Lab #3-Competition Studies of Substitution and Elimination Reactions
Section: CHM2123 A
TA: Stephanie Ruth
Student: Jeel Patel-8237838
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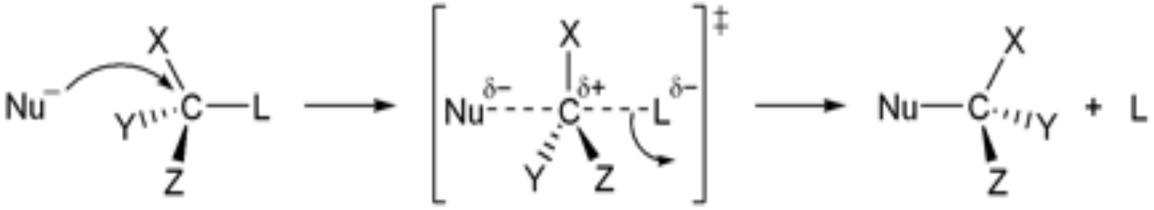
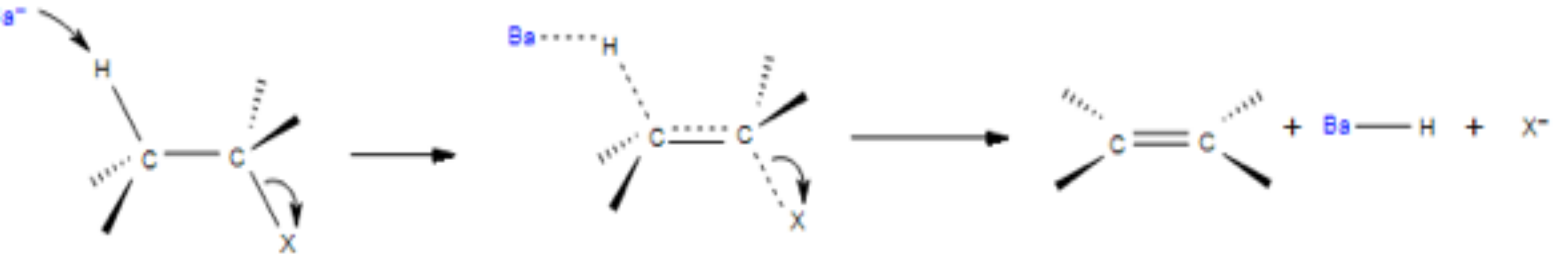
Introduction

Like many reactions in chemistry, substitution and elimination reactions usually do not yield a single product. More often than not, there are multiple products and not all possible products are made. The diversity of organic molecules, allows them to undergo more than one reaction pathway, these pathways are usually competing with one another. The term *conversion* is used to quantify the amount of reactants that have converted to products. Similarly, the concept of *selectivity* is used to represent the ratio between two or more possible products. The product with greatest selectivity will be called the major product and the other products will be referred to as minor. One example of competing reactions are E2 and Sn2 which will be explored in this experiment.

Substitution reactions involve a nucleophile, with excess electron density, attacking an electrophile with a deficit of electrons. The result is a bond formation between the E+ and Nu. There are two mechanisms for substitution reactions known as Sn1 and Sn2. The former reaction is characterized as unimolecular and proceeds through a carbocation intermediate. Sn1 reactions do not require strong nucleophiles unlike Sn2 reactions which as characterized as bimolecular reactions. The focus of this experiment will be on Sn2 reactions. In Sn2 reactions the Nu attacking and the departure of the leaving group are concerted steps. Tertiary alpha carbons do not undergo Sn2 pathways because their transition states would indicate a pentavalent carbon atom which is highly improbable.



The other competing pathway that this lab explores is E2. This is similar to Sn2 in the sense that they are both bimolecular and do not proceed via carbocation intermediates. However, E2 reactions require a strong base to deprotonate a beta carbon in order to form a double bond and simultaneously break the carbon leaving group bond. Chemists often favour E2 products over Sn2 by increasing the temperature of the reaction; Sn2 products have lower entropy than E2 products and thus E2 pathway require greater energy to overcome the activation energy barrier. Due to the acid-base reaction, the E2 products yield an additional product which increases the reaction entropy as discussed above. For an E2 reaction to take place the hydrogen to be deprotonated and the leaving group need to be anti-periplanar to one another. This arrangement is required for the proper overlap of orbitals to form the new bonds.



This experiment will involve conducting two trials with 1-bromobutane (electrophile) and one trial with 2-bromobutane (electrophile), with the nucleophile as KOH which will be kept constant. Properties of gases such as the ideal gas law will be used to calculate the amount of gaseous E2 product made (butene). Important techniques such as reflux and suction filtration will be utilized to help measure the conversion and selectivity of the reactions.

Experimental Procedure

Please refer to "CHM2123 Laboratory of Organic Chemistry II" pg.45-52
Modification: the procedure didn't mention to measure the value of P* so the values were created assuming that the total length of the eudiometer tube is 654.05 mm.

Table of Reagents

Compound	Molar Mass (g/mol)	Moles (n)	Quantity	Density (g/ml)	Equivalent
Potassium Hydroxide	56.1056	0.143 0.144 0.143	8.04g 8.08g 8.04g	1.046	Different for 3 trials (as shown)
95% Ethanol	46.06844	-	40ml	-	3 trials
Water	-	-	1L	-	3 trials
1-Bromobutane	137.02	0.0137	1.5ml	1.255	2 trials
2-Bromobutane	137.02	0.00733	0.8ml	1.255	1 trial

Table of Results

Reaction Condition	1-bromobutane at reflux	1-bromobutane at 19 Degrees	2-bromobutane at reflux
Pressure of Gas (atm)	0.9691	0.9157	0.9298
Volume of Gas (ml)	49.6-6.1 =**43.5**	0.6-0.4 =**0.2**	12.1-0.8 =**11.3**
Mass of KBr (g)	1.57	0.23	0.47
Moles of KBr (mol)	0.0132	0.00193	0.00395
Moles of Butene (mol)	1.74x10^-3	7.57x10^-6	4.34x10^-4
Moles of Butanol (mol)	0.011458	0.001922	0.003516
% Yield	96%	14%	54%
% Conversion	96%	14%	54%
Selectivity (E2:Sn2)	13% butene 87% butanol	0.4% butene 99.6% butanol	11% butene 89% butanol

Table of Observations

Key Step	Observation
1-bromobutane @ Reflux	
Steps 1 to 3- Preparation	-8.04g of KOH obtained (white, shiny and solid) -35ml of 95% EtOH obtained -takes significant time for KOH to dissolve and heat produced in process of dissolving
Steps 12 to 16-Reflux and Reaction	-before addition, a full eudiometer tube was filled with gas -the starting volume of gas in the second tube was 6.1ml -final volume after adding 1-bromobutane was 49.6ml -bubbling was faster initially then gradually slowed down
Steps 17 to 18-Suction Filtration	-flask takes long time to cool-meanwhile white crystals forming and are visible -1st filtration is improper-visible KBr in mother liquor (clear and yellow) -2nd filtration was much better-mother liquor was clear -no visible KBr in mother liquor the second time around
Step 19-Mass of KBr	-product was a powder and had a slight yellow hue -mostly white and soft -mass of product= 44.32g-42.75g=1.57g
1-Bromobutane @ 50 Degrees	
Steps 1 to 3- Preparation	-8.08g of KOH obtained -35ml of EtOH -temperature of water bath was 19 degrees
Steps 12 to 16-Reflux and Reaction	-starting volume of gas in eudiometer tube is 0.4ml -final volume is 0.6ml -very little to NO bubbling seen during reaction -the solution in the flask was cloudy and not as warm as previous part -flask placed in an ice bath to promote crystal formation -no visible crystals in flask but still cloudy
Step 19-Mass of KBr	-product is white and powder-like (similar to previous part) -0.23g of KBr
2-bromobutane @ Reflux	
Steps 1 to 3- Preparation	-8.04g of KOH obtained -35ml of EtOH obtained
Steps 12 to 16-Reflux and Reaction	-initial volume of gas in eudiometer is 0.8ml -final volume of gas is 12.1ml -visible white crystals formed and solution is cloudy
Step 19-Mass of KBr	-0.47g of KBr weighed

Calculations: 2-bromobutane @ reflux

Assumptions:

1) Standard eudiometer length is 654.05 mm
2) Roughly 100 mm of the eudiometer was submerged in the water
3) 1 ml of water is equivalent to 13.08 mm in a standard eudiometer tube

P of Gas

$$mm_{gas} = (13.08mm)(11.3ml)$$
$$= 147.804mm$$

$$mm_{H2O} = 654.05 - 100 - 147.804$$
$$= 406.246mm$$

$$mmHg_{H2O} = 406.246mm \div 13.6mm$$
$$= 29.871mmHg$$
$$= 0.0393atm$$

$$P_{gas} = P_{atm} - P_{water} - P^{*}$$
$$= 0.9948atm - 0.0257atm - 0.0393atm$$
$$= 0.9298atm$$

Moles of Butene

$$n_{butene} = \frac{PV}{RT}$$
$$= \frac{(0.9298atm)(0.0113L)}{(0.08206)(294.85K)}$$
$$= 4.342X10^{-4}mol$$

Moles of Butanol

$$n_{butanol} = n_{KBr} - n_{butene}$$
$$= 0.00395 - 4.34X10^{-4}$$
$$= 0.003516mol$$

%Conversion

$$\%C = \frac{4.34X10^{-4} + 0.003516}{0.00733}(100)$$
$$= 54\%$$

Selectivity

$$selectivity = \frac{n_{butene}}{n_{total}}(100)$$
$$= \frac{4.34X10^{-4}}{0.00395}(100)$$
$$= 11\%butene$$

$$\%Butanol = 100 - 11$$
$$= 89\%$$

Discussion

The overall goal of this experiment was to compare the differences in conversion and selectivity among E2 and Sn2 products involving bromobutane and potassium hydroxide. The experiment was divided into 3 trials with varying reactions conditions, trial one was between 1-bromobutane and KOH at reflux, trial two was done between the same two products but at 19 degrees (no reflux), and lastly, trial three was preformed using 2-bromobutane and KOH at reflux conditions. For all trials, roughly 8 g of KOH was dissolved in 95% ethanol and was allowed to reach reflux (except trial 2). The initial volume of gas was noted prior to adding the electrophile into the reflux flask containing the nucleophile. Lastly, the final volume of gas was noted to calculated the amount of gas produced. The reaction flask was allowed to cool to room temperature and then the inorganic KBr salt was collected via suction filtration and weighed. The mass of KBr for the three trials were: 1.57 g, 0.23 g, and 0.47 g. For all three reactions, the E2 mechanism yields 1-butene which is a gaseous product while the Sn2 product is 1-butanol. To better understand the details of each trial, they will be discussed separately below.

Referring to the table of results, the conversion for this trial was 96% with 13% of butene (E2 product) and 87% butanol (Sn2 product). Firstly, it is understandable that the % conversion is high because the reaction was heated and the nucleophile was a primary haloalkane which has very minimal steric hindrance. Heating the flask meant that the molecules were given enough energy to overcome their activation energy barriers resulting in a greater percentage of reactants converting into products. Theoretically, introducing heat in a reaction favours the formation of the E2 products because the activation barrier for these products is higher than Sn2 products. This is because the E2 pathway has larger entropy than the Sn2 pathway. And additionally, E2 mechanism involves acid-base reactions which are much faster than nucleophilic substitutions. However, the results for this trial do not seem to correlate well with the known theory since there were more moles of butanol than butene produced. One very likely reason for this is the impurity of the KBr crystals when they were weighed. The crystals had a slight yellow colour after filtration, which indicates that some butanol somehow become incorporated into the crystal structure of KBr, additionally the KBr was not completely dry. Both these factors would have given a greater mass of KBr and thus greater moles than what was actually present. The moles of butanol were calculated by subtracting the moles of butene from moles of KBr, however, since the KBr moles was higher, the resulting value for moles of butene was also higher than reality! This would have in-turn falsely indicated that the reaction had more selectivity for butanol, when in reality it should be selective for butene. To summarize, this trial favoured the formation of butene which is the E2 product; it would have favoured the E isomer over the Z isomer to reduce steric effects between neighbouring groups on either side of the double bond.

The second trial was conducted with the same reactants however, there was no heating mantle present and the reaction was not under reflux conditions. This reaction took place in a water bath whose temperature was 19 degrees. The bath was on a stir plate but no additional heat was added to the reaction. All other steps were consistent with trial one. The conversion for this trial was 14% with 0.4% selectivity for butene and 99.6% selectivity for butanol. The mass of KBr after filtration was only 0.23 g. As explained for trial one, the lack of heat favours the formation of the Sn2 product because the E2 pathway requires heat to overcome the activation energy barrier. This theory was proven by the evidence that there was a clear selectivity for butanol versus butene in this trial. the conversion however, was much lower than trial one, it was only 14%! Once again this is because of the lack of heat. Most endothermic reactions require heat to overcome the activation barrier. Even though Sn2 requires less energy than E2 it still requires heat nonetheless. Since this trial was performed in a water bath at 19 degrees there was not sufficient energy for even Sn2 reactions to occur for all reactant molecules simply because they didn't have enough speed in order to collide and make bonds. The results for this trial coincide with the known theory and there were no significant sources of errors for this trial.

The final trial was conducted under reflux conditions with KOH and 2-bromobutane as reactants. The same procedure was applied as trial one. The conversion was 54% with 11% selectivity for butene and 89% for butanol. Due to the fact that this trial was under reflux (heat present) and that KOH is a strong nucleophile and base, it is most likely to have mixture of E2 and SN2 products. Since 2-bromobutane has a secondary alpha carbon, the steric hindrance increases compared to the previous trials with 1-bromobutane. The activation energy is higher for the Sn2 pathway than the E2 for secondary alpha carbons, hence E2 should theoretically be the major. According to the results and % conversion this was not the case. A plausible explanation is that the KOH is such a strong nucleophile that is acted as a nucleophile rather than a base. This would explain why the majority of products followed the Sn2 pathway. In order to favour the E2 products it would be a good idea to use a strong base that is not a strong nucleophile for example, potassium tert-butoxide.

Overall this experiment was yield products that correlated with the known theory. However, the last trial seems to deviate from the expected results and in order to bettie understand the reasoning behind this there should be multiple trials conducted. Additionally the trials should involve keeping the 2-bromobutane constant while chasing the nature of the nucleophile to really understand how E2 can be favoured over Sn2 with a secondary alpha carbon. For comparison purposes, similar trials should be done with tertiary alpha carbon to see if the selectivity of the reaction changes.

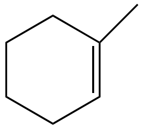
<u>**Ouestions**</u>

1. At 100% Conversion, the moles of 1-bromobutane is equal to moles of butene produced. Using the ideal gas law we get the following:

$$\frac{1.255g}{1ml} = \frac{?}{1.5ml} \qquad n = \frac{1.8825g}{137.02g/mol} \qquad V = \frac{(0.0137n)(0.082057)(298.15K)}{1atm}$$

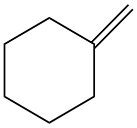
$$? = 1.8825g = 1bromobutane \qquad n = 0.0137 \qquad V = 0.335L$$

2. a)



NaBr HOCH$_3$

b)



KBr HOC(CH$_3$)$_3$

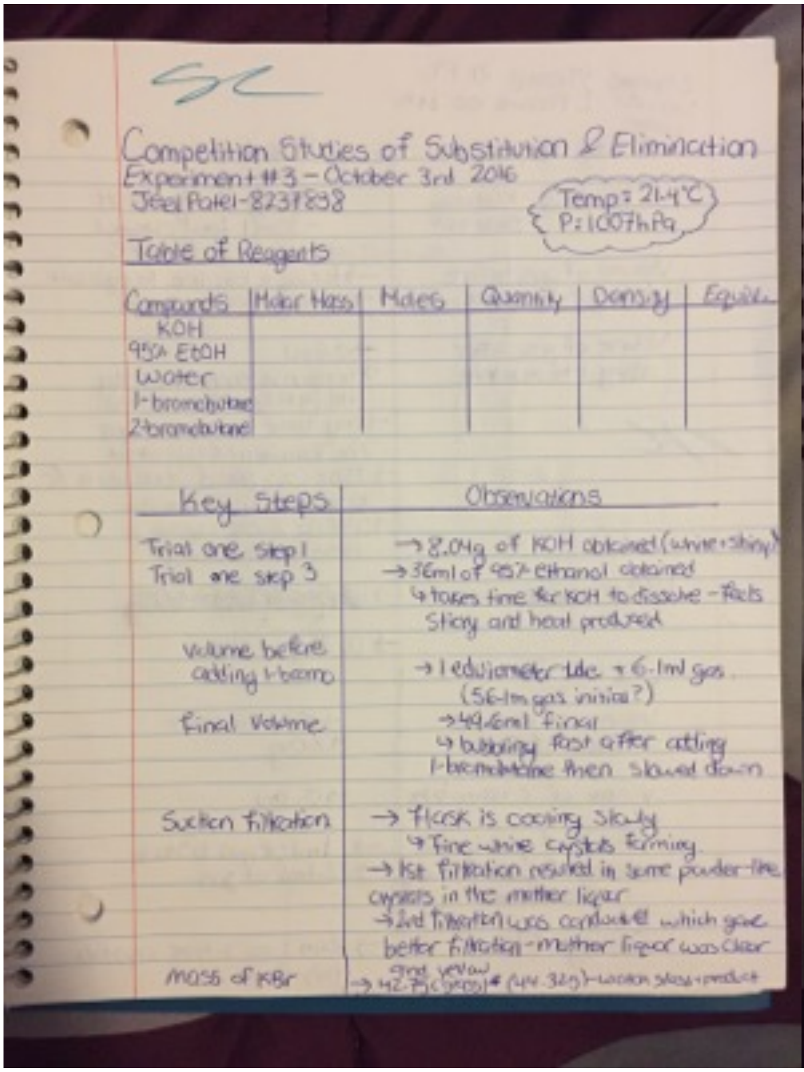
3.

a) Elimination
b) Substitution
c) Substitution

4. To promote the formation of 1-pentene from 1-bromopentane as the starting material, you can use a strong base that is a weak nucleophile such as potassium tert-butoxide and add heat to the reaction. 1-pentene is an elimination product whereas 1-pentanol is a substitution product.

Chemists often favour the formation of elimination over substitution by using a strong base to promote deportation versus nucleophilic attack. They also add heat which divers the formation of a double bond (desired product here).

Raw Data



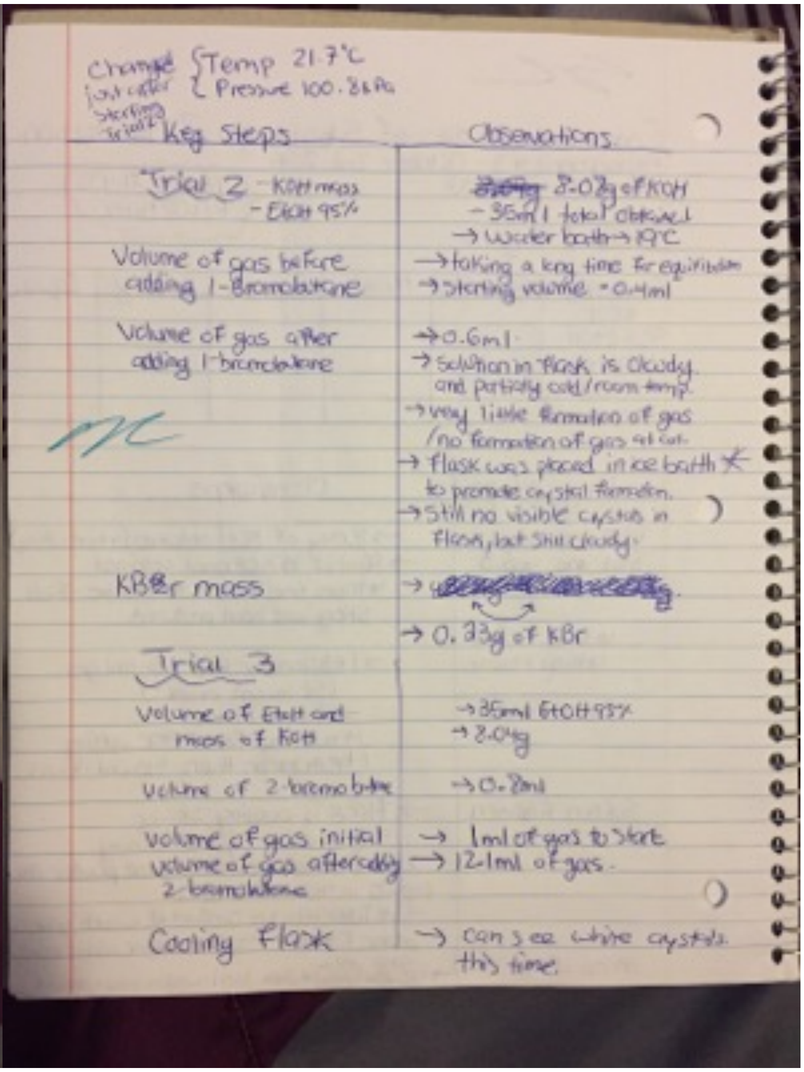
Competition Studies of Substitution & Elimincation
Experiment #3 – October 3rd 2016
Jeel Patel-8237838

Temp: 21.4°C
P: 1007hPa

Table of Reagents

Compounds	Molar Mass	Moles	Quantity	Density	Equiv.
KOH					
95% EtOH					
water					
1-bromobutane					
2-bromobutane					

Key Steps	Observations
Trial one step 1	→ 8.04g of KOH obtained (white + shiny)
Trial one step 3	→ 36ml of 95% ethanol obtained ↳ takes time for KOH to dissolve – feels sticky and heat produced
volume before adding 1-bromo	→ 1 eudiometer tube + 6.1ml gas (56.1m gas initial?)
final volume	→ 49.6ml final ↳ bubbling fast after adding 1-bromobutane then slowed down
Suction filtration	→ flask is cooling slowly ↳ fine white crystals forming. → 1st filtration resulted in some powder-like crystals in the mother liquor → 2nd filtration was conducted which gave better filtration – mother liquor was clear and yellow
mass of KBr	→ 42.75(g)(SPDS)# (44.32g) – watch glass + product



Change just after starting trial 2 { Temp 21.7°C
Pressure 100.8kPa

Key Steps	Observations
Trial 2 – KOH mass – EtOH 95%	~~8.04g~~ 8.02g of KOH – 35ml total obtained → water bath → 19°C
Volume of gas before adding 1-Bromobutane	→ taking a long time for equilibrium → starting volume = 0.4ml
Volume of gas after adding 1-bromobutane	→ 0.6ml → Solution in flask is cloudy and partially cold/room temp. → very little formation of gas /no formation of gas at all. → flask was placed in ice bath * to promote crystal formation. → Still no visible crystals in flask, but still cloudy.
KBr mass	→ [illegible]. → 0.23g of KBr
Trial 3	
Volume of EtOH and mass of KOH	→ 35ml EtOH 95% → 8.04g
volume of 2-bromobutane	→ 0.8ml
volume of gas initial	→ 1ml of gas to start
volume of gas after adding 2-bromobutane	→ 12.1ml of gas.
Cooling flask	→ can see white crystals this time.