KINETIC INVESTIGATION OF UNIMOLECULAR SOLVOLYSIS

EXPERIMENTAL OBJECTIVES

To examine the kinetics of a unimolecular solvolysis reaction

LEARNING OBJECTIVES

- To learn how to determine rate constants from reaction rates
- To demonstrate how the rate constant changes with temperature
- To calculate an activation energy of a reaction based upon rate constant data

PRE-LAB EXERCISES

1. Read this handout carefully.
2. Review unimolecular solvolysis reactions in your Wade text.

BACKGROUND

The speed at which a reaction takes place is of particular importance in chemistry because it provides information about the detailed path over which reactants travel on their way to becoming products (the reaction mechanism). The correct interpretation of rate data depends on knowledge of those factors that can influence the rate, and these include (1) the structure of the compound or compounds entering into the reaction, (2) the temperature, (3) the type of solvent in which the reaction is carried out, and (4) for many reactions, the concentrations of the reacting species.

We shall investigate some of these effects on a simple but very important process in organic chemistry, unimolecular solvolysis, sometimes designated as S_N1. Such a reaction can be written in two steps. These steps are illustrated with the reaction we are to study in this experiment-namely, the hydrolysis of *tert*-butyl chloride (I).
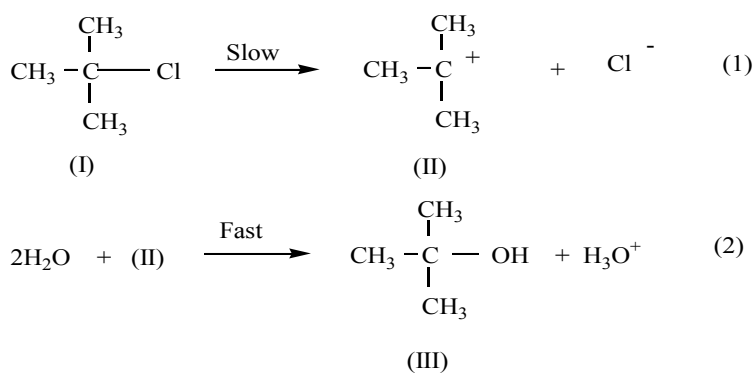
Equation (1) represents the breaking of the carbon-halogen bond of *tert*-butyl chloride in such a way as to form a reactive intermediate carbocation (II) and a chloride ion. The carbocation then reacts rapidly with water to form *tert*-butyl alcohol (III) and a hydronium ion.

If a reaction goes through several steps, the rate of the slowest step represents the overall rate of the reaction. Thus Equation (1) represents the rate-determining step of this reaction.

In the experiment a solution of *tert*-butyl chloride in acetone is quickly added to aqueous sodium hydroxide which contains a bromphenol blue indicator (blue at pH $\geq$ 4.6). The amount of hydroxide is equivalent to 10% of the total amount of *tert*-butyl chloride. Solvolysis begins at the time of mixing and proceeds to give *tert*-butyl alcohol and hydronium ion at a characteristic rate. When the hydronium ion has neutralized the sodium hydroxide, the indicator changes from blue to yellow and the time required for this change represents the time for 10% reaction.

GENERAL PROCEDURE

Repeat the following procedure **three times** and record the time for 10% reaction, the solvent composition (by volume), and the temperature. Determine the average time and the average deviation in seconds.

1.   Pipet 3 mL (5-mL graduated pipet) of a 0.1 M solution of *tert*-butyl chloride in acetone in a 50-mL Erlenmeyer flask and place the flask on white paper. *Take no more than 50 mL of solution in a 100 mL beaker. Pipet from the beaker with the Mohr pipet and bulb.*

2.   Pipet 0.3 mL (1-mL graduated pipet) of 0.1 M sodium hydroxide solution into a second 50-mL flask and then add 6.7 mL of deionized water. *Similarly, take no more than 5 mL of solution into a 50 mL beaker to pipet from.* Add several drops of bromphenol blue indicator solution.

3.   Note the time and quickly pour the acetone solution into the water solution, swirl for a second, and immediately pour the solution back into the other flask. (This procedure will insure complete mixing.) Note the time when the indicator changes color. *Before beginning each experiment, the two flasks should be rinsed with acetone and drained.*

QUESTION 1 How many millimoles (mmols) each of *tert*-butyl chloride and hydroxide ion are present in each flask prior to mixing?

QUESTION 2 Does the acetone participate directly in the reaction? Does the water participate in the reaction? Explain.

QUESTION 3 The relationship between the rate constant for a unimolecular reaction and the percent reaction is given by the expression

$$kt = \ln \frac{1}{1 - (\%\text{reaction}/100)}$$

Calculate the value of k (in sec^{-1}) for the data from Part A.

TEMPERATURE DEPENDENCE

(This part will be done in cooperation with your partner sharing the fume hood. One person will do part #1 and the other do part #2.)

The tendency of the carbon-chlorine bond to rupture will depend on whether a sufficient amount of energy (in the stretching vibration of the bond) is available in the *tert*-butyl chloride molecules. For the following experiments, use the procedure of Part A.

      1. Prepare a water bath from a large beaker and adjust the temperature (crushed ice) to about $10°$ below room temperature. Again follow the procedure of Part A but before you mix the two solutions, allow the temperature of the Erlenmeyer flasks to equilibrate in the water bath for about 5 min. (A piece of copper wire wound around the neck of the flasks and hooked over the edge of the beaker provides a convenient support.) Try reaction three times.

2. Warm a large beaker of water to about $10°$ above room temperature and repeat the preceding experiment three times.

Each person will record all the results from both experiments in their own notebook.

QUESTION 4 What conclusion do you draw about the effect of temperature on the S_N1 reaction rate constant? Do you think your results would be qualitatively true for other reactions?

QUESTION 5 Calculate the rate constant (in sec^{-1}) for each of the temperatures used.

ACTIVATION ENERGY

Because molecules of reactant must have a certain minimum energy before a reaction can take place, we can define an energy of activation that is related to the rate constant by Equation 3, in which c is constant, E_a is the activation energy in calories per mole, R is the gas constant (1.99 cal/K mol), and T is the absolute temperature.

$$k_1 = c e^{-Ea/RT} \tag{3}$$

By taking the natural logarithm of both sides of Equation 3, we obtain Equation 4, which indicates that a plot of ln k versus $1/T$ should give a straight line with slope equal to $-E_a/1.99$. (Note that Equation 4 has the form $y = mx + b$, the general equation for a straight line in which m is the slope, defined as dy/dx.)

$$\ln k_1 = -(E_a/1.99)(1/T) + \ln c \tag{4}$$

QUESTION 6 Plot the data from Exercises 3 and 6 and record your approximate value for *Ea* in kcal/mol. Make sure you plot ln k on the y axis, and $1/T$ (in Kelvins^{-1}) on the x-axis. Don't forget to label.