Introduction:

This experiment studies the difference between elimination and substitution reactions. There are two types of elimination reactions, E1 and E2, and two types of SN1 and SN2 reactions. We will be studying E2 and SN2 more closely in this particular experiment.

An E1 reaction is a unimolecular reaction that occurs step by step as a carbocation occurs as the leaving group leaves, and then an alkene is formed as the beta hydrogen is removed by the solvent, which in an E1 reaction is preferred to be polar protic. All elimination reactions are preferred to include heat. This reaction prefers a weak base. It will not be relevant in this experiment which in which we are using a strong base.

The other elimination reaction is an E2 reaction. This is a bimolecular, concerted reaction which favours the use of a polar aprotic solvent, like acetone, for example, but can still work in a polar protic solvent, like ethanol, or methanol. It requires a strong base with a pK_{aH} of at least 10 which can be small or large hindered. The use of a small, strong base, like NaOH, will result in the most substituted product, called the Zaitsev product, whereas the use of a large hindered base like KO*t*Bu will result in the a least substituted alkene product called a Hofmann product. This occurs because a more hindered strong base will wants to attach on to where there are more H^+ rather than carbons because it is easier for it to attack there because of its steric hindrance which interfered less on the least substituted carbon. An antiperiplanar conformation between the leaving group and the desired proton is also required in order for an E2 reaction to be carried out. As stated before, an elimination reaction such as this one prefers heat.

Figure 1 is an elimination reaction, E2, with 1-bromobutane as the electrophile with a strong, hindered base of KOH in ethanol.

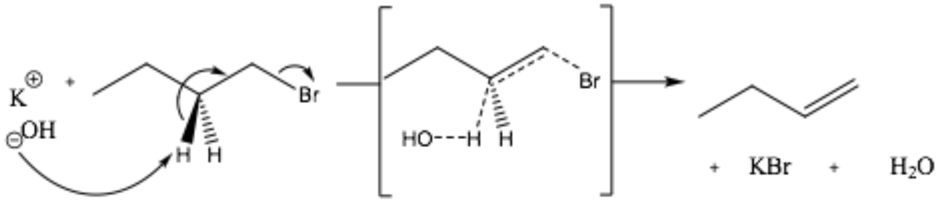


Figure 2 shows an elimination reaction, E2 with 2- bromobutane and KOH in ethanol which produces most substituted alkenes, trans-2-butene and cis-2-butene as shown below. The major product between the cis and trans products is the trans product as it is less hindered.

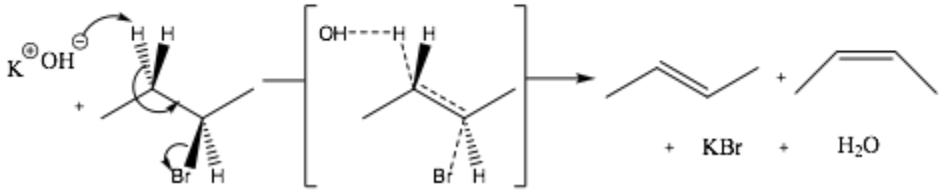
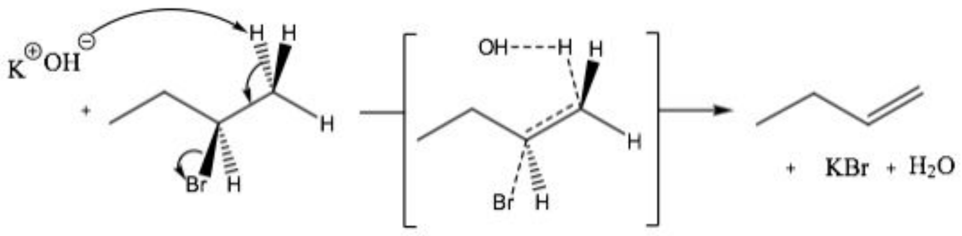


Figure 3 shows an elimination reaction, E2 with 2- bromobutane and KOH in ethanol which produces least substituted alkene 1-butene as shown below which is the minor product as the base is strong and hindered favouring to attack the least hindered carbon due to it being hindered itself to avoid the most steric hindrance as possible.



One substitution reaction is an SN1 reaction.This substitution mechanism is unimolecular and occurs step by step. It requires a weak nucleophile, generally neutral, which is usually a strong acid such as HBr and requires a polar protic solvent such as MeOH. This type of reaction is stereospecific and can generate enantiomers, as seen in figure 3. This occurs as its stereochemistry is lost upon the removal of the leaving group. This reaction is also not demonstrated in this experiment as it uses a strong acid (a weak base), and in this experiment we are using a strong base.

An SN2 reaction is a bimolecular, concerted reaction which favours the use of a polar aprotic solvent, and uses a strong nucleophile preferably with a negative charge which happens to be a stronger base. Anything with a salt, such as K, Li or Na ends up having a negative charge and ends up being a strong base and a good nucleophile. An SN2 reaction has a specific stereochemistry associate with it as in the one step in which this reaction takes place, the substitution attack occurs from the back of the leaving group resulting in an inversion of stereochemistry.

Figure 4 is the mechanism for an SN2 reaction with 1-bromobutane as the electrophile and KOH as the nucleophile, a strong hindered base in a ethanol, a polar protic solvent.

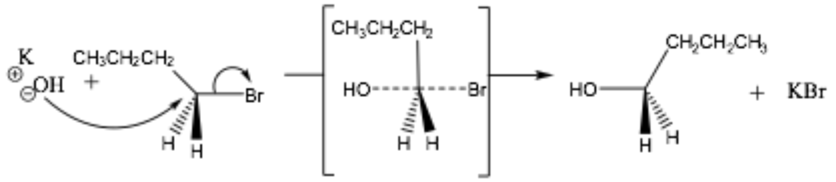
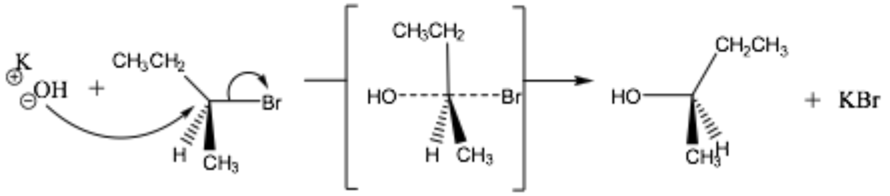


Figure 5 shows the mechanism for an SN2 reaction with 2-bromobutane and KOH in ethanol.



E2 and SN2 reactions are very similar in their guidelines and these are the two reactions that will be looked at in this experiment. A key difference between these two is that an SN2 reaction prefers a methyl halide and a primary halide, respectively, whereas an E2 reaction prefers a tertiary halide. A secondary halide provides competition between these two and further analysis can determine which reaction may be favourable.

Since these two reactions are so similar it is difficult to get a 100% yield of either one, but there are some tweaks in electrophile, nucleophile and temperature that can be applied to favour one reaction over the other.

Since a nucleophile can react as a base it creates competition between substitution and elimination reactions. In order to favour an elimination reaction is to use a non-nucleophilic base like a strong hindered base. A nucleophile with a charge will favour a substitution reaction over an elimination reaction.

Temperature is a large determining factor to which type of reaction will occur. A substitution reaction usually has a lower activation energy than an elimination reaction. When heat is added to a reaction, it favours an alkene formation and is more likely to reach the required threshold for an elimination reaction. In this case a beta proton is more accessible than the alpha carbon and an elimination reaction is favoured.

The goal of this experiment is to determine how much of an E2 product and a SN2 product was generated under various conditions with various solvents. This was split into three parts. In part 1, we react a strong small base and strong nucleophile KOH with 1-bromobutane at room temperature (with reflux). For the second part, 2-bromobutane was reaction with KOH at room temperature (at reflux). In part 3 we react a strong small base and strong nucleophile KOH with 1-bromobutane at a higher temperature of 55 degrees celsius. Reflux is when a constant heat is applied to a solution resulting in no liquid being lost in an evaporation. We will use an eudiometer to collect the gas formed in the reaction. Assuming the gas formed is an ideal gas we can use the following equations to determine the amount of product formed from each reaction. To calculate this we use a couple of equations as shown below.

1. P*= (amount of water between the waters edge of the beaker and the highest point it reaches in the eudiometer above the water, in mm)/(13.6mm)

    a. Pressure given in mmHg

2. $P_{gas} = P_{atm} - P_{water} - P^*$ (See table 3.3 for P_{water} values, see table 3.4 for P* value calculations).

3. $Pv = nRT$

4. $n_{KBr} = n_{gas} + n_{butanol} = n_{E2} + n_{SN2}$

Using the first equation we get the pressure needed to find the pressure of the gas collected, with equation 2. Assuming this is a noble gas, and that the pressure is in KPa we can use the third equation to isolate for the amount of moles of butene collected. From this value, we can determine the moles of butanol collected using equation 4, given the mass of KBr used in this experiment, and the moles of butene calculated. Stoichiometrically, the ration between the moles of KBr reaction is 1:1 with the amount of electrophile consumed in the reaction. Knowing the number of moles of KBr produced we can calculate the percent of butene and its complement butanol produced because we know that one mole of the electrophile substrate which reacts with the base/nucleophile which is KBr will produce one mole of the product containing a combination of the elimination product (alkene gas) and the substitution product (butanol), based on stoichiometry. We use equation 4 for this as well and we also make the assumption that all the electrophile is reacted in the 20-25 minutes during which the reaction occurred.

Experimental Procedure:

Refer to lab manual of CHM2523 pg. 47-54, experiment 3.

Modifications:

- Step 7: use 700 mL of water instead of 1000 mL.
- Proceed with step 19 before step 18.

Reagent Table:

Table 1: Table of reagents for 1-bromobutane with KOH at room temperature at at 55℃.

Compound	**Molecular mass (g/mol)**	**Quantity (g or mL)**	**Density (g/mL)**	**Mmol**	**Equivalents**
KOH	56.1056	8.04 g	2.12	0.143	13
EtOH	46.0684	40.0 mL	789 000	N/A	N/A
1-bromobutane	137.02	1.5 mL	1.27	0.0109	1

Table 2: Table of reagents for 2-bromobutane with KOH at room temperature.

Compound	**Molecular mass (g/mol)**	**Quantity (g or mL)**	**Density (g/mL)**	**Mmol**	**Equivalents**
KOH	56.1056	8.04 g	2.12	0.143	39
EtOH	46.0684	40.0 mL	789 000	N/A	N/A
2-bromobutane	137.02	0.51 mL	0.5	0.00365	1

Observations:

Step	**Observation**
3. (Part 1: 1-bromobutane at room temperature)	- 8.04 g KOH - KOH are oval white crystals - EtOH appears clear and colourless - KOH does not dissolve in ethanol
10.	- Bubbles start to form when the magnet starts to turn - Crystals dissolve and more bubbles are created - Water column empties quickly - Had to add more water to the water column - All KOH dissolved and bubbles in the water column stop forming - Initial volume in the water column is 0.0 mL
12.	- Solution turns white with bubbles - Water column level lowers as air bubbles form - Gas released from the balloon in white vapour.
19.	- KOH mass = 8.04 g
12.	- Water column level went down ⅓ of the way really quickly the slowed

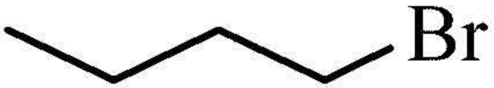
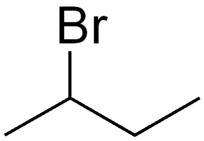
	down - Stopped reaction - 25 mL gas
16 - Filtration	- Steam forms when adding solution to be filtered - Rinsed with EtOH to maximize the solution being filtered
17.	- 1.29 g of KBr product measured
12. (Part 2: 2-bromobutane)	- KOH mass = 8.04 g - Initial volume in water column = 2.0 mL // - Had to restart this part because the water column emptied too soon for us to note the final volume. - New KOH mass : 7.99 g - Initial volume = 0.0 mL - Final volume = 49.0 mL - Had to refill water tube, blocked has from escaping with thumb but some escaped anyways.
17.	- KBr product mass = 0.49 g - Filtered twice to maximize product
12. (Part 3: 1-bromobutane + water bath (55℃))	- Initial volume : 6.5 mL - Tried to keep temperature constant at 55℃ - Temperature fluctuated between 53℃ and 60℃ - Slight vapour formed in the balloon - KOH not dissolving - No visible precipitation forming in the balloon - Dismounted the stand because no change occurred after ~25 minutes - No filtration was conducted as we had no solution to filter

Results:

Reaction Conditions	**Gas Pressure (atm)**	Gas volume (mL)	Moles of Butene (mol)	Mass of KBr (g)	Moles of KBr (mol)	Moles of Butanol (mol)	Butene Yield (%)	Butanol Yield (%)
1-bromobutane at reflux	0.00153922	25	(1.01×10^{-3})	1.29	0.01084	(9.83×10^{-3})	9.31	90.69
1-bromobutane at 55°C	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
2-bromobutane at reflux	(4.025×10^{-3})	56.5	(2.28×10^{-3})	0.49 g	(4.12×10^{-3})	(1.84×10^{-3})	55.26	44.74

Discussion:

This lab analysed how different factors can affect the competition between substitution and elimination products, in this case SN2 and E1. Depending on if the reactant in question, in this case KOH, acts as a nucleophile or a base based on the environment given for the reaction, the major product will be a substitution product or an elimination product. Two main factors that affect the outcome and proportion of each product is the hindrance on the electrophile as well as the temperature. The two different electrophiles used in this experiment are 1-bromobutane and 2-bromobutane. As can be observed in figures 6 and 7, 1-bromobutane is less hindered than 2-bromobutane. 1-bromobutane is also a primary halide which highly favours the formation of an SN2 product because a nucleophile is more willing to attack a less sterically hindered alpha carbon as it attacks the leaving group alpha carbon from behind. An E2 reaction preferred more substituted alpha carbons because it increases the alkene stability determined by enthalpy of hydrogenation of the alkenes. Whereas 2-bromobutane is a secondary halide which creates competition between an SN2 and E2 reaction. In order to determine which product was more prevalent, the amount of butene and butanol product was measured and calculated where butene product indicates an E2 reaction and a butanol product indicates an SN2 reaction.

Figure 6.	Figure 7.
1-bromobutane	2-bromobutane
	

For the first part of the experiment consisting of the electrophile 1-bromobutane, KOH as its nucleophile in a solvent of ethanol at room temperature we got an experimental yield of butene gas (E2 product) of 9.31% and a yield of butanol, SN2 product, of 90.69%. This indicates that the major product was SN2 and the minor product was E2. (Refer to figure 1, figure 2 and figure 4 found in the introduction for the mechanisms of these reactions). The electrophile used in this case is 1-bromobutane which is a primary halide, meaning the alpha carbon is only connected to one other carbon (and bromide in this case). This is an ideal situation to have an SN2 reaction occur as the lack of hindrance around the alpha carbon allowed for an efficient attack of the nucleophile with minimal interference from any hindering groups nearby and allowing for the leaving group to leave simultaneously resulting in a favoured butanol product. An SN2 can only occur with an attack coming from the opposite plane from which the leaving group is situated due to it being a concerted reaction. A primary halide is the second most preferred substitution on the alpha carbon for an SN2 reaction, the first being a methyl substituted alpha carbon which carries even less hindrance to allow for an even simpler back attack of the nucleophile. The nucleophile used is KOH which is a good nucleophile due to the fact that its positively charged potassium and ionically stable allowing for an easy separation between the K^+ and the OH^- allowing for substitution to occur as the OH forms butanol. A good nucleophile like this one is favourable for an SN2 reaction.

Calculations showed that E2 products still occurred but with a much lower yield of only 9.31%. An E2 reaction can still occur even though an SN2 is favoured. The nucleophile used for the SN2 reaction, KOH, also happens to be a strong small base which is ideal for an E2 reaction. Because 1-bromobutane is a primary halide it is not the most ideal condition for an E2 reaction. An E2 reaction prefers a tertiary alpha carbon, or the most substituted carbon as possible. It prefers tertiary over secondary but can still work relatively well under both those conditions. With a primary halide, an E2 reaction will have a harder time competing with other more favourable reactions, such as SN2, but it can still form. This is because an E2 reaction prefers to form a more stable alkene which consists of a more substituted alpha carbon. It will gladly use a strong small base like KOH, but the explanation for its low percent yield is the primary halide. An E2 reaction can form 2 types of alkenes, a zaitsev product (forming the most substituted alkene) or a hofmann product (forming the least substituted alkene) but we cannot conclude which of these are formed in what ratio in this particular experiment. At room temperature, with no added heat, an E2 reaction will not be advantageous due to enthalpy as previously mentioned.

The polar protic solvent used in this experiment, ethanol, does not significantly favour one reaction to form over the other as both E2 and SN2 reactions form well with a polar protic solvent. This solvent may only have a small effect on the nucleophile as the protic solvent can form hydrogen bonding with the nucleophile which can result in the reduction of its nucleophilicity. This should not have much of an effect in this case because of the other factors involved in this reaction.

Experimentally, a 9.31% : 90.69% ratio of E2:SN2 products is in line with the theory of the competition between these two products and their theoretically predicted outcomes.

The second part of this experiment had 2-bromobutane as the electrophile with KOH in a solvent of ethanol at room temperature. The yield of butene gas, the E2 product is 55.26% and the yield of butane, the SN2 product is 44.74%. These results are drastically different from those in part 1. This is due to the structure of 2-bromobutane versus that of 1-bromobutane. 2-bromobutane is a secondary halide. This is not the most prefered environment for an E2 or an SN2 reaction but still functions well enough for both of them and causes a relatively equal competition between these two reactions as can be proven from the yield results. A secondary halide increases the steric hindrance around the alpha carbon, making it a little harder for an SN2 attack to occur as further elaborated upon, earlier. The secondary halide also does not create the most stable alkene in an E2 reaction but still works just fine, just not the most favourably. The small degree of variance in the yields of the two products can be caused by the slight disadvantage the SN2 reaction has in the polar protic solvent, as explained above. This could have E2 favoured slightly over SN2 along with potential sources of error which will be discussed later.

For the third part of the experiment consisting of 1-bromobutane as the electrophile at a higher temperature of 55 degrees celsius with KOH and ethanol, no reaction was observed after about 25 minutes when we ran out of time. Theoretically, this reaction will be similar to that in part 1, but with a higher yield for the E2 product. This is because of the higher temperature in this part which allows for higher activation energy and allows for elimination to be more favoured than it was in part one. This added heat phenomenon is explained to greater lengths at the beginning of the discussion. The elimination product would still be the minor product due to the primary halide of 1-bromobutane as discussed in part one.

A few sources of error can have quite an effect on the experimental yield. First, we assumed that the mass of KBr produced in our experiment is the full amount that is produced in this reaction. However, if we had let the reaction run longer than we did (~20 - 25 minutes) we may have produced more KBr product. This is important because we rely on the value of KBr to get our value for the amount of butene gas produced in the reaction as well as butanol produced in this reaction. An underestimate of the amount of KBr will underestimate the amount of butene gas formed and overestimate the amount of butanol formed. This would imply a higher yield of E2 and a lower yield of SN2 then there actually is in this.

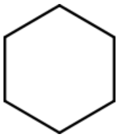
Another source of error comes from when we had to change the eudiometer as it empties and more water was required. A removal of the eudiometer during the reaction was required and even as we followed through with preventative methods of covering the opening of the gas as the eudiometer was being filled up. Despite our actions some gas was still able to escape. This is the butene gas that escapes and means that less of it is accounted for in the analysis of the reaction. This source of error also causes a lower yield of E2 and a higher yield of SN2 than there actually was based on how the calculated product of SN2 relies on how much E2 product (butene gas) is observed and collected.

Questions:

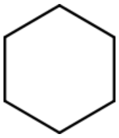
1.
Temperature = 25°C = 298.15 K
Pressure = 1 atm = 101.325 KPa
Universal gas constant = 8.3144598 L kPa K^{-1} mol^{-1}
Volume of 1-bromobutane = 1.50 mL
Density of 1-bromobutane = 1 276 g/mL
Molar mass of 1-bromobutane = 137.02 g/mol
Volume of butene gas = **(2.10 x 10^{-4}) L^3**

Mass of 1-bromobutane = volume x density = 1.50 mL x 1 276 g/mL = 1.176 g
Moles of 1-bromobutane = mass / molar mass = 1.176 g / 137.02 g/mol = 0.008579 mol
therefore moles of butene = 0.008579 mol
V=nRT/P = (0.008579 x 8.314 x 298.15)/(101 325) = 2.10 x 10^{-4} L^3

2.
a)



b)



3.
a) Elimination.
b) Substitution.

c) Substitution.

4. A substitution reaction occurs to produce 1-pentanol. If we want 1-pentene, the creation of an alkene, we want an elimination reaction to occur. In this case, 1-pentene is a least substituted alkene (hofmann product) which indicates an E2 reaction. For this to occur, the NaOH (a strong small base in the case of an elimination reaction) should be replaced with a strong hindered base like $KOC(CH_3)_3$. Another way to ensure an elimination reaction is to add heat to the reaction which increases the activation energy of the reaction which is favoured for an elimination reaction over a substitution reaction, as explained in the introduction.