RELATIVE RATES OF SUBSTITUTION REACTIONS

PROCEDURE

The reactions below will investigate the effects of structure, solvent, and concentrations on both S_N1 and S_N2 reactions. Because of the hazards posed by some of the chemicals, wear gloves at all times. Use caution when shaking tubes; keep the cork in place with your thumb, don't shake too vigorously, and shake only in your hood. Use caution, as pressure may build up, forcing the cork out. All tubes used in the experiment should be clean and dry to prevent competing side reactions.

A. Factors Affecting Rates of S_N2 Reactions

Measure 2 mL of 15% NaI in acetone into each of three small test tubes. To one tube add two drops of *n*-butyl bromide, to a second tube add two drops of *sec*-butyl bromide, and to the last tube add two drops of *tert*-butyl bromide. Cork the tubes and shake. Cloudiness or precipitation indicates a reaction has occurred (the precipitate is NaBr, which is less soluble in the acetone). (If you do not observe a reaction, you might add more drops of the alkyl halide.) Observe closely during the first 15-20 minutes and then at intervals throughout the period; remember you are trying to compare the rates of the reactions, but record other observations as well. From your data, determine the effect of substrate structure on the rates. Justify your conclusions based on theory.

To three test tubes add 1 mL 15% NaI in acetone. Into one tube add two drops *n*-butyl bromide, to a second tube add two drops isobutyl bromide, and to the third tube add two drops neopentyl bromide. Again, shake, record your observations, and determine the effect of structure on rates of these reactions. Justify your conclusions based on theory.

Measure 1 mL of 15% NaI in acetone into each of two test tubes. To one add two drops of *n*-butyl bromide and to the second add two drops of *n*-butyl chloride. Shake, and record your observations. The difference is easier to see if you try to perform both tests as simultaneously as possible. Determine the effect of leaving group on rates of these reactions. Justify your conclusions based on theory.

B. Factors Affecting Rates of S_N1 Reactions

Measure 2 mL of a 0.1 M solution of ethanolic $AgNO_3$ into each of three test tubes. Add one drop of *n*-butyl bromide to one tube, one drop of *sec*-butyl bromide into the second, and one drop of *tert*-butyl bromide into the third. Cork and shake the tubes continually, looking closely for evidence of reaction. Record your observations and determine the effect of structure on rates of these reactions and justify.

Measure 2 mL of 0.1 M $AgNO_3$ in ethanol into to test tubes. Chill the tubes in ice for a couple minutes. To one tube add one drop of *tert*-butyl bromide and to the other add *tert*-butyl chloride. Compare the rates of the reactions. Again, the difference is easier to see if you try to perform both tests as simultaneously as possible. Determine the effect of leaving group on the rate of these reactions and justify.

To each of four test tubes, add 1 mL of the following 1:1 mixtures: methanol/water, ethanol/water, propanol/water, and acetone/water. Place three drops of 0.5 M NaOH and three drops 1% phenolphthalein into each tube. Add three drops of *tert*-butyl bromide to each tube, shake once to mix, and then exactly time the disappearance of the pink phenolphthalein color. Record observations and determine the effect of solvent on this reaction and justify.

C. Kinetic Study of an S_N2 Reaction

Prepare 4.0 mL of a 25% v/v solution of *n*-butyl bromide in acetone using the stock solutions available. Also prepare 10.0 ml of a 7.5% solution of NaI in acetone by diluting the 15% solution available.

To determine the order with respect to the substrate, measure 1 mL of 15% NaI in acetone into each of two test tubes. To one, add one drop of acetone and one drop of the 25% *n*-butyl bromide solution. Mix thoroughly and begin timing the reaction from the instant you add the substrate. Watch for the appearance of a precipitate or cloudiness; stop timing at that point. Record your time. Repeat with the second tube but add two drops of the 25% *n*-butyl bromide solution (and no acetone). Measure and record the time it takes for precipitation.

To determine the order with respect to the nucleophile, measure 1.0 mL of 15% NaI in acetone into a test tube. Add two drops of the 25% *n*-butyl bromide solution and time the reaction. Repeat for the 7.5% NaI/acetone solution.

Use the data to determine the rate law for the reaction.