

Reminder: These notes are meant to supplement, not replace the laboratory manual.

## SN1 Reaction Notes

### Background and Application

Substitution Nucleophilic First Order (SN1) reactions are one of the most common type of organic reactions. SN1 reactions can be used to make a wide variety of new compounds. In this experiment, t-amyl alcohol will be converted by a SN1 mechanism to 2-chloro-2-methylbutane.

### Safety Precautions

Concentrated Hydrochloric Acid is 12M. It will cause visible destruction of tissue upon contact. Wear eye goggles at all times during this experiment. Keep HCl away from skin, clothes, eyes. Neutralize any spilled HCl with sodium bicarbonate (baking soda) and wipe up immediately.

Gasses will be released when sodium bicarbonate is added to your separatory funnel. Do not stopper funnel after the addition of sodium bicarbonate solution. Vent separatory funnel frequently while shaking. Do not vent sep funnel toward another person or yourself. Liquids may spray out while venting.

Chlorinated hydrocarbons tend to be toxic materials. The target organs are the liver and kidneys. Be careful not to breathe product or get on skin.

#### 1. Some terminology related to SN1 Reactions:

**Synthesis:** A reaction which results in the formation of a new product.

**Mechanism:** A step by step description of bond breaking and bond breaking as one compound is transformed into another compound.

**Leaving Group:** This is the part of a molecule which may break away, taking the electrons from the bond with it. The more stable the leaving group as an independent assemblage, the more readily it will depart the molecule.

**Carbocation:** A carbon with only 6 shared valence shell electrons. A full positive charge resides on the carbon. Carbocations are electrophiles.

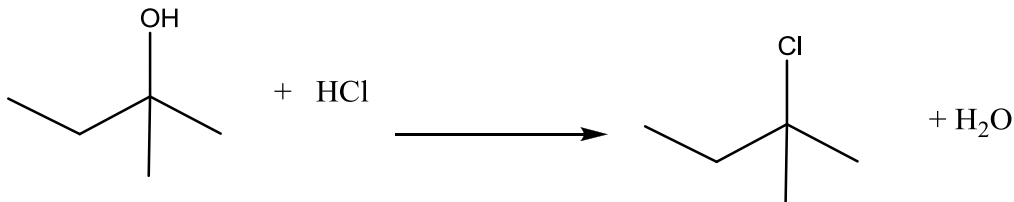
**Nucleophile:** An atom or assemblage of atoms which will donate electrons to form a new covalent bond. Strong nucleophiles are strong Lewis bases.

**Electrophile:** An atom which will accept electrons and form a new covalent bond. Electrophiles have either a formal positive charge or a partial positive charge. They have a low electron density and hence will accept electrons from a nucleophile.

**SN1 mechanism:** A two step Nucleophilic substitution mechanism which is rate dependent only on the starting alkyl concentration.  $K = k_1[R-LG]$ . The first step, the leaving group leaves forming a carbocation. This is the slow rate determining step (RDS). In the second step, a nucleophile forms a new covalent bond with the electrophile.

2. This is a synthetic experiment. Today each of you will make a new compound by reacting two starting materials together. 2-methyl-2-butanol (t-amyl alcohol or t-pentyl

alcohol) is converted to 2-chloro-2-methyl butane (t-amyl chloride or t-pentyl chloride). The overall reaction is as follows.



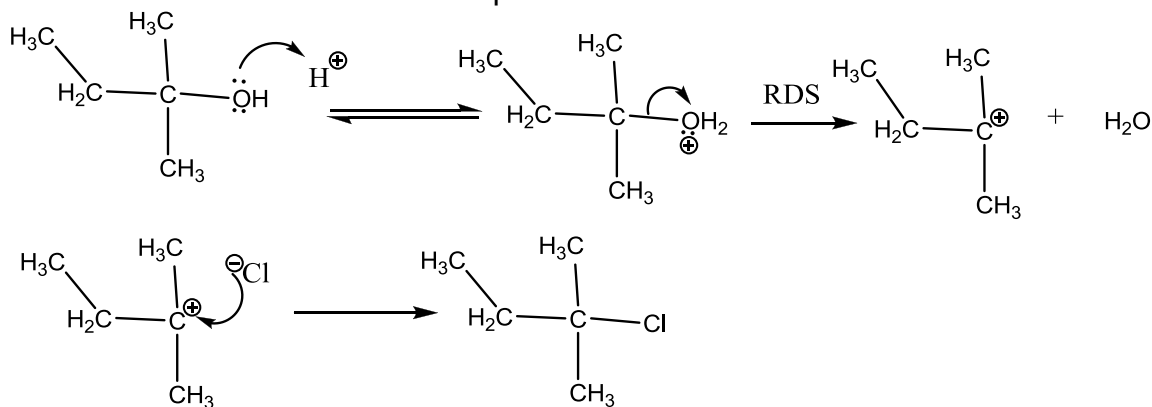
3. This reaction is carried out in the presence of excess concentrated hydrochloric acid. HCl is highly corrosive. Goggles and gloves should be worn at all times. Care should be taken to not get acid on skin. Hydrochloric acid is a strong acid (pK<sub>a</sub> = - 3.9) which means the acid completely dissociates.



4. Most chlorinated organic materials have increased toxicity to humans. The target organs are usually the liver and kidney. Minimize direct contact with these materials.

5. S<sub>N</sub>1 reactions are nucleophilic substitution reaction with first order kinetics in regard to the organic substrate. This is a three-step mechanism. First the acid protonates the alcohol to form a good leaving group; then water (the leaving group) departs, forming a carbocation. This is the rate determining step (RDS). The last step is a Lewis acid-base reaction in which the nucleophile combines with the carbocation to form the product.

The entire mechanism is depicted below.

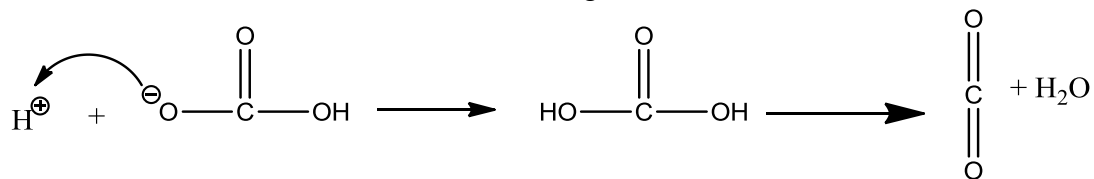


6. 2-methyl-2-butanol is soluble in water. 2-chloro-2-methylbutane is insoluble in water (<1.0 g/100mL)<sup>1</sup>. When 2-chloro-2-methylbutane forms it immediately separates from the aqueous layer and creates a new organic layer. The solubility in water of these two compounds is different because the hydroxyl group is both a hydrogen bond donor and a hydrogen bond acceptor, whereas chlorine is neither a hydrogen bond donor or acceptor. The hydroxy group permits the t-amyl alcohol to be soluble in water.

7. If two or more layers exist in a separatory funnel, you can determine the identity of the aqueous layer by adding drops of water to the funnel and observing the layer into which the droplets merge.

<sup>1</sup> National Institutes of Standards and Testing, <http://www.nist.gov/srd/PDFfiles/jpcrd560.pdf> April 1, 2009

8. Sodium bicarbonate is baking soda. Sodium bicarbonate solution is simply baking soda dissolved in water. It is a weak base and will neutralize any excess acid present. When sodium bicarbonate reacts with an acid, it forms carbonic acid which dissociates into water and carbon dioxide which is a gas.



9. Saturated sodium chloride (NaCl) solution is simply salt water, also called brine. The high ionic nature of the brine decreases the formation of emulsions and promotes the separation of organic material from the water layer.

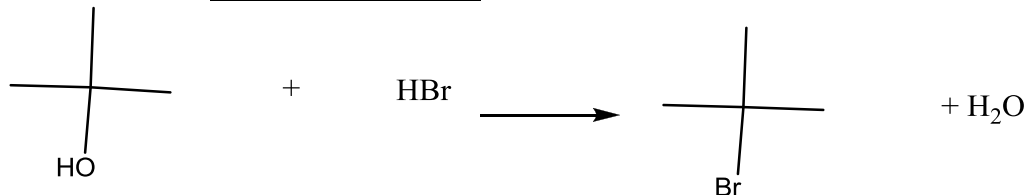
10. Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ) is a dehydrating (drying) agent. It absorbs water from materials with which it comes in contact. Sodium sulfate is often used to dry liquids. This does not mean to remove all the liquid, but simply to remove the water ( $\text{H}_2\text{O}$ ) from that liquid.

11. Percent yield is the amount of material actually formed divided by the theoretical maximum amount of product that could form (the theoretical yield). This is a common calculation in second semester organic lab.

$$\text{Percent yield} = \frac{\text{mass}_{\text{product}_{\text{actually}_{\text{formed}}}}}{\text{theoretical}_{\text{maximum}_{\text{mass}_{\text{of}_{\text{product}}}}} \times 100\%$$

12. The theoretical maximum mass of product is calculated based on the starting amount of reactants and the stoichiometry of the reaction. This reaction has a one to one stoichiometry. The volume of alcohol must be converted into grams of alcohol using density. The grams of alcohol must be converted into moles of alcohol using the molecular weight. The moles of alcohol must be converted into moles of alkylchloride using the reaction stoichiometry. The moles of alkylchloride must be converted into grams of alkylchloride using the molecular weight of the chloride. The moles of acid used is determined by multiplying the volume of acid solution used (in L) by the concentration in Molarity. The units of Molarity is moles per liter. The liters cancel and moles of acid remain. The moles of acid is converted into moles of product by the reaction stoichiometry. The moles of product is converted into grams of product by multiplying by the molecular weight.

13. An example of calculating the theoretical maximum amount of product which can form is illustrated below on a different but similar reaction.



	2-methyl-2-propanol	Hydrobromic acid	2-methyl-2-bromopropane
Molarity	-	12.1	-
Mol Wt (g/mol)	74.15	80.9	137.05
Density (g/mL)	0.781	na	1.198

“t-BuOH” will indicate 2-methyl-2-propanol

“t-BuBr” will indicate 2-methyl-2-bromopropane

If 4.76 mL of 2-methyl-2-propanol were reacted with 13.59mL of 4.5 M HBr, what is the maximum amount of product which could form? If 4.5681 grams of product were made, what is the percent yield?

Calculate the maximum theoretical amount of product that could be made based on each starting material.

The theoretical maximum amount of product based on the alcohol is.....

$$\frac{\text{starting\_volume(mL)}}{1\_mL} \times \frac{\text{Density (g/mL)}}{1\_mL} \times \frac{1}{\text{mol.\_wt(g/mol)}} \times \frac{\text{Reaction\_Stoichiometry}}{1\_mol\_tBuOH} \times \frac{\text{Mol.Wt.Product(g/mol)}}{1\_mol\_tBuBr} = \text{gram\_pr}$$

Keeping good track of units and identifiers will help to solve the problem.

$$\frac{4.76\_mL\_tBuOH}{1\_mL} \times \frac{0.781\_g\_tBuOH}{1\_mL} \times \frac{1\_mol\_tBuOH}{74.15\_g\_tBuOH} \times \frac{1\_mol\_tBuBr}{1\_mol\_tBuOH} \times \frac{137.05g\_tBuBr}{1\_mol\_tBuBr} = 6.87gtBuBr$$

The theoretical maximum amount of product based on the alcohol is.....

$$\frac{13.59\_mL\_HBr\_sln}{1000\_mL\_HBr\_sln} \times \frac{1\_L\_HBr\_sln}{1\_L\_HBr\_sln} \times \frac{4.5\_mol\_HBr}{1\_L\_HBr\_sln} \times \frac{1\_mol\_tBuBr}{1\_mol\_HBr} \times \frac{137.05g\_tBuBr}{1\_mol\_tBuBr} = 8.4gtBuBr$$

Since 6.87 g is less than 8.4 g, that means the maximum amount of material that can be made is 6.87 grams and the 2-methyl-2-propanol is the limiting reagent.

The percent yield is the amount of product actually produced divided by the theoretical maximum amount of product that could be produced times 100%.

$$\text{Percent\_Yield} = \frac{\text{amount\_of\_product\_made}}{\text{theoretical\_maximum\_amount\_of\_product}} \times 100\% = \frac{4.5681\_g}{6.87\_g} \times 100\% = 66.5\%$$

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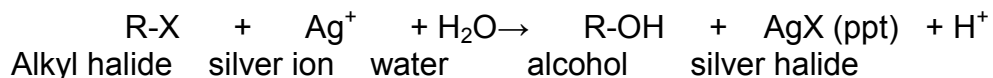
14. Physical properties necessary to carry out the calculations for the synthesis of 2-chloro-2-methyl butane are below.

2-methyl-2-butanol density = 0.806 g/mL mol. Wt. =88.15

Concentrated Hydrochloric Acid Molarity = 12.1 M

2-chloro-2-methylbutane density = 0.866 g/mL mol. Wt=106.59

15. Silver nitrate is one of the very few water-soluble silver salts. When silver nitrate reacts with an alkyl halide, a silver halide forms. This is insoluble and will appear as a white cloud or a white precipitate.



If silver nitrate is reacted with an unknown material and a white precipitate results, then the unknown material must have contained a halide. When Silver Nitrates contacts skin, it becomes reduced and turn black-brown. This will not wash off. Be careful to avoid skin contact.

Revised: slweaver October 28, 2011