A Kinetic Study of a Solvolysis Reaction Part II

(by Jyotsna Pradhan Ph.D. updated Oct. 1998)

In today's experiment, we shall investigate some effects on the solvolysis of t-butyl chloride in water-acetone solvent, a representative example of a simple but important class of reactions in organic chemistry. The major product of the solvolysis of t-butyl chloride in water-acetone is t-butyl alcohol, with a small amount of isobutylene being formed as a by-product. The overall reactions involved are represented as follows:

$$(1)\ (CH_3)_3C\text{-}Cl \ + \ 2H_2O \ \rightarrow \ (CH_3)_3C\text{-}OH \ + \ H_3O^+ \ + \ Cl^-$$

$$(2)\ (CH_3)_3C\text{-}Cl \ + \ H_2O \ \rightarrow \ (CH_3)_2C{=}CH_2 \ + \ H_3O^+ \ + \ Cl^-$$

The first of these is a nucleophilic substitution of OH for Cl in the t-butyl chloride, the second an elimination of the elements of hydrogen chloride. You will observe that hydronium ion is formed as a product in both reactions. This will enable you to follow the rate of the combined reactions by noting the time required for neutralization of a fixed amount of sodium hydroxide added to the reaction mixture.

On the basis of a vast array of evidence, both experimental and theoretical, chemists have proposed two general types of mechanisms for nucleophilic substitution and elimination reactions of this type. In the first of these, the initial step is a slow solvent-aided ionization of the halide into a carbocation and chloride ion:

$$(3)\ (CH_3)_3C\text{-}Cl \ \rightarrow \ (CH_3)_3C^+ \ + \ Cl^- \ \text{(slow)}$$

This is followed by rapid reaction of the carbocation with water, to form the corresponding alcohol in the case of the substitution reaction, and isobutylene in the case of the elimination reaction. For t-butyl carbocation these two reactions are as follows:

$$(4)\ (CH_3)_3C^+ \ + \ 2H_2O \ \rightarrow \ (CH_3)_3C\text{-}OH \ + \ H_3O^+ \ \text{(fast)}$$

$$(5)\ (CH_3)_3C^+ \ + \ H_2O \ \rightarrow \ (CH_3)_2C{=}CH_2 \ + \ H_3O^+ \ \text{(fast)}$$

It is a well-established principle of kinetics that if a reaction goes through several steps and one of these is very much slower than the others, then the rate of the slowest step represents the overall rate of the reaction. The slowest single step, whose rate determines the overall rate of a stepwise reaction, is called the rate-determining step. Thus, in this first general mechanism proposed for nucleophilic substitution and elimination reactions in alkyl halides, equation (3) represents the rate-determining step for both the nucleophilic substitution and the elimination reaction, as applied to t-butyl chloride.

Any reaction in which the rate-determining step involves the making or breaking of a covalent bond in only one particle is designated a unimolecular reaction. In both the nucleophilic substitution reaction and the elimination reaction only a single particle, a molecule of the halide, is undergoing a change in covalence in the rate-determining step (3). Hence, both reactions are said to be unimolecular reactions.

A nucleophilic substitution reaction of this type is called S_N1, substitution nucleophilic unimolecular. The corresponding elimination reaction is called E1, elimination unimolecular. It is this combination of reactions which t-butyl chloride undergoes in today's experiment.

In the second general type of mechanism proposed for these reactions, the single, and therefore, rate-determining, step in each case involves a collision of two particles, a halide molecule and a hydroxide ion. These reactions are therefore bimolecular since both particles are undergoing a simultaneous change in covalent bonding.

In the substitution reaction, it is postulated that hydroxide ion attacks the halogen-bearing carbon atom as the halide ion is simultaneously liberated. If such a reaction were to occur for t-butyl chloride, it would be represented as follows:

$$(6)\ HO^- + (CH_3)_3C\text{-}Cl \rightarrow HO\text{-}C(CH_3)_3 + Cl^-$$

Such a reaction is designated as S_N2, substitution nucleophilic bimolecular. This type of mechanism is operative with primary halides in the reaction with hydroxide ion, but it does not take place with tertiary halides.

In the bimolecular elimination reaction, according to the proposed mechanism, the hydroxide ion removes a β-hydrogen as a proton, with synchronous shift of an electron pair and elimination of the halide ion to form the corresponding olefin. For t-butyl chloride, this may be represented as follows:

$$(7)\ HO^- + H\text{-}CH_2(CH_3)_2C\text{-}Cl \rightarrow HOH + CH_2{=}C(CH_3)_2 + Cl^-$$

Such a reaction is designated as E2, elimination bimolecular. This is the predominant reaction of t-butyl chloride when it is heated with concentrated sodium hydroxide solution. However, very little, if any of the t-butyl chloride is consumed in this manner in today's experiment, since the concentration of hydroxide ion used is small.

We shall first test the effect of concentration on the reaction rate. Then we shall make further studies on the effect of temperature and of the nature of the solvent medium on the reaction rate.

Experimental

In today's experiment, you will use 0.1M solution of t-butyl chloride in acetone, a 0.1M solution of sodium hydroxide, and a solution of bromothymol blue indicator. The amount of sodium hydroxide added in each reaction mixture will represent exactly 10 mole percent of the total amount of t-butyl chloride, and timing of the reaction should begin at that instant.

As solvolysis of the t-butyl chloride proceeds, the acid produced [see equations (1) and (2)] will be neutralized by the sodium hydroxide. As long as some sodium hydroxide is present, the solution containing bromothymol blue indicator will remain deep blue. The acidity of the solution will increase rapidly after the sodium hydroxide is completely neutralized and, if mixing is efficient, the entire solution will instantly turn greenish-yellow. You will determine the length of time required for the change—which represents the time required for the reaction of one-tenth of the total sample of t-butyl chloride—by means of the sweep-second hand of a watch.

A. Measurement of Time for 10% Solvolysis of t-Butyl Chloride in 70% water-30% Acetone Solvent

Label the indicated containers and take them with you to obtain from the stock bottles in the hood the following materials:

1. About 35 mL of a 0.1M solution of t-butyl chloride in acetone (in a small Erlenmeyer flask; keep it stoppered when it is not in use).
2. About 10 mL of a 0.1M aqueous solution of sodium hydroxide (in a 25-mL Erlenmeyer flask).
3. About 30 mL of a 30 percent solution of acetone in water. (This can be made by adding 21 mL of water to 9 mL of acetone. Keep this solution, which will be needed in Part B, in a stoppered Erlenmeyer flask).

Before beginning each run, be certain to rinse the Erlenmeyer flasks with acetone and dry them.

Prepare **flask #1** by pipeting 3.00 mL of a 0.1M solution of t-butyl chloride in acetone into a 25-mL Erlenmeyer flask. Place the flask on a sheet of white filter paper (to aid you in observing changes in the color of the solution).

Now, prepare **flask #2** by pipeting 0.3 mL (using a 1-mL pipet) of 0.1M sodium hydroxide solution and add 6.7 mL (using a 10-mL graduated cylinder) of distilled water (this water may need to be boiled first to remove dissolved CO_2—ask your instructor). Finally, add a drop of bromothymol blue indicator.

Quickly pour the water solution into the acetone solution, at the same time noting the positions of the second hand and the time. Swirl the mixture for just one or two seconds and immediately pour the combined solutions back into the other flask, in order to insure complete mixing of the two solutions.

Swirl the solution continuously over the white filter paper. Note the position of the second hand and the time at the instant the solution turns greenish-yellow. Repeat this experiment two more times and write the results in your notebook as indicated in Record A.

Record A
Solvent: 70% Water-30% Acetone

Run Number	Temperature	Time for 10% reaction
1		
2		
3		

Average time: ___________sec

B. Measurement of Time for 10% Solvolysis of t-Butyl Chloride in 70% Water-30% Acetone at One-half the Concentration Used in Part A.

Follow exactly the experimental procedure used in Part A, except that before the two solutions are mixed, add 10 mL (using a graduated cylinder) of 30% solution of acetone in water to the Erlenmeyer flask which contains the aqueous sodium hydroxide solution. The experiment will then be carried out with the concentrations of t-butyl chloride and sodium hydroxide at exactly one-half the values used in Part A.
Repeat the experiment two more times and tabulate the results as in Part A.

Record B
Solvent: 70% Water-30% Acetone
(One-half the concentration of Part A)

Run Number	Temperature	Time for 10% reaction
1		
2		
3		

Average time: __________sec

C. Effect of Temperature on the Rate of Solvolysis of t-Butyl Chloride

Prepare a water bath by pouring 300-400 mL of water into a large beaker. By means of crushed ice and vigorous stirring maintain the temperature uniformly at about 10 degrees below room temperature. Now, in the two Erlenmeyer flasks, prepare the two solutions as directed in Part A. Before you mix the two solutions, however, allow the temperature of the flasks and their contents to equilibrate by suspending the flasks in the water bath for 10 minutes. A strip of copper wire looped over the edge of the beaker and wound around the neck of the flask provides a convenient means of support. Now proceed, as directed in Part A, to mix the solutions and time the reaction. Repeat the experiment once more.
Next, warm a large beaker of water to about 10 degrees above room temperature. Try and maintain a uniform temperature. Add the solutions to the Erlenmeyer flasks as directed in Part A. Allow the temperature of the flask and their contents to equilibrate in the water bath as before then proceed as in Part A. Repeat the experiment once more, making sure the temperature is the same (or as close as possible) as for the first data point.

Record C
Solvent: 70% Water-30% Acetone
(Below room temperature trial)

Run Number	Temperature	Time for 10% reaction (sec)
1		
2		

Average time: __________sec

Solvent: 70% Water-30% Acetone
(Above room temperature trial)

Run Number	Temperature	Time for 10% reaction (sec)
1		
2		

Average time: ___________sec

From the data that you have now collected for the $t_{1/10}$ you will calculate k for the reaction at three temperatures using:

$$\mathbf{\ln A_t - \ln A_o = -kt}$$

Where A_t is the amount of starting material left over at time t.

Temperature (^oC)	Rate Constant (k)	ln k	Temperature (K)	1/T (K^{-1})

Then using the Arrhenius Equation:

$$\mathbf{\ln k = -(E_a/R)(1/T) \quad + \quad \ln A}$$

Plot a graph of ln k vs. 1/T for the data at the three temperatures and determine the activation energy (E_a) for this reaction and also the collision frequency factor (A) where T is the temperature in Kelvin and R=8.314 J/mol•K.

Adapted from "Unitized Experiments in Organic Chemistry", 3rd ed., by Brewester, Vanderwerf and McEwen.

Kinetics Part II Data Sheet

Record A

Solvent: 70% Water-30% Acetone

Run Number	Temperature	Time for 10% reaction
1		
2		
3		

Average time: ___________sec

Record B

Solvent: 70% Water-30% Acetone

(One-half the concentration of Part A)

Run Number	Temperature	Time for 10% reaction
1		
2		
3		

Average time: ___________sec

Record C

Solvent: 70% Water-30% Acetone

(Below room temperature trial)

Run Number	Temperature	Time for 10% reaction
1		
2		

Average time: ___________sec

(Above room temperature trial)

Run Number	Temperature	Time for 10% reaction
1		
2		

Average time: ___________sec

Run	Average time (sec)	k	ln k	Temperature (K)	1/T (K^{-1})
Room temp –10^{o}C					
Room temp					
Room temp +10^{o}C					

Activation Energy (E_a):___________________________________

Collision Frequency Factor (A):___________________________