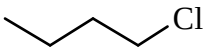
S_N1 and S_N2 reactions of alkyl halides

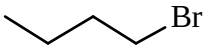
Introduction

The two primary mechanisms for substitution reactions are the S_N1 and S_N2 reactions. Today we will be studying these reactions for all of the compounds shown below. You should work in pairs today. One of you can do all the S_N1 reactions and the other one can do all the S_N2 reactions.



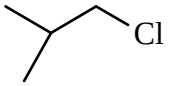
1-chlorobutane

A



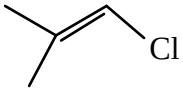
1-bromobutane

B



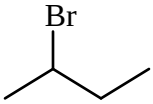
1-chloro-2-methylpropane

C



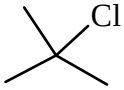
1-chloro-2-methyl propene

D



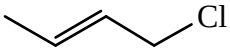
2-bromobutane

E



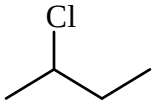
2-chloro-2-methyl propane

F



1-chloro-2-butene

G



2-chlorobutane

H

S_N2: $\text{R-X} \xrightarrow[\text{acetone}]{\text{NaI}} \text{R-I} + \text{NaX}\downarrow$

S_N1: $\text{R-X} \xrightarrow[\text{OH}]{\text{Ag}^+} \text{R}^+ + \text{AgX}\downarrow \rightarrow \text{R-O}$

To test the S_N2 reactions we will use a solution of NaI in acetone. Acetone is an aprotic solvent that is fairly polar and I^- is a reasonable nucleophile. If a reaction occurs, we will form Br^- or Cl^-, both of which will combine with the Na^+ to form either NaBr or NaCl. NaI is soluble in acetone, while NaCl and NaBr are not soluble and will form a precipitate. So if you see any precipitate, it indicates that the S_N2 reaction has occurred. More precipitate means more reaction.

To test the S_N1 reactions, we will use a solution of $AgNO_3$ in ethanol. Ethanol is a **very** polar protic solvent, and the silver ion forms very strong bonds with Br^- or Cl^-. So the silver ion helps to remove the halide and form the carbocation and the silver halide salt. The carbocation reacts with the ethanol to form the ether; and the AgCl and AgBr are insoluble (remember exp. 5 from

101A?) and will form a precipitate. As above, if you see any precipitate, it indicates that the SN1 reaction has occurred. More precipitate means more reaction.

Experimental Procedure:

For both procedures, you will need a 50 ˚C water bath, so fill a 100 mL beaker half full with water, place it on a hot plate and heat it until the water is 50-55 ˚C. If the bath becomes too hot, you can periodically lower the temperature by adding some ice or cool water to the bath.

SN2 reactions:

Place about 0.1 mL of each of the halides in small labeled test tubes. Then quickly add 1 mL of a 9% solution of NaI in acetone. Be sure to keep track of the time, so that you will know exactly how long it takes to form a precipitate. The length of time to form precipitate is a measure of the reactivity of the alkyl halide. **Make sure that you add all of the NaI/acetone solution and mix the solution before you look for any precipitate. You will often see a small amount of precipitate when you the first drop of the NaI/acetone solution hits the alkyl halide. This is because the NaI is not soluble in the alkyl halide. After all the solution is added, the NaI should all be soluble because there is much more acetone than alkyl halide.** Allow the reaction to sit at room temperature for 5 minutes, while occasionally flicking the test tube to mix everything. If no reaction has occurred after 5 minutes, place the test tubes in a 50 ˚C water bath for 5-10 minutes and look for any precipitate. Record the time it takes each of the compounds to form a precipitate. Some of the compounds may not form a precipitate.

SN1 reactions:

Place about 0.1 mL of each of the halides in small labeled test tubes. Then quickly add 1 mL of a 1% solution of $AgNO_3$ in ethanol, and mix the solution thoroughly. Be sure to keep track of the time, so that you will know exactly how long it takes to form a precipitate. The length of time to form precipitate is a measure of the reactivity of the alkyl halide. Allow the reaction to sit at room temperature for 5 minutes, while occasionally flicking the test tube to mix everything. If no reaction has occurred after 5 minutes, place the test tubes in a 50 ˚C water bath for 5-10 minutes and look for any precipitate. Record the time it takes each of the compounds to form a precipitate. Some of the compounds may not form a precipitate.

Calculations/Discussion

There will be no formal lab report for this lab, but we will all compare our results. Before the lab, try to rank all of the halides in terms of their reactivity in both SN1 and SN2 reactions (one list for each reaction). It may be difficult to rank all of them, but don't worry if you can't predict all of them with 100% confidence. The experiment will tell us which factors are most important!

After you and your partner have completed the lab, rank all your compounds in terms of the time of reaction (1 = fastest reaction, 8 = slowest reaction) for both the SN1 and SN2 reactions. Place your ranking next to the letter for each compound on the board. Then we can see how well all of our results agree! We will discuss and rationalize our results in the lab.