S_N1 and S_N2 Reactions
Substrate and Solvent Effects

Adapted from: OPERATIONAL ORGANIC CHEMISTRY, 3/e, John W. Lehman, Prentice Hall, 1999.

The purpose of this collection of experiments is to determine what effects the leaving group, carbon substitution pattern and solvent have on the rate of reaction for two different nucleophilic substitution mechanisms, S_N1 and S_N2. You will be joining a research team: *alpha-1 or alpha-2*, *beta–1 or beta-2*, *or gamma-1, or gamma-2, or gamma-3*, which are part of a larger research group studying the overall mechanism and kinetics of nucleophilic substitution reactions.

The alpha and beta teams are to investigate a series of various different alkyl and aryl halides using either *Procedure A* or *B*, where the halide (X) is either chlorine (Cl) or bromine (Br); the gamma teams will study a series of different solvent systems using *Procedure C*. Read through all three procedures. Consider whether the respective procedure favors an S_N1 or an S_N2 mechanism, and check the appropriate box below for each. When complete see Dr. R. for your team and procedure.

Procedure A:	S_N1 S_N2	*Procedure B:*	S_N1 S_N2	*Procedure C:*	S_N1 S_N2

 A and B Procedures: *(Where X is either Cl or Br.)*

Procedure A (alpha groups): *#1 = - Cl; #2 = - Br*
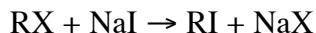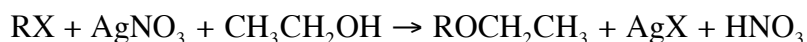
$$RX + NaI \rightarrow RI + NaX$$

Determine what compounds are available for your assigned halide. (They are located together in the lab.) Draw their structures on the form that was provided your team. Check with Dr. R. before proceeding with the experiment.

Gather clean, dry small test tubes with stoppers or parafilm for each halide. Add 1.0 mL of a 15% sodium iodide in acetone solution to each test tube. Add 2 drops of the first halide on your list to one test tube. Record the time. Cover or stopper and shake the tube. Observe closely the time it takes for cloudiness to appear. If there is no precipitate formed after 5 minutes place the test tube in a water bath at 45ºC for 10 minutes. Cool to room temperature and record if a precipitate forms. Repeat with each of the remaining halides.

1) Graph your results. 2) Write a structure for the product of each reaction that was observed. 3) Arrange the halides in order of reactivity and explain how this relates to the mechanism. 4) Compare your results to your predictions. 5) Clearly state a conclusion as to how the substrate effects the reaction rate and how this relates to the mechanism.

After completing all of the above, compare your results with the other *alpha* group and jointly prepare a short 10-15 minute presentation. It should be a consolidated summary of the results including a list of general statements that address the effects of carbon substitution patterns and the leaving group on nucleophilic substitution reaction rates which are supported by your results. Answer the remaining question(s) on the form

Procedure B (beta groups): *#1 = - Cl; #2 = - Br*

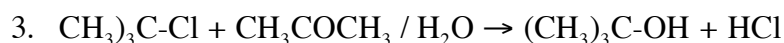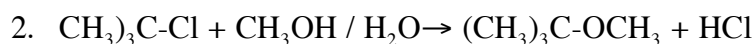$$RX + AgNO_3 + CH_3CH_2OH \rightarrow ROCH_2CH_3 + AgX + HNO_3$$

Determine what compounds are available for your assigned halide. (They are located together in the lab.) Draw their structures on the form that was provided to your team. Check with Dr. R. before proceeding with the experiment.

Gather clean, dry small test tubes with stoppers or parafilm for each halide. Add 2.0 mL of a 0.1M solution of silver nitrate in ethanol to each test tube. Add one drop of the first halide on your list to a test tube. Record the time. Cover or stopper and shake the tube. Observe closely the time it takes for cloudiness to appear. (The formation of a silver halide precipitate.) If there is no precipitate formed after 5 minutes place the test tube in a boiling water bath for 10 minutes. Record if a precipitate forms. Repeat with each of the remaining halides.

1) Graph your results. 2) Write balanced equations for each reaction that you observed. 3) Arrange the halides in order of reactivity and explain how this relates to the mechanism. 4) Compare your results to your predictions. Reconcile any differences from the predicted and actual results. 5) Clearly state a conclusion as to how the substrate effects the reaction rate and how this relates to the mechanism.

After completing all of the above, compare your results with the other *beta* group, reconcile any differences and prepare a short 10-15 minute presentation. It should be a consolidated summary of the results including a list of general statements that address the effects of carbon substitution patterns and the leaving group on nucleophilic substitution reaction rates which are supported by your results. Answer the remaining question(s).

Procedure C (gamma groups): *(Solvolysis: MeOH, EtOH, H₂O)*

1. $(CH_3)_3C\text{-}Cl + CH_3CH_2OH / H_2O \rightarrow (CH_3)_3C\text{-}OCH_2CH_3 + HCl$

2. $(CH_3)_3C\text{-}Cl + CH_3OH / H_2O \rightarrow (CH_3)_3C\text{-}OCH_3 + HCl$

3. $(CH_3)_3C\text{-}Cl + CH_3COCH_3 / H_2O \rightarrow (CH_3)_3C\text{-}OH + HCl$

Identify the nucleophile in each of the three reactions. If not already prepared for you, prepare the solvent mixtures in the solvent ratios for your assigned reaction. Consult the form that was provided your team. Check with Dr. R. before proceeding with the experiment.

Gather clean, dry small test tubes with stoppers or parafilm for each. Have one test tube for each solvent concentration. Add 2.0 mL of the solvent system plus 3 drops of a 0.5M sodium hydroxide solution with one drop of phenolphthalein indicator to each. Place the test tubes in a water bath at 35°C for 4-5 minutes. Add 3 drops of tert-butyl chloride to each test tube. Record the time. Cover or stopper and shake each tube and replace in the bath. Observe closely the time it takes for the pink color to disappear. (The neutralization of the NaOH by the HCl formed.) Record the time elapsed.

1) Graph your results and compare them to your predictions. Reconcile any differences from the predicted and actual results. 2) Write a mechanism for your reaction. 3) Define *dielectric constant* and rank your solvent mixtures in increasing order of dielectric constant for the mixture. 4) Clearly state a conclusion as to how the nature of the solvent effects the reaction rate and how this relates to the mechanism based on your results.

After completing the above, compare your results with the other *gamma* groups, reconcile any differences and prepare a short 10-15 minute presentation. It should be a consolidated summary of the results that includes a list of general statements regarding the effects of solvent and nucleophile on nucleophilic substitution reaction rates which are supported by your results.

Answer the accompanying questions.