaction and determine the constant of the reaction ($k_{observed}$) and the order of the reaction.

In titrating the NaOH solutions, the results showed that the concentrations labelled on the bottles were correct. The concentration of the 0.3M NaOH was found to be 0.308M. The result showed that 0.2 M NaOH solution actual concentration was 0.19M. In the graphs 1.1 to 3.2, the time versus the volume change is recorded. In these graphs, the hypothesized logarithmic

trendline is observed. However, the data varied greatly between each individual trial. This combined with the low R^2 values indicates that there were some errors in the experiment. Although the values observed were inconsistent, they were plausible and used to determine the K constant and exponent of the rate equation. In the graphs, the slope represents the m exponent and the k is represented by the y- intercept. The final K value based on the experimental results is 0.0871. The value of m calculated was 0.0763. There was no literature available to compare theoretical values of K or m. But based on the amount of errors and setbacks as discussed in the section below, it is most likely that the K value and the m exponent are not correct. In the graphs *1.4, 1.5, 1.6, 2.3, 2.4, 3.3, 3.4* show the straightened curves of the ln(volume)/time graphs. These straight lines represent the slope of the $K_{observed}$ for each NaOH catalytic concentrations.

In the first week of the experiment, no useful data was obtained. This occurred because of the large amounts of alcohol and catalyst that were used. The mencius would overflow and the whole reaction would take less than six minutes to complete. The large ratios were cause the reaction to happen very quickly. This in combination with the small measurements of burette made it impossible to observe the full reaction. To correct this, the following week, a smaller ratio of 100 ml of NaOH was used with 1 ml of diacetone alcohol.

Inaccurate readings of the change in volume in the capillary were a source of error in the experiment. The change in volume was too small to read with the equipment provided. Due to human error in the readings, an inaccurate change in volume was observed. The physical setup of the experiment also affected the results. The reaction began as soon as the catalyst and alcohol were combined but the recording of the volume change did not start at the same time. This

happened because the meniscus had to be found and the dilatometer had to be set up again. This is resulted in an inaccurate timing of the reaction. Inconsistent temperature readings might have also impacted the results of the experiment. Although the thermostated bath was set to 25 $\circ C$, it was observed that the temperature of the water between the two tanks was inconsistent. This could have been resolved by using a physical thermometer to verify that the temperature was accurate. The main experimental shortcoming resulted from human error. The inability to accurately record the initial start time of the reaction and read the values correctly caused results that could only be approximated. This could be improved by using a dilatometer that allows the two chemicals to be mixed without manipulating the set up of the experiment.

Conclusion

In conclusion, the rate equation found is equation 5.

$$-\frac{d}{dt} = (0.0871)x[OH]^{0.0763} \quad (5)$$

The actual rate constant was found to be 0.0871 and the exponent for the concentration of OH was 0.0763. The volume as a function of time gave the proper logarithmic relationship when graphed but varied between trials of each concentration. When straightened, the relationships were slightly linear but based on the low R^2 value on each graph, the relationship was weak. The average slopes were found to be 0.08555 for a OH concentration of 0.4M, 0.0631 for a OH concentration of 0.3M, and 0.0939 for a OH concentration of 0.2M. The log of these values were then plotting versus the log of their OH concentration for a linear trendline to solve for the OH

exponent m and the actual rate constant k. The trendline between the point had a very small positive slope of 0.0763 representing the OH exponent in the rate law. The graph had a y-intercept at -1.06 and k was solved using the log(k) to find a rate constant of 0.0871. Although the values for the experiment are skewed with high error the general trends align with those assumed in the introduction. The numbers are all physical plausible and show that the volume change of the reaction mixture is proportional to the concentration change and can therefore be used to solve for the overall rate equation of the depolarization of diacetone in alcohol in excess NaOH catalyst.

References

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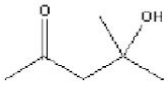
Experiment N
Kinetics of the Depolymerization of Diacetone Alcohol via Basic Catalysis

The empirical rate equation of the depolymerization of diacetone alcohol (**1**) via basic catalysis is:

$$-\frac{\partial x}{\partial t} = kx^n [OH^-]^m \quad (1)$$

where k is the rate constant, and the exponents n and m are the order of the reaction with respect to the diacetone alcohol of concentration x and to the hydroxyl ions.



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Goal

The goal of this experiment is to determine the hydroxy-dependent rate constant k_{obs}, the value of the exponent m and the rate constant k.

Available Materials and Equipment

- Diacetone alcohol
- 0.3 M NaOH solution
- 0.4 M NaOH solution
- 0.1 M HCl solution
- Phenolphthalein
- Dilatometer
- Thermostated baths
- Burette

Guiding Questions and Answers

1. What is the rate law when hydroxide ions are present in excess?

$$-\frac{\partial x}{\partial t} = kx^n$$

2. Write a simple expression for the hydroxyl-dependent rate constant k_{obs}.

$$k_{obs} = k[OH]^m$$

3. What rate law results if you assume the reaction is first order with respect to diacetone alcohol.

$$-\frac{dX}{dt} = k_{obs} X$$

4. Give the integrated rate law of the pseudo-first-order rate law determined in question 3:

$$-k_{obs} t = \ln\left(\frac{X}{X_0}\right)$$

5. How can you determine the value of k_{obs}?

Solve if initial and final concentrations are known over a specific period of time

6. What calculations or graphical analysis are required to determine the rate constant k and the order of the reaction with respect to $[OH^-]$?

Using experimental data, graph concentration vs. time, using functions for each order, find which will straighten the curve, that will be the order of reaction. ($[X]_0 - [X]_t$, 1st - $\ln(x)$, 2nd $1/x$) The slope of the linear curve will be K, the rate constant.

7. How can you determine the rate of the depolymerization of the diacetone alcohol given the available materials and equipment listed above? Which physical property could you monitor? (Hint: consider the reaction stoichiometry too).

Procede the reaction in the dilatometer with a known initial volume and volume would be monitored and recorded at times to solve for the rate

$$\ln(V_t - V_\infty) = -k_{obs}t$$

8. How can you determine what volumes of NaOH and diacetone alcohol to mix in order for the reaction to be complete in about two hours? (Hint: remember that the reaction mixture must contain a large excess of NaOH). In which order should you mix the reagents?

Based on a ratio of 1:100 taking approximately 30 min, reduced the ratio to 1:25 should take about 2 hours. you should add the alcohol to the ~~temperature set~~ base.

9. Give the volumes of NaOH and diacetone alcohol that you have determined to satisfy the above conditions:

We used 1 mL of diacetone alcohol to 100 mL of NaOH, reactions did not go for 2 hours.

10. Do you need to know the change in concentration with time of the alcohol to determine the rate constant k_{obs} or can you use another variable that is directly proportional to this concentration and more straightforward? If you need to know the actual concentrations, how will you determine them? What experimental data must you obtain and what calculations or graphical analysis are necessary? (Hint: refer to your answer to question 7).

Volume can be used instead of concentration since it will be measured by the meter. once you have the changes in volume at each time, the k_{obs} can be observed from graphing the data since the slope of the curve is k_{obs}

11. The thermostated bath temperature is set at 25°C. Why is it important to maintain the temperature of the reaction constant?

Rate is dependent on temperature therefore it must be kept constant analyse the rate

12. What NaOH concentrations could be used to determine the rate constant and order of the reaction?

The concentration used are 0.2M, 0.3M and 0.4M

13. How frequently and for long should you monitor the reaction?

Reaction should proceed for about 2 hours and volume should be taken every 5minutes

14. In your procedure, what should you be particularly careful about in order to obtain accurate and reproducible results?

The initial volumes added should be measured very precisely to ensure the results are exact. Also the water bath must be used to ensure constant temperature to not change the rate constant during the experiment.

Discussion

Give a mechanism for the depolymerization of diacetone alcohol via basic catalysis that is supported by experimental data collected.

Mechanism for reaction is found in introduction.