Experiment 2: The Kinetic Study of Nucleophilic Substitution

September 18th, 2018
Section C00

Introduction:

The rate of a reaction is dependent on the concentration of reactants because the more molecules there are, the more chances there are for bond breaking and formation between these molecules ("Experiment 2," n.d.). This is demonstrated by the equation for the rate of a reaction:

$r=k[A]^x[B]^y$ where $A+B \rightarrow C+D$ ("Experiment 2," n.d.).

As shown here, the rate of the reaction is also dependant on the rate constant and the order of the reaction, which is the addition of the values of x and y. Thus, the individual exponents correspond to the order for the individual reactants. If a reaction has a rate order total of zero, that means that the concentration of the

reactants has no influence on the rate of the reaction. If a reaction is first order, one of the reactants will have an exponent of one, and demonstrated on a graph will have a negative slope when ln[A] is on the y-axis and time is on the x-axis ("Experiment 2," n.d.). A second order reaction will either have one exponent as a factor of two or each exponent will be to the power of one ("Experiment 2," n.d.). This graph would show a positive slope of k when1/[A] is on the x-axis versus time ("Experiment 2," n.d.). Temperature can also influence the rate of a reaction because the value of k is influenced by the temperature as shown in the Arrhenius Equation for the rate constant, k:

$k=Ae-Ea/RT$ (Lower, 2016).

Catalysts can also influence the rate of a reaction because as shown in the above equation is the value *Ea* (Lower, 2016). This number stands for the Activation Energy and catalysts influence this value by lowering it so that less energy is required for the reaction to proceed (Lower, 2016).

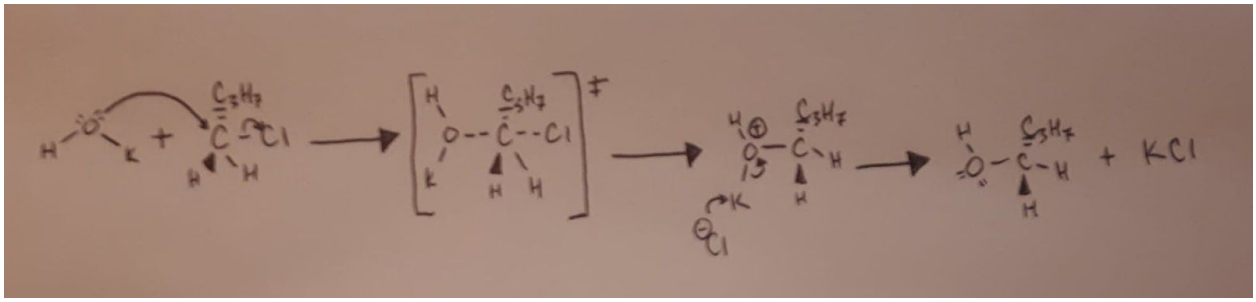
Sn-1 reactions occur when there is a nucleophilic substitution and there is only one reactant involved in the rate-determining step, this is the slowest step in the reaction where the leaving group first separates from the a-carbon ("Experiment 2," n.d.). This leaves the molecule as a positive carbocation, since there are only three bonds attached to the carbon. The result of this positive charge is the attack of a nucleophile, increasing stability of the carbocation and satisfying the nucleophiles attraction to positive charges by donating its lone pair of electrons. The rate of the reaction for an Sn-1 reaction is only dependant on the electrophile and the leaving group has to separate before the attack of the electrophile so the reaction is unimolecular("Experiment 2," n.d.). Since the rate of the reaction is only determined on the concentration of the substrate it is a first order reaction ("Experiment 2," n.d.).

Sn-2 reactions have no carbocation intermediate, but the nucleophile attacks the electrophile and the leaving group separates in one step ("Experiment 2," n.d.). As a result, the rate of the reaction is dependent on the nucleophile and electrophile. Therefore, this nucleophilic substitution reaction is bimolecular because the rate determining step involves two molecules(Lower, 2016). Since the rate of the reaction is determined by the substrate and the concentration of the reaction it is a second order reaction ("Experiment 2," n.d.).

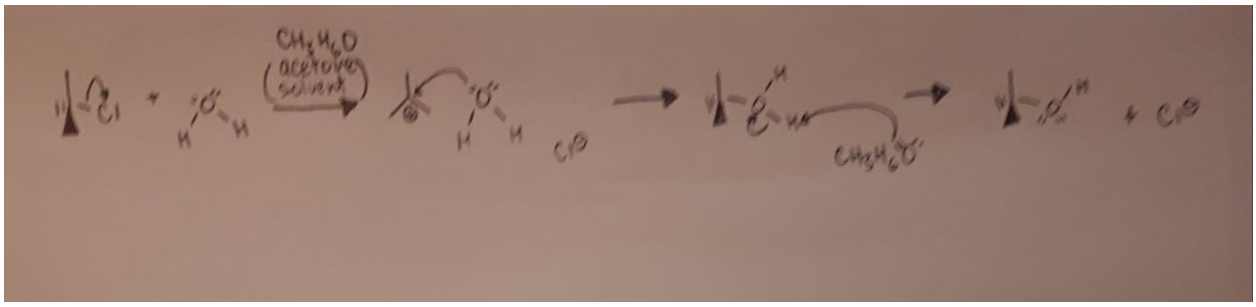
In Part A of the experiment, the goal was to determine how the leaving group would effect the rate of the reaction for chlorobutane and KOH ("Experiment 2," n.d.). Another goal of the experiment is to determine the order of the reaction and the rate constant by plotting time verses [KOH], ln[KOH], and 1/[KOH]. This was done through titration, where the amount of acid needed to arrive at the visual cue of neutralization was used to measure the amount of KOH in the aliquot. In Part B of the experiment, the goal was to determine the effect of the solvent system on the rate of the reaction for different concentrations of tBuCl. From this, another goal was to determine the order of the reaction and graph each order like in Part A. The initial tBuCl concentration can then be multiplied by the amount of percentage that is not used to measure the amount of tBuCl remaining ("Experiment 2," n.d.).

Mechanism:

Part A



Part B



<u>Part A: Hydrolysis of 1-chlorobutane</u>

Table of Reagents and Solvents:

Table 1: Table of reagents showing all the solvents and reagents used in part A along with their respective volume, molecular mass, density, number of mol and equivalents.

Reagent	**Amount (ml)**	**Molecular Mass (g/mol)**	**Density (g/ml)**	**Mol**	**Equivalents**
0.5 M 1-chlorobutane	40	92.56	0.89	0.02	1

2.0 M KOH	10	56.11	2.12	0.02	1
EtOH	5	46.07	0.789	NA	NA

Experimental Procedure:

Refer to the CHM2123Protocol2.pdf on the CHM2123 lab course on TopHat

Results and Observations:

i) Observations:

Table 2: Steps and observations for part A of the hydrolysis of 1-chlorobutane.

Steps	Observations
Fill a 25 mL burette with 0.1 M HCl	HCl has a very strong pungent smell
Once the solution has started to reflex	Bubbling is seen in the solution
Pour the aliquot into a 50 mL Erlenmeyer flask and add 2-3 drops of phenolphthalein indicator to the solution	Solution in the Erlenmeyer flask tends to turn pink as we add drops of phenolphthalein indicator
Begin titrating the aliquot with 0.100 M HCl from the burette, noting accurately how much HCl is required to reach the end point	After having added a certain volume of 0.1 M HCl to the solution inside the Erlenmeyer flask, the pink solution then became a clear solution as it has titration was complete

ii) Results:

Table 3: Concentration of KOH neutralized at 5 different time intervals using HCl as our titrant and phenolphthalein as our indicator

Reaction Time	2 Minutes	15 Minutes	30 Minutes	45 Minutes	60 Minutes
V aliquot (mL)	5	5	5	5	5
Vi HCl (mL)	0	0	0	0	0
Vf HCl (mL)	16	16	14.5	15	14.1

ΔV HCl (mL)	16	16	14.5	15	14.1
mMoles of HCl Titrated (cΔV)	1.6	1.6	1.46	1.5	1.41
mMoles of KOH neutralized in the titration	1.6	1.6	1.46	1.5	1.41
[KOH] neutralized	0.32	0.32	0.29	0.30	0.28
ln[KOH]	-1.14	-1.14	-1.24	-1.20	-1.27
1/[KOH]	3.125	3.125	3.448	3.333	3.571

Table 4: Average [KOH] titrated by all students with respect to the time we had titrated the solution at. ln [KOH] and 1/[KOH] are calculated from average [KOH] and these results are for 1-chlorobutane

Time (min)	Average [KOH] (M)	ln [KOH]	1/[KOH]
2	0.369	-0.997	2.710
15	0.336	-1.091	2.976
30	0.326	-1.121	3.067
45	0.339	-1.082	2.950
60	0.327	-1.118	3.058

Table 5:Average [KOH] titrated by all students with respect to the time we had titrated the solution at. ln [KOH] and 1/[KOH] are calculated from average [KOH] and these results are for 1-bromobutane.

Time (min)	Average [KOH] (M)	ln [KOH]	1/[KOH]
2	0.2015	-1.602	4.963
15	0.1579	-1.846	6.333
30	0.1223	-2.101	8.177
45	0.1000	-2.303	10.00

60	0.0530	-2.937	18.87

Calculations:

i) Sample calculation for mmol HCl titrated, mmol KOH neutralized in the titration, [KOH] neutralized, ln[KOH], and 1/[KOH] in table 3 at time = 2min:

Concentration of HCl from given = 0.100 M

Δ**V HCl** = Vf - Vi = 16 - 0 = 16mL

mmol of HCl titrated = (concentration of HCl)(ΔV HCl)
= (0.100M)(16mL)
=1.6 mmol

mmol of KOH neutralized in the titration = 1.6 mmol
Since our reaction is a 1:1 reaction, then we can say that number of moles of KOH is the exact same as the number of moles of HCl and so we can say that number of mmol KOH = 1.6 mmol

[KOH] neutralized = nmol [KOH] / Volume aliquot
= 1.6 mmol / 5 mL
= 0.32 M

ln[KOH] = ln (0.32M)
= -1.14

1/[KOH] = 1/(0.32M)
= 3.125

ii) Sample calculation for average [KOH], ln[KOH] and 1/[KOH] calculated in table 4 at time = 2min:

From the class data provided by our TA, we were able to find the average for each time by adding the [KOH] values at each specific time and dividing it by the total number of [KOH] values per each time interval. For time = 2 min, we had a concentration of [KOH] to be 0.48 M, 0.32 M and a concentration of [KOH] to be 0.308 M. Average [KOH] for time = 2min will be (0.48 + 0.32 + 0.308) / 3 which gives us 0.369

ln[KOH] = ln(0.369)
= -0.997

1/[KOH] = 1/(0.369)
= 2.210

iii) Sample calculation for average [KOH], ln[KOH] and 1/[KOH] calculated in table 5 at time = 2 min:

From the class data provided by our TA, we were able to find the average for each time by adding the [KOH] values at each specific time and dividing it by the total number of [KOH] values per each time interval. For time = 2 min, we had a concentration of [KOH] to be 0.184 M and a concentration of [KOH] to be 0.219 M. Average [KOH] for time = 2min will be (0.184 + 0.219) / 2 which gives us 0.2015

ln[KOH] = ln(0.2015)
= -1.602

1/[KOH] = 1/(0.2015)
= 4.963

Graphs:

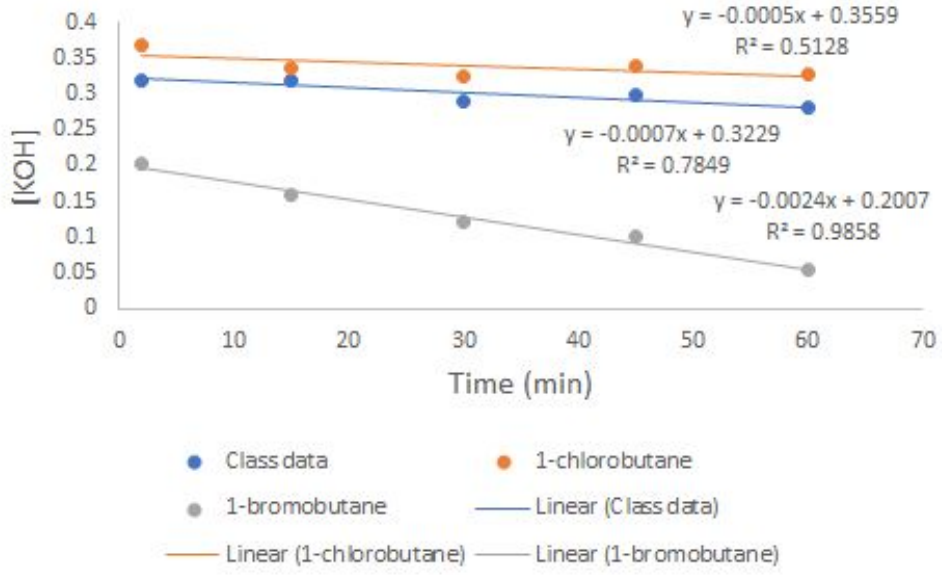


Figure 1: Concentration of KOH versus time for zero order kinetics of 1-chlorobutane, 1-bromobutane and class data from the data collected from the class.

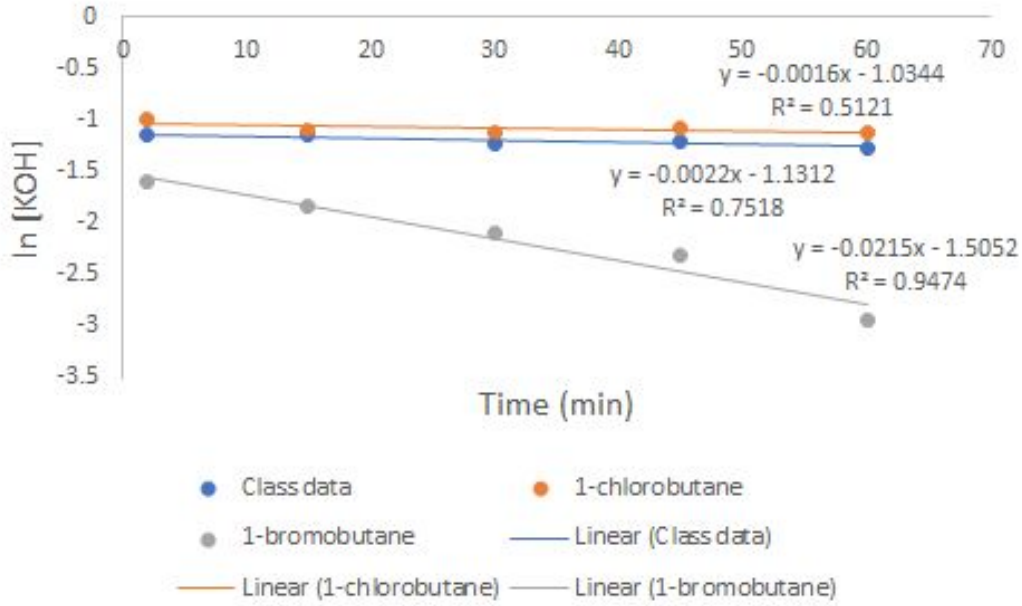


Figure 2: ln of the concentration of KOH versus time for first order kinetics of 1-chlorobutane, 1-bromobutane and class data from the data collected from the class.

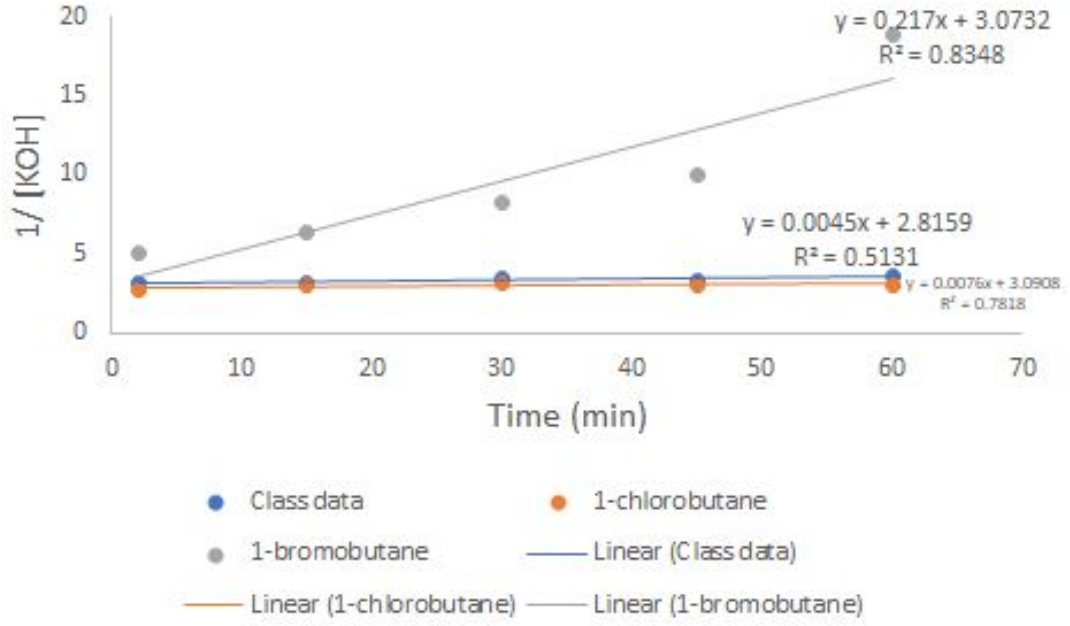


Figure 3: Inverse of the concentration of KOH versus time for second order kinetics of 1-chlorobutane, 1-bromobutane and class data from the data collected from the class.

Discussion:

In part A, our goal was to analyze the effects of the addition of KOH on the rate of reactions of the leaving groups of 1-chlorobutane and 1-bromobutane. In this experiment, our group chose to use 1-chlorobutane instead of 1-bromobutane. During the experiment, 1-chlorobutane was added into a round bottom flask and was then boiled and KOH was added to the boiled mixture. When the 1-chlorobutane boils, we then know the leaving group, chlorine, has broken off the carbon and attached to the K+ ion that had broken off from the OH- ion of KOH. This reaction mechanism is SN2 and what this means is that one bond is broken, and one bond is formed synchronously in one step. SN2 is a kind of nucleophilic substitution reaction mechanism. At the different time intervals, we measured out 5.0 mL of our aliquot and placed it in a Erlenmeyer flask and added 3 drops of phenolphthalein indicator to the flask and that made the contents turn pink. HCl is titrated into the solution to make the solution clear again. For all time intervals, we notice very little change in concentration of KOH compared to that of 1-bromobutane as Bromine is a much better leaving group than chlorine. In order to determine the differences in the rates of reactions between the two halides, we had to graph three plots per halide for a zero order, first order and second order reaction. The data used was the average class data given by the TA. While looking at our zero-order graph, concentration of KOH versus time, we can see that that the 1-chlorobutane produced a linear curve but has a negative slope. For our first order graph, ln concentration of KOH versus time, we can see that the 1-chlorobutane also has a linear curve but a negative slope. For our second order, 1/concentration of KOH versus time, we can see that the 1-chlorobutane has a linear curve as well as a positive slope and thus we can say that our reaction is a second order reaction. The reason to why we may have had many straight lined curves for 1-chlorobutane could be because chlorine, being the harder leaving group, holds on closer to its electrons than Bromine. While looking at our zero-order graph, concentration of KOH versus time, we can see that the 1-bromobutane produced a linear curve but has a negative slope. For our first order graph, ln concentration of KOH versus time, we can see that the 1-bromobutane does not have a linear curve and has a negative slope. For our second order, 1/concentration of KOH versus time, we can see that the 1-bromobutane does not have a linear curve but has a positive slope and thus it will be harder to determine which order this reaction favors but because our curve is almost linear and our curve is positive, we can say that our reaction is a second order reaction. Our concentrations tended to decrease as Bromine is a better leaving group than chlorine and thus we have more bromine leaving the reaction than chlorine.

Part B

Table of reagents

Table 6: Table of reagents showing all the solvents and reagents used in part B along with their respective volume, molecular mass, density, number of mol and equivalents for a 85:15 H2O:Acetone solution.

Reagent	Amount (ml)	Molecular Mass (g/mol)	Density (g/ml)	Mol
0.1 M tert-butylchloride	3	92.57	0.84	0.0003
0.02 M NaOH	1.5, 3.0, 4.5, 6.0	39.997	2.13	0.00003, 0.00006, 0.00009, 0.00012
water	15.5, 14.0, 12.5, 11.0	18.05	0.9982	NA

Table 7: Table of reagents showing all the solvents and reagents used in part B along with their respective volume, molecular mass, density, number of mol and equivalents for a 70:30 H2O:Acetone solution.

Reagent	Amount (ml)	Molecular Mass (g/mol)	Density (g/ml)	Mol
0.1 M tert-butylchloride	3	92.57	0.84	0.0003
0.02 M NaOH	1.5, 3.0, 4.5, 6.0	39.997	2.13	0.00003, 0.00006, 0.00009, 0.00012
water	15.5, 14.0, 12.5, 11.0	18.05	0.9982	NA
acetone	3	58.08	0.791	NA

Experimental procedure:

Refer to the CHM2123Protocol2.pdf on the CHM2123 lab course on TopHat

Results and Observations:

i) Observations:

Table 8: Steps and observations for part B

Steps	Observations
Add 2 – 3 drops of bromothymol blue indicator and place the flasks in the water bath.	The addition of bromothymol blue gave the solution a pale blue colour. Gently mixing made this colour uniform in the flask.
Pour 3.0 mL of the 0.10 M tBuCl in acetone solution into each flask.	Shortly after adding tBuCl in acetone the blue solution would fade back to faint yellow.

ii) Results:

Table 9: Results obtained for part B

	85:15 Acetone:water	70:30 Acetone:water
First order rate constant from group's data	0.008	0.0015
First order rate constant based on global average	0.0055	0.0015
% difference	45.455	0.00
Order of reaction	1	1

Calculations:

% difference: $\%\ difference = \frac{(theoretical - actual)}{theoretical} * 100 = \frac{0.0055 - 0.008}{0.0055} * 100 = 45.455\%$

Graphs:

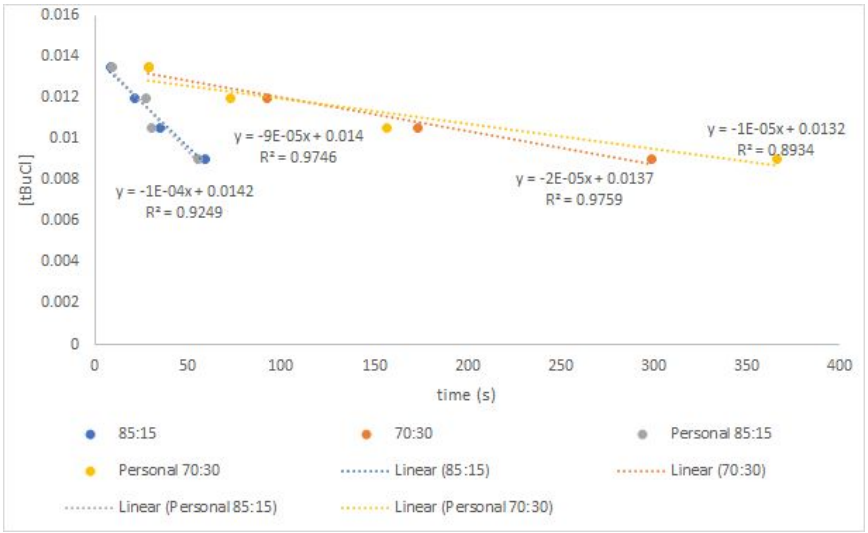


Figure 4: A plot of the concentration of t-butyl chloride in solution with time for both a 85:15 and 70:30 Water:Acetone solution based on the group's results

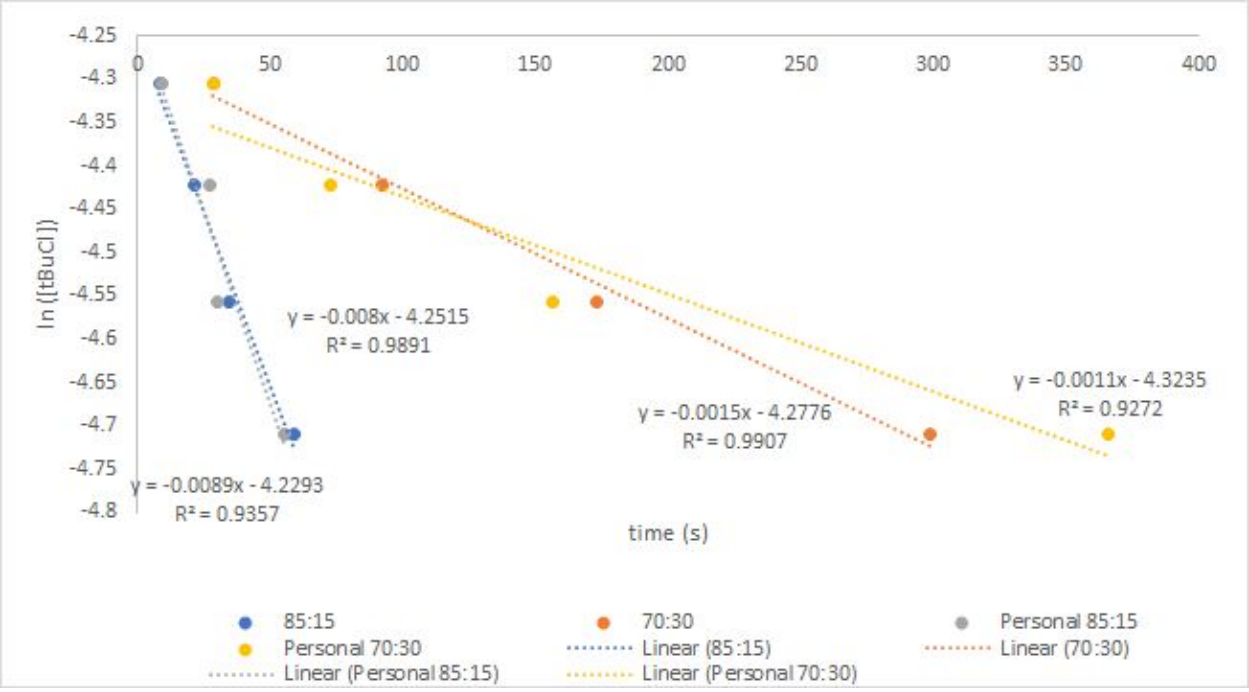


Figure 5: A plot of ln of the concentration of t-butyl chloride in solution with time for both a 85:15 and 70:30 Water:Acetone solution based on the group's result

Discussion:

Part B aimed to determine whether the hydrolysis of t-butyl chloride by sodium hydroxide is an SN_1 or SN_2 reaction, and to analyze the kinetics of the reaction to determine the rate constant and the order of reaction. The reaction went much quicker in an 85:15 water:acetone solvent than in a 70:30 water:acetone solvent. Water is polar protic solvent whereas acetone is a polar aprotic solvent. SN_1 reactions are promoted by polar protic solvents, which leads to believe the hydrolysis of t-butyl chloride is an SN_1 reaction. The linear graphs we obtained also show that it is a first order reaction as the slope for ln of the concentration of t-butyl chloride in solution with time provided the rate constant for the rate law. The group's data was consistent with the global data, with the rate constant being exactly the same for the 70:30 solution, even though the 85:15 solution's data was off, with a 45% percent difference. This error is very likely due to human errors such as inaccurate burette volume dispensal, uncertainty in when to stop the timer, etc. A bigger amount of trials would have made the group and global data closer. The experiment was performed by dispensing the same volume of 0.1M tbutyl chloride in acetone in flasks with different concentrations of NaOH, along with bromothymol blue indicator, to measure how long the concentration of OH^- took to change. The indicator is blue at a more basic pH, and turns to a faint yellow colour when all the OH^- has been consumed, meaning the reaction is over. The flasks were kept in a water bath, to maintain a desired temperature, since a temperature raise would promote elimination and lead to formation of isobutylene instead of t-butanol.

References

Experiment 2. (n.d.). In *Top hat*. Retrieved September 26, 2018, from https://app.tophat.com/e/833666/assigned/

Lower, S. (2016, April 5). Reaction rate. In F.-D. Odufalu, P. Chacha, G. Mudda, & A. Iskandar (Eds.), *LibreTexts*. Retrieved from https://chem.libretexts.org/Textbook_Maps/Physical_and_Theoretical_Chemistry_Textbook_Maps/Supplemental_Modules_(Physical_and_Theoretical_Chemistry)/Kinetics/Reaction_Rates/Reaction_Rate