CHM 2123 Section E
Kinetic Study of Nucleophilic Substitution
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September 27, 2019

Introduction 12/12

This experiment examines the rate of the reaction; part A determines the effect of a leaving group on the rate of a substitution reaction, and part B determines the effect of a solvent on the rate of a substitution reaction.

The rate of a reaction can be expressed by the equation $\mathrm{r} = \mathrm{k}[A]^x[B]^y$ where $A + B \rightarrow C + D$, k is the rate constant and x and y are the orders of the reaction; the sum of x and y is the overall order of the reaction. In part A the order of the reaction is dependant on the concentration of KOH and in part B the order is dependant on the concentration of tBuCl. The order of the reaction can be expressed as $\frac{d[A]}{dt} = -k[A]^x$ where x is the order, 0, 1 and 2 respectively and t is the time. These equations are referred to as the rate laws and can be used to determine k by plotting [A] v. t, ln[A] v. t and 1/[A] v. t respectively. Whichever equation can be plotted as a straight line corresponds to the order of the reaction and k is equal to the slope of that line multiplied by negative one.

A nucleophilic substitution reaction occurs when a nucleophile replaces a leaving group on a carbon atom. Two common substitution reactions are SN1 and SN2 reactions. These are abbreviations where S is substitution, N is nucleophilic, and the number refers to whether the reaction is unimolecular or bimolecular. In the SN1 reaction the rate is determined by the concentration of one molecule and the reaction occurs in two steps (the first being the rate determining step), whereas in the SN2 reaction the rate is determined by the concentration of two molecules and the reaction occurs in one step. The first step of the SN1 reaction is the formation of a carbocation upon removal of the leaving group, therefore an SN1 reaction requires either a tertiary alpha carbon or a resonance stabilized alpha carbon to form a sufficiently stable carbocation. Since the SN2 reaction occurs in one step it generally requires a primary alpha carbon so that it is able to approach from the opposite side of the leaving group without steric hindrance. These “requirements” categorise 1-chlorobutane and 1-bromobutane as SN2 reagents and tBuCl as an SN1 reagent. In addition, SN1 reactions favour weak bases and polar protic solvents while SN2 reactions favour strong bases and polar aprotic solvents.

In part a of the experiment reflux is used to maintain the high temperature required for the reaction of 1-bromobutane (or 1-chlorobutane) and KOH without losing substances as vapour. Reflux requires the use of a condenser, a glass tube with a cold jacket that has cool water running through it. The condenser is connected to a round bottom flask containing the reactants, underneath the flask is a thermowell that heat the contents of the flask. If the contents of the flask evaporate they rise into the condenser where they are cooled and condense back into the flask. In addition, a magnetic stir bar can be placed inside the flask to further assist the reaction.

As the reaction of 1-Bromobutane and KOH progresses, the progress is measured using titrations. The mixture of reactants is basic and adding phenolphthalein results in a pink appearance, as HCl is added the colour becomes lighter until it is clear, indicating that the mixture has been neutralised. As the reaction progresses and there are less reactants present in the flask, the amount of HCl required to neutralise the mixture decreases. This makes it possible to quantify the amount of products in samples at different times throughout the reaction and determine the rate of the reaction. The HCl reacts with the KOH with a 1:1 ratio so by calculating the moles of HCl titrated the moles of KOH which reacted is found and since the volume of the aliquot is known the concentration of KOH can be calculated for each time in the reaction.

In part b of the experiment the hydrolysis of tBuCl is compared in a solvent ratio of 70:30 H_2O:Acetone vs 85:15 H_2O:Acetone. For each solvent the time taken to reach 10%, 20%, 30% and 40% completion (controlled by the amount of NaOH). HCl is a byproduct of the reaction so the time taken to reach the % completion can be observed by adding bromothymol blue to the mixture and taking note of when the indicator changes colour (indicating the mixture is acidic). The concentration of tBuCl can be calculated by multiplying the initial concentration by the percentage not consumed (100%-completion).

<u>Mechanism</u>

Figure 1.a: Mechanism for 1-bromobutane with potassium hydroxide (SN2)

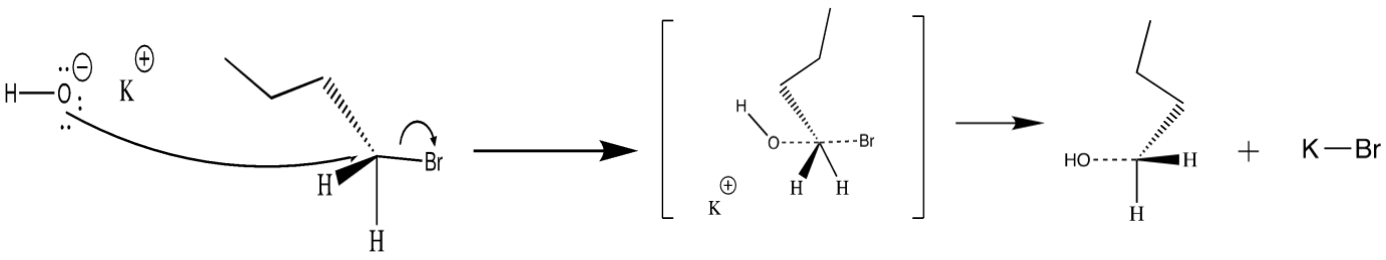

Figure 1b: Mechanism for 1-chlorobutane with potassium hydroxide (SN2)

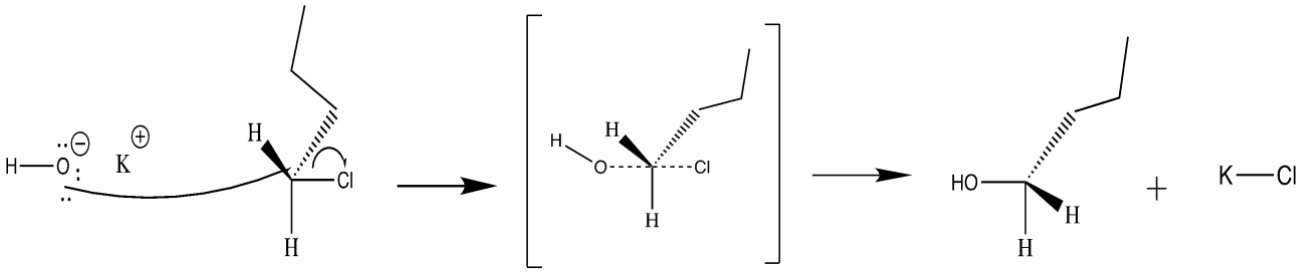

Figure 1.c: Mechanism for tBuCl with water (SN1)

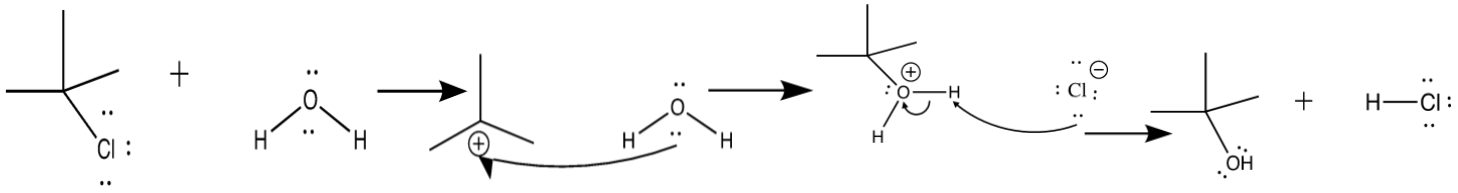

Table of Reagents

Table 1.a.: Part A reagents involved in the reaction 4/4

Reagent	Molar Mass (g/mol)	Quantity	Density (g/mL)	Mmol	Equivalent
1-Bromobutane	137.02	40 mL	1.27	20	1
KOH	56.106	10 mL	2.04	20	1
EtOH	46.07	5 mL	0.789	85.1	-

Table 1.b.: Part B reagents involved in the reaction

Reagent	Molar Mass (g/mol)	Quantity (mL)	Density (g/mL)	Mmol	Equivalent
Distilled Water	18.01	12.5	1.00	694.4	25.5
tBuCl	92.57	3	0.9	27.3	1
Acetone	58.08	3	0.791	40.7	-
NaOH	39.997	1.5	2.13	80.3	2.9

Protocol

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The experimental procedure of this experiment for both part A & B can be found on TopHat in the Experiment 2 rubric.

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Observation & Results 4/4

Table 2.a: Observations obtained from part A and B of the experiment

1-Bromobutane and KOH- Part A Physical characteristics of the substances	**Observation:** - Both KOH & 1-bromobutane were collected and observed to be of a colorless liquid.
Reflux- Part A: Reaction mixture reaching reflux	**Observation:** - It was remarked the formation of bubbles and the volumetric flask was found to be very hot
Titration- Part A: Once the titration materials were all set up, 2-3 drops of Phenolphthalein were added to the solution	**Observation:** - The addition of Phenolphthalein drops caused the solution to turn into a light-ish pink color
Titration- Part A: In order to know when to stop adding HCL	**Observation:** - The light-ish pink color changed to a cloudier transparent color
Indicator- Part B: Addition of bromothymol blue indicator drops	**Observation:** - The addition of bromothymol blue indicator drops caused the transparent solution to turn into a blue color
Hydrolysis of tBuCl- Part B: Repetition of the hydrolysis by 20, 30 & 40% (85:15 H2O : Acetone)	**Observation:** - The time needed for the change in color was observed to be dependent of the percentage conversions. As, the percentage conversions increased, the change in color would occur much later.

Table 2.c: Concentration of KOH at different times (1-bromobutane)

Reaction time (min)	2	15	30	45	60
V aliquot (mL)	5.0	5.0	5.0	5.0	5.0
Vinitial HCL (mL)	0.0	14.5	7.0	10.9	10.5
Vfinal HCL (mL)	14.5	23.8	14.8	16.9	15.8
ΔV (Vfinal-Vinitial) HCL (mL)	14.5	9.30	7.8	6.00	5.30
Moles of HCL titrated*(mol)	$1.45x10^{-3}$	$9.30x10^{-4}$	$7.8x10^{-4}$	$6.00x10^{-4}$	$5.30x10^{-4}$
Moles of KOH neutralized in the titration* (mol)	$1.45x10^{-3}$	$9.30x10^{-4}$	$7.8x10^{-4}$	$6.00x10^{-4}$	$5.30x10^{-4}$
[KOH] neutralized * (mol/L)	0.29	0.186	0.16	0.120	0.106
LN[KOH] (mol/L	-1.24	-1.68	-1.83	-2.12	-2.24
1/KOH M^1	3.44	5.38	6.25	8.33	9.43
Class Average *(mol/L)	0.231	0.196	0.148	0.130	0.107

**sample calculations would be provided*

Table 2.c.: Average time and concentration obtained at 70:30 H2O:Acetone

% Conversion	10%	20%	30%	40%
0.10 M tBuCl in acetone	3.0 mL	3.0 mL	3.0 mL	3.0 mL
0.02 M NaOH in water	1.5 mL	3.0 mL	4.5 mL	6.0 mL
Distilled Water	15.5 mL	14.0 mL	12.5 mL	11.0 mL
Time to colour change #1 (s)	8.59	19.02	50.07	60.02

Time to colour change #2 (s)	5.50	23.23	56.64	60.34
Time to colour change #3 (s)	4	18.54	60.21	>600
[tBuCl] remaining in solution (M)	0.0135	0.012	0.0105	0.009
Ln([tBuCl]) (M)	-4.305	-4.423	-4.556	-4.711
1/ [tBuCl] (M^-1)	74.07	83.33	95.24	111.11
Average time of trials 1-3 in seconds (personal data)	6.03	20.26	55.83	78
Average time of trials 1-3 (Group data)	13.63	27.14	55.73	82.69

Table 2.d: Average time and concentration obtained at 70:30 H2O:Acetone

% Conversion	10%	20%	30%	40%
0.10 M tBuCl in acetone	3.0 mL	3.0 mL	3.0 mL	3.0 mL
0.02 M NaOH in water	1.5 mL	3.0 mL	4.5 mL	6.0 mL
Distilled Water	12.5 mL	11.0 mL	9.50 mL	8.0 mL
Acetone	3.0 mL	3.0 mL	3.0 mL	3.0 mL
Time to colour change #1 (s)	35	180	290	594
Time to colour change #2 (s)	47	120	>600	607

Time to colour change #3 (s)	34	85	-	-
[tBuCl] remaining in solution (M)	0.0135	0.012	0.0105	0.009
Ln([tBuCl]) (M)	-4.305	-4.423	-4.556	-4.711
1/ [tBuCl] (M^-1)	74.07	83.33	95.24	111.11
Average time of trials 1-3 (personal data)	38.67	128.33	290	615.5
Average time of trials 1-3 (Group data)	40.42	102.23	195.36	303.06

- *: no more time*

Calculation 3/4

Calculations Part A:
The following data are taken from the 2-minutes column

Sample Calculation of Moles of HCL Titrated

V=14.5 mL = 0.0145 L
n=c/v
n= 0.1/0.0145
n=1.45x10^{-3} moles of HCL

Sample Calculation of Moles of KOH Titrated

It is a 1:1 ratio, therefore their number of moles is equivalent, meaning they have the same value of moles

n=1.45x10^{-3} moles of KOH

Sample Calculation of [KOH] neutralized

Aliquot Volume= 5mL = 0.005 L
c=n/v
c= 1.45x10^{-3}/ 0.005
c= 0.231 mol/L

reaction order? rate

Calculations Part B:

The following data are taken from the 10% conversion

Sample Calculation of [tBuCl] remaining in solution (M) / Zero Order

c1: 0.1 v1: 0.003 L c2: ? v2: 0.020 L

c1v1=c2v2

(0.1 x 0.003) = (c2 x 0.020)

c2= 0.015 M

→ As the data chosen was the 10% conversion, the remaining [tBuCl] is calculated to be:

1) 100%-10%=90%
2) remaining [tBuCl] = 0.90 x 0.015 = 0.0135 M

Sample Calculation of Ln([tBuCl]) / First order & 1/[tBuCl]/Second order

1) Ln[0.0135]= -4.305 M
2) 1/ [0.0135]= 74.07 M^-1

Graph

Part A

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Figure 2.a: Graph of the zero order reaction rate of 1-bromobutane/1-chlorobutane

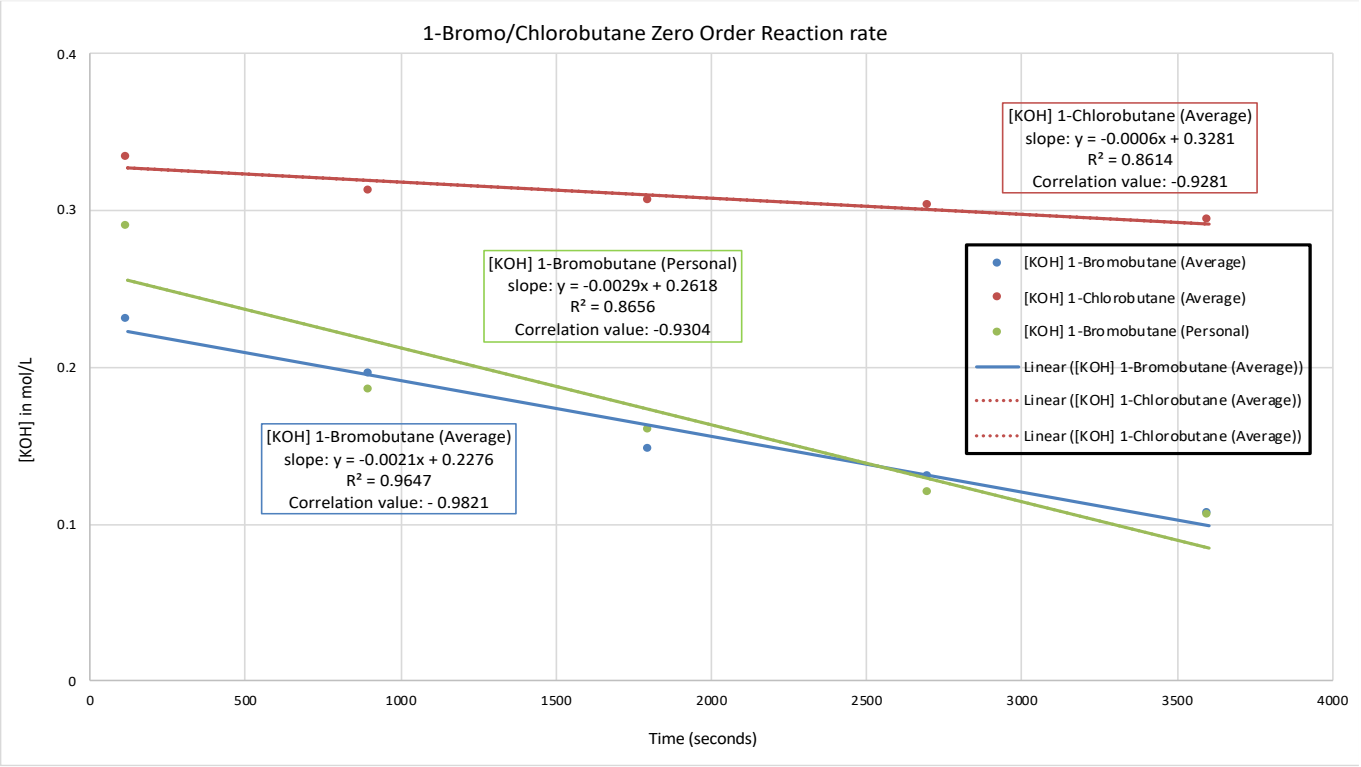


Figure 2.b: Graph of the first order reaction rate of 1-bromobutane/1-chlorobutane

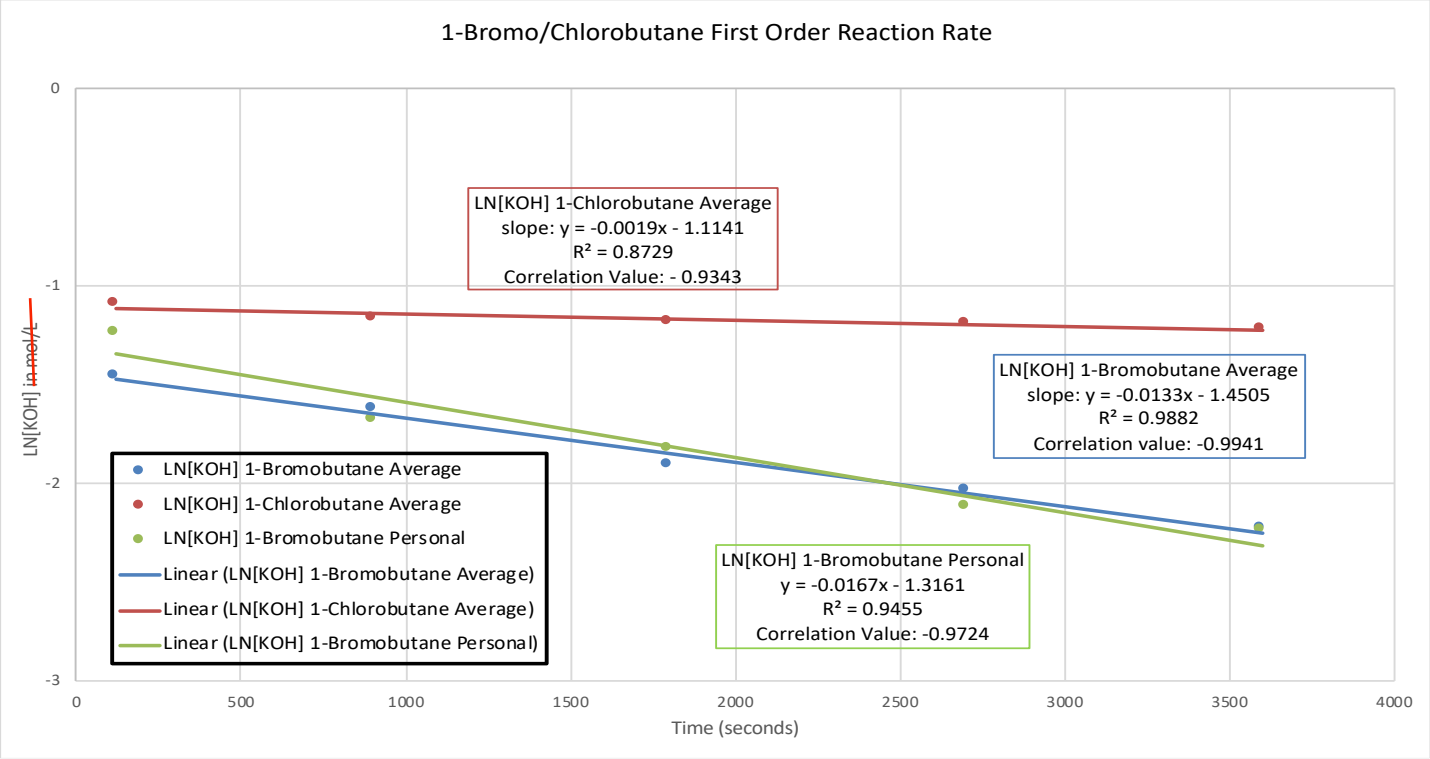
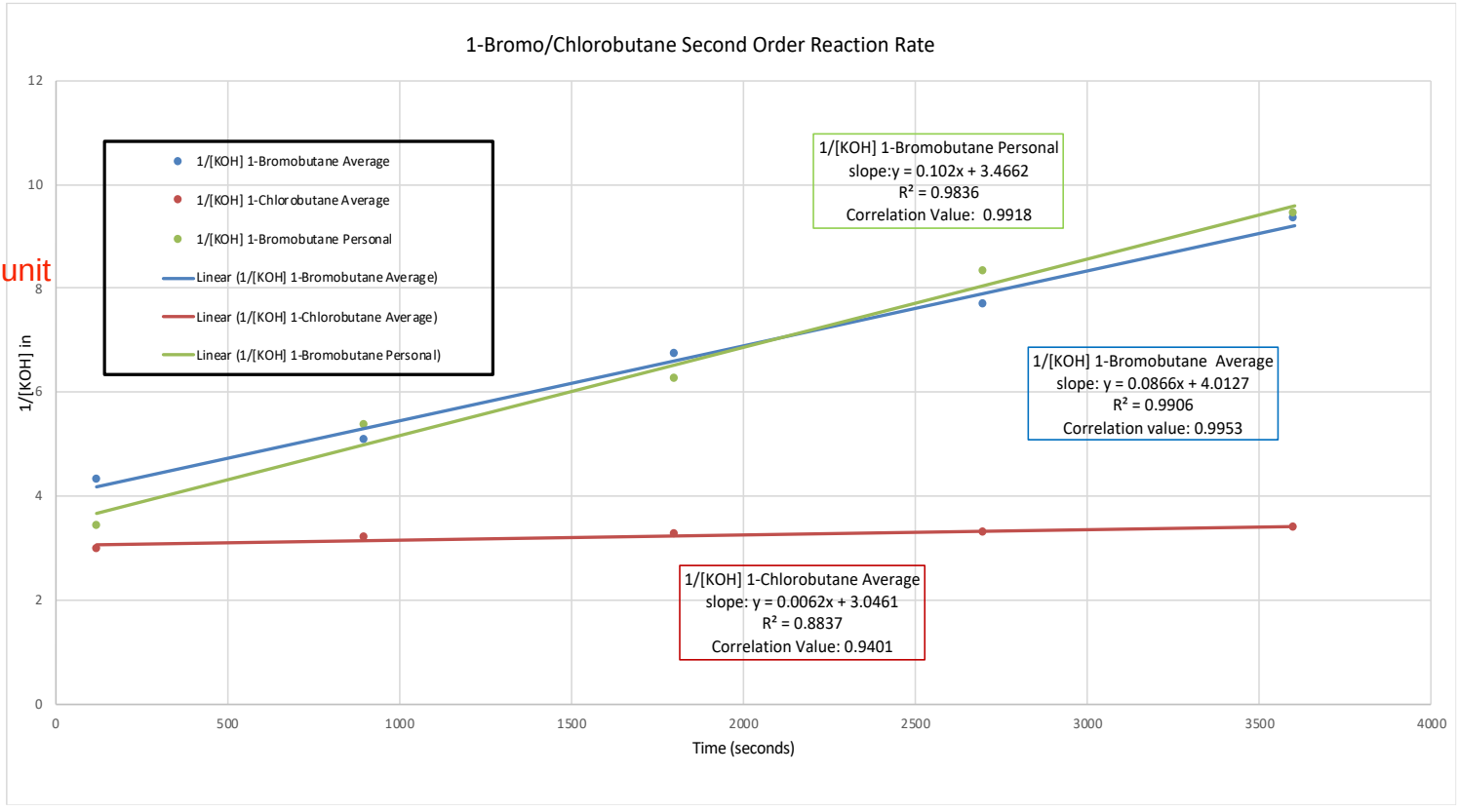


Figure 2.c: Graph of the second order reaction rate of 1-bromobutane/1-chlorobutane



Part B

Figure 3.a: Graph of the zero order reaction average rate

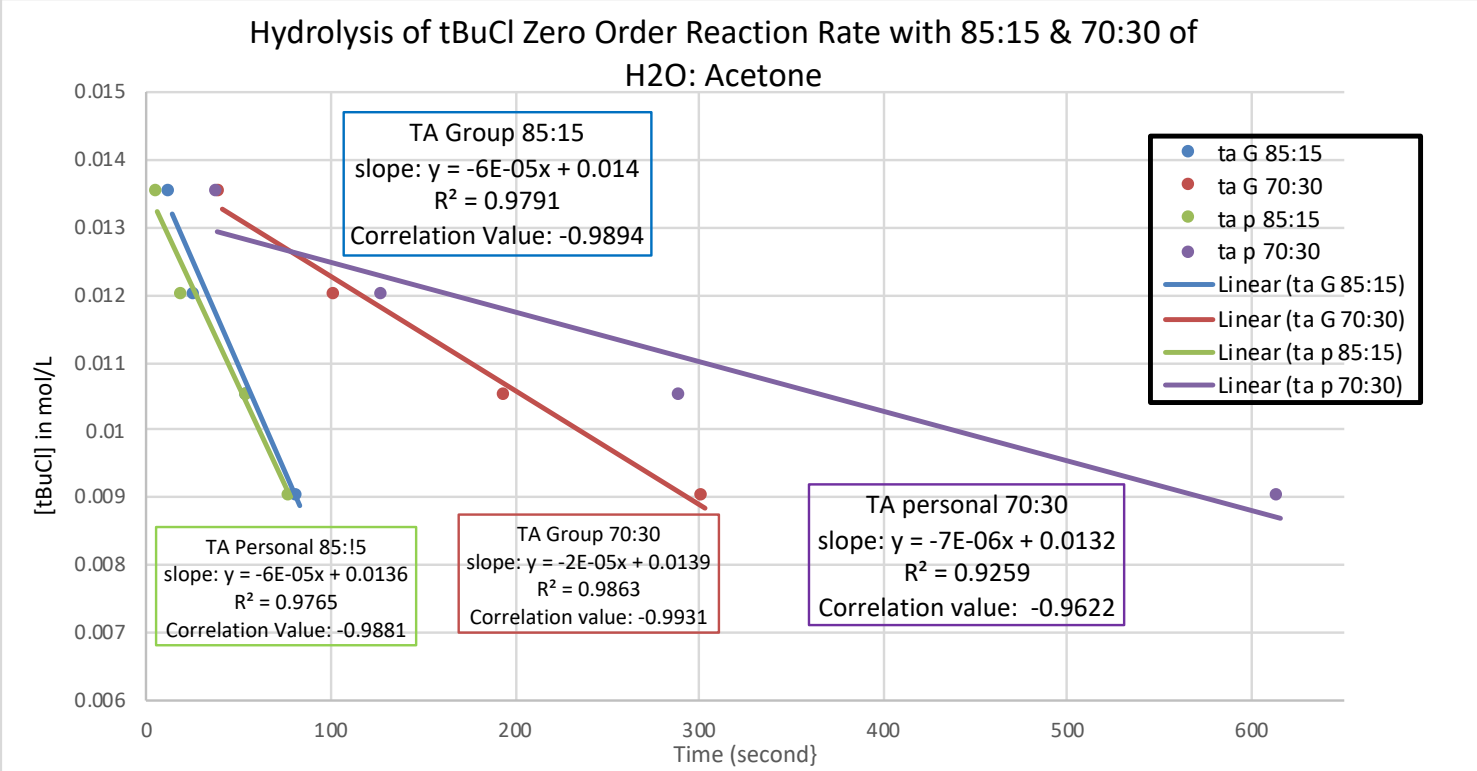
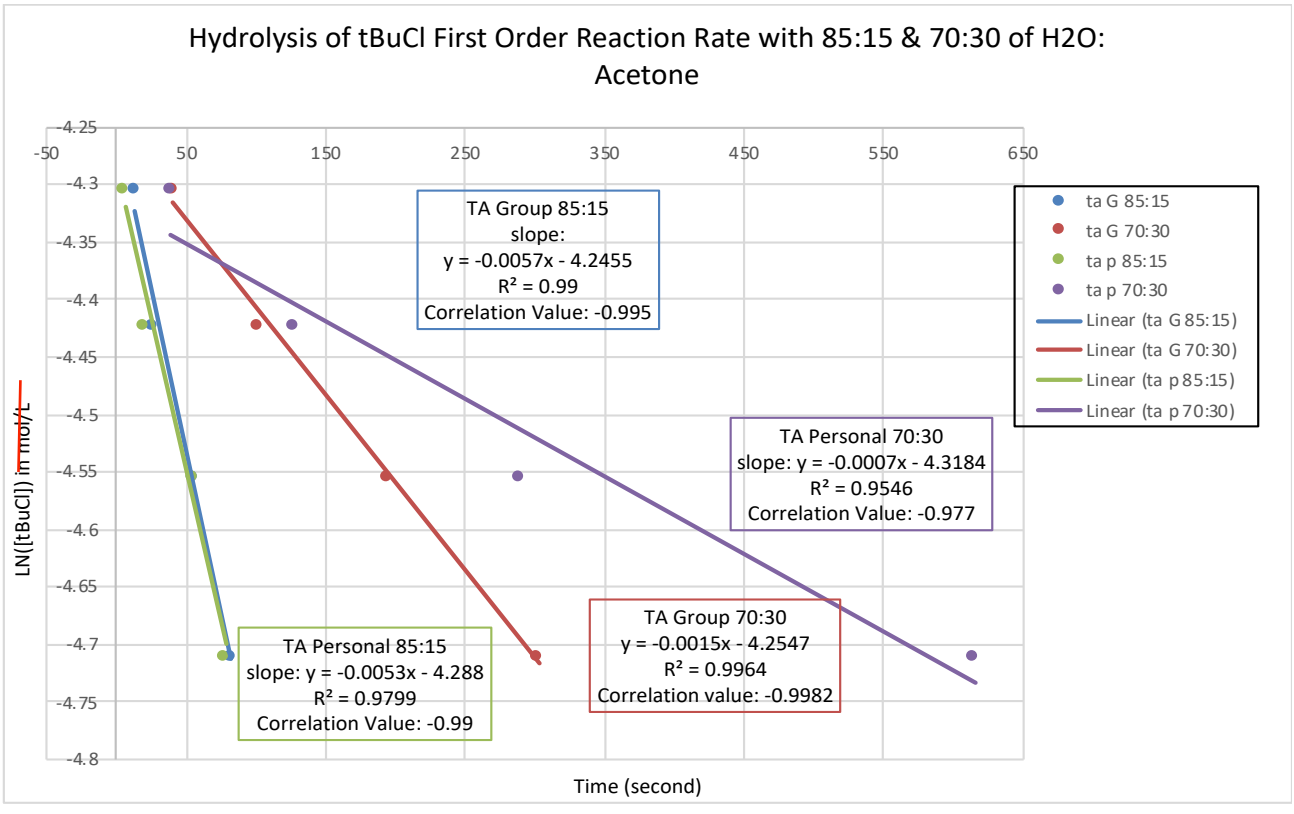


Figure 3.b: Graph of the first order reaction average rate



Discussion

Part A:

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In this experiment, the main goal was to be able to find the reaction order and rate of, in our case, the hydrolysis of 1-bromobutane and tert-butyl chloride depending on different solvent mixture ratios to different effects of leaving groups. In the first part of the experiment, we are dealing with a nucleophilic substitution, SN2, where a nucleophile such as potassium hydroxide, a strong base, will attack and attach itself at the electrophile (1-bromobutane) carbon-alpha's site before it's leaving group, bromine which is known as a weak base, leaves. To set up the equipment, it is specified to add a reflux condenser where it's presence can be explained by the need of avoiding any kind of loss from our prepared solution that could occur due to vaporization. As the material was set up and the 1-bromobutane collected and, subsequently, transferred into the volumetric flask already equipped with a magnetic stir bar, the flask started to gradually heat, which will cause an increase in reaction rate later on, and reaching reflux where bubbles were observed. Once this step was complete, an adequate amount of potassium hydroxide in H2O was likewise transferred in order for it to get dissociated into its ionic form and to attack the electrophile. As a polar aprotic solvent is necessary for an ideal SN2 reaction, EtOH was lastly added. After two minutes, an aliquot volume of the solution was pipetted out to be used for the first titration trial which will determine the concentration of OH present and, the rest of the solution, would go and continue reflux. This step was repeated for the next 15, 30, 45 and 60 minutes, necessary in order to conclude the reaction rate. In terms of the titration, after setting up the equipment and adding HCl to the burette, to notice when the titration completed where hydroxide is neutralized, drops of phenolphthalein indicator was added to the solution mixture. As seen in the results of part A, three graphs of zero, first and second order were plotted where concentrations taken in different time slots are being compared in order to be able to conclude the rate of the reaction based on the obtained correlation value of each linear regression lines, known as trendlines. It can be concluded, that the hydrolysis of 1-bromobutane runs a second reaction order as the data points fit a linear regression and by comparing the correlation values

of the three graphs, the second order graph has a positive strong correlation values very close to 1 such as 0.9918 for personal data of 1-bromobutane and 0.9953 for average global data of 1-bromobutane, which shows also that our values are very close and similar to the global average data one. For the two other graphs, the correlation values are negative where it defines slightly not existing correlation. Lastly, the k value, which is found in the slope equation on each graph, is found to be 0.0062 for 1-chlorobutane (global data) and 0.087 (global data) or 0.102 (personal data) for 1-bromobutane.

Part B

which one is better leaving group? bromo or chloro?

An SN1 reaction is a unimolecular nucleophilic substitution with 2 steps. The first step of the reaction is the formation of a carbocation, a very unstable transition state which since the carbocation is very unstable the first step of reaction is the rate determining step. tBuCl has a tertiary alpha carbon which provides enough stability to form a carbocation and too much steric hindrance for an SN2 reaction, therefore it undergoes an SN1 reaction. SN1 reactions favour polar protic solvents because the dipole helps to stabilize the carbocation. Water is an example of a polar protic solvent that increases the rate of an SN1 reaction because of its significant dipole. Polar aprotic solvents also have a dipole, however it is significantly weaker than a polar protic solvent because they do not have the highly polarised hydrogen. This effect is clearly shown on the graphs for part b. The time required to reach the same completion is consistently shorter for the reaction with the solvent system of 85:15 water: acetone when compared to the 70:30 water:acetone mixture. Since water is a polar protic solvent and acetone is a polar aprotic solvent, these results are consistent with the properties of an SN1 reaction. As described in the introduction the order of the reaction can be determined by looking at the R2 value of the graphs. For each set of data the R2 value is consistently closer to 1 in graph b which used the rate law for a first order reaction. Using the rate law to plot the data is used to determine the order of the reaction because k is a constant that should be represented by the negative slope of the graph. In order for k to be constant the data needs to be linear. This means that the greater accuracy of the R2 value for the line in graph b shows that the graph of the first order rate law better represents k as a constant; therefore this is a

first order reaction. The graphs also show a clear difference between the group's results and the personal results when using a solvent system of 70:30 water:acetone. A possible explanation for this difference was that nearing the end of the experiment there was not enough time to complete three trials and therefore the last two plot points for this mixture were only the mean of two trials and therefore less accurate. In addition, as the reaction took longer to progress the differences between the times measured for each trial increased. This could be because of the inherit chance involved in a molecule having the necessary combination of factors to react, and this chance diminishing in a less favorable solvent system and after the concentration of reactants has already decreased. Human error could also be a factor, perhaps after more time passed people became less diligent in mixing and watching the reaction. A contributing factor for these errors could be that with their partner doing part a, it was difficult to complete the experiment on time and maintain focus.

Reference

1. Experiment 2 Laboratory Manual. Retrieved from TopHat.

https://app.tophat.com/e/896767/assigned/

writing style 4/4

2. Robinson, Bill. Integrated Rate Laws,

https://www.chem.purdue.edu/gchelp/howtosolveit/Kinetics/IntegratedRateLaws.html.

Raw Data