



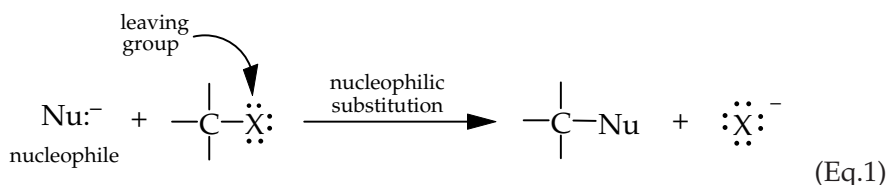
The Kinetics of Solvolysis of 2-Chloro-2-methylpropane

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PURPOSE OF THE EXPERIMENT Monitor the solvolysis reaction of 2-chloro-2-methylpropane in 2-propanol–water through product analysis. Determine whether the reaction rate is directly proportional to the concentration of 2-chloro-2-methylpropane in the mixture.

BACKGROUND REQUIRED You should know how to conduct a titration using a standard base solution and an acid-base indicator.

BACKGROUND INFORMATION An **alkyl halide** is a compound containing a halogen atom bonded to an sp^3 -hybridized carbon atom, and is given the symbol RX. **Nucleophilic substitution** is any reaction in which one nucleophile is substituted for another. Some nucleophiles are anions, while others are neutral compounds. In Equation 1, Nu^- is the nucleophile and X is the leaving group.



Two mechanisms for nucleophilic substitutions have been proposed, S_N1 and S_N2 . A fundamental difference between them is the timing of bond breaking between carbon and the leaving group and bond forming between carbon and the nucleophile.

S_N2 Mechanism In one mechanism, the bond breaking processes are concerted, meaning that they occur simultaneously. Thus, departure of the leaving group is assisted by the incoming nucleophile. This mechanism is designated S_N2 , where S stands for substitution, N stands for nucleophilic, and 2 stands for bimolecular. A **bimolecular reaction** is one in which two reactants are involved in the rate-determining step.

In an S_N2 reaction, the reaction rate of RX depends on both the concentrations of RX and the nucleophile; that is, the reaction follows second-order kinetics. The reaction is first order with respect to alkyl

halide and first order with respect to nucleophile. Equation 2 shows the rate equation for an S_N2 reaction, where $[RX]$ is the alkyl halide concentration, t is the time, and k is the rate constant.

$$\text{rate of reaction of RX} = -\frac{d[RX]}{dt} = k[RX][\text{Nu}^-] \quad (\text{Eq. 2})$$

Figure 1 shows an S_N2 mechanism for the reaction of hydroxide ion and chloromethane to form methanol and chloride ion. The nucleophile is shown attacking from the side of the molecule opposite the leaving group, resulting in an inversion of configuration at the carbon center.

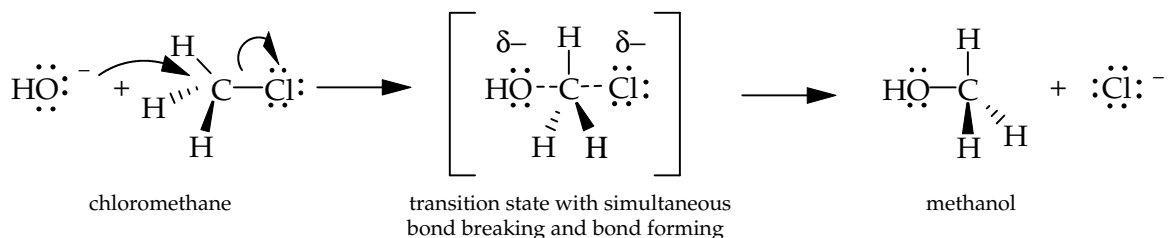


Figure 1 The S_N2 mechanism

S_N1 mechanism In the other mechanism, termed S_N1 , bond breaking between carbon and the leaving group is entirely completed before bond forming with the nucleophile begins. In the designation S_N1 , 1 stands for unimolecular. A **unimolecular reaction** is one in which only one reactant is involved in the rate-limiting step.

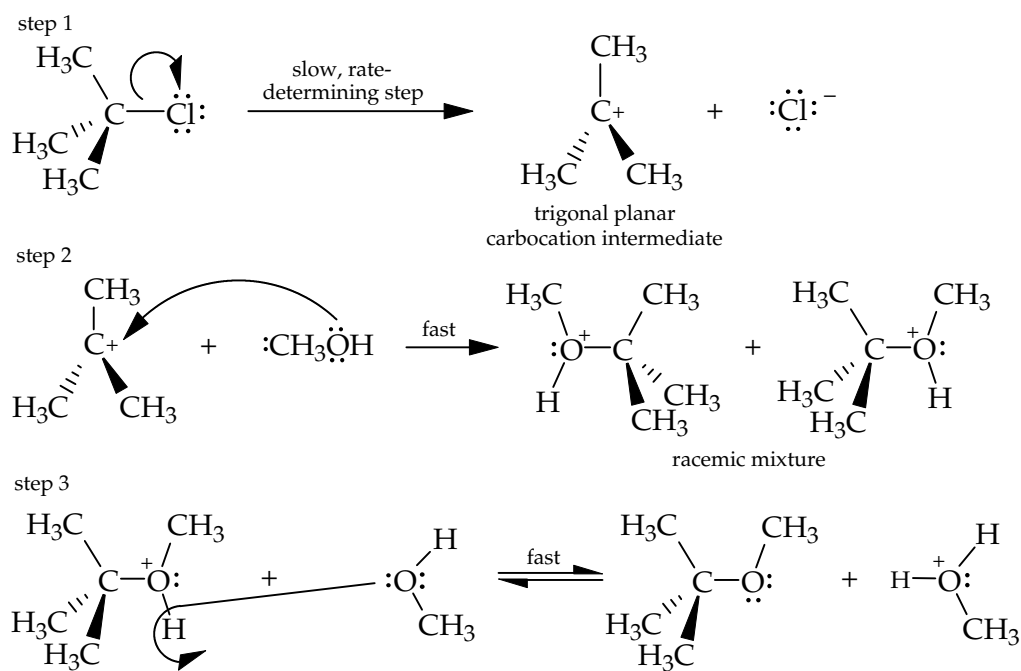
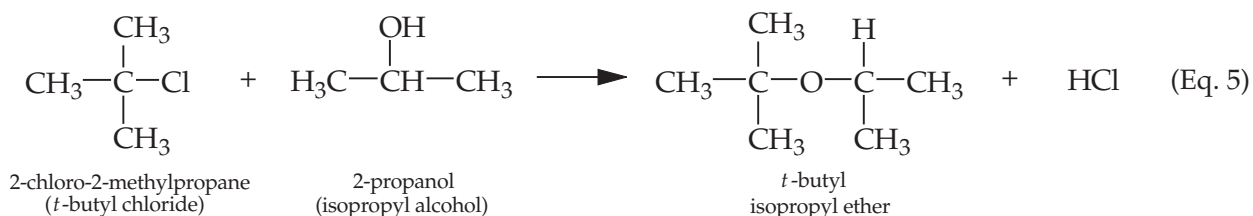
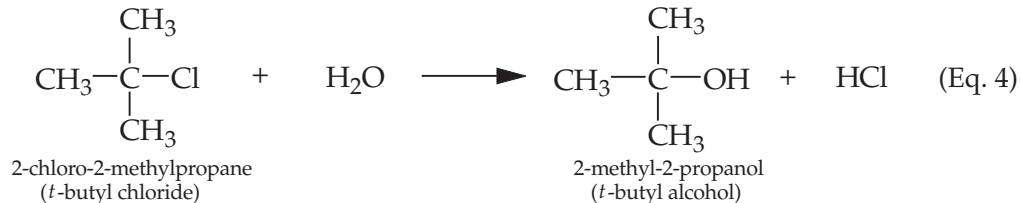
The reaction rate of RX in an S_N1 reaction depends only on the concentration of RX ; it is independent of the concentration of the nucleophile. This reaction follows first order kinetics, as shown in Equation 3. The reaction is first order with respect to alkyl halide and zero order with respect to nucleophile.

$$\text{rate of reaction of RX} = -\frac{d[RX]}{dt} = k[RX] \quad (\text{Eq. 3})$$

The S_N1 mechanism is illustrated by the solvolysis reaction between 2-chloro-2-methylpropane (*t*-butyl chloride) and methanol to form *t*-butyl methyl ether, as shown in Figure 2 on the next page. **Solvolysis** is a reaction in which the solvent serves as the nucleophile. In step 1, the $C-Cl$ bond breaks forming a tertiary (3°) carbocation intermediate. In step 2, the carbocation reacts with methanol, the nucleophile, to form an oxonium ion. Because the carbocation is planar, attack of the nucleophile occurs from either face of the carbocation with equal probability. A racemic mixture results. In step 3, loss of H^+ by proton transfer from the oxonium ion gives *t*-butyl methyl ether.

Kinetics In this experiment, you will study the solvolysis of 2-chloro-2-methylpropane (*t*-butyl chloride) in a mixed solvent of water and 2-propanol (isopropyl alcohol). Water and 2-chloro-2-methylpropane are not miscible, but both compounds are soluble in 2-propanol.

The organic product of the reaction of 2-chloro-2-methylpropane with water is 2-methyl-2-propanol (*t*-butyl alcohol), as shown in Equation 4. The organic product resulting from the reaction of 2-chloro-2-methylpropane with 2-propanol is *t*-butyl isopropyl ether, as shown in Equation 5.

Figure 2 The S_N1 mechanism

In either case, one mole of HCl is produced for each mole of 2-chloro-2-methylpropane reacting. Thus, by following the rate at which HCl is formed, the rate at which 2-chloro-2-methylpropane undergoes solvolysis can be measured.

The number of moles of HCl produced as a function of time is measured by titrating the reaction mixture with standard NaOH solution to neutralize the HCl, as shown in Equation 6.



Phenolphthalein indicator, which is colorless in acidic solution and pink in basic solution, is used to determine the end point. When the pink color just persists, the solution has reached the end point.

The solvolysis of 2-chloro-2-methylpropane (t -BuCl) is assumed to be an S_N1 reaction; that is, it is first order in t -BuCl and zero order in nucleophile, as shown in Equation 7.

$$\text{Reaction rate of } t\text{-BuCl} = -(\text{d}[t\text{-BuCl}] / \text{d}t) = k[t\text{-BuCl}] \quad (\text{Eq. 7})$$

Equation 7 can be re-expressed in terms of moles of t -BuCl in Equation 8, where

$$\begin{aligned} A &= \text{moles of } t\text{-BuCl} \text{ present at the start of the reaction,} \\ P &= \text{moles of } t\text{-BuCl} \text{ reacted} = \text{moles of HCl formed at elapsed} \\ &\quad \text{time, } t, \text{ after the start of the reaction,} \\ A - P &= \text{moles of unreacted } t\text{-BuCl} \text{ present at elapsed time, } t, \text{ after the} \\ &\quad \text{start of the reaction:} \end{aligned}$$

$$-(\text{d}[t\text{-BuCl}] / \text{d}t) = k[A - P] \quad (\text{Eq. 8})$$

Equation 8 gives the relationship between the rate of solvolysis and the concentration of t -BuCl remaining in the reaction mixture.

A and P cannot be measured directly using the titration method. Instead the volume, V , of NaOH delivered and the elapsed time, t , are measured. Equation 9, then, expresses a mathematical relationship between rate of solvolysis of t -BuCl and the experimentally measured quantities, where

$$\begin{aligned} V &= \text{volume of NaOH added at elapsed time, } t \\ V_{\infty} &= \text{volume of NaOH added after all } t\text{-BuCl} \text{ has reacted and} \\ &\quad \text{all HCl has been neutralized} \\ (1 - V/V_{\infty}) &= \text{fraction of RX remaining at elapsed time, } t. \end{aligned}$$

$$-(\text{d}[t\text{-BuCl}] / \text{d}t) = k(1 - V/V_{\infty}) \quad (\text{Eq. 9})$$

Integrating this expression and rearranging gives Equation 10.

$$\ln(1 - V/V_{\infty}) = -kt \quad (\text{Eq. 10})$$

Equation 10 has the straight-line equation form $y = mx + b$, where

$$y = \ln(1 - V/V_{\infty}), \quad m = -k, \quad x = t, \quad b = 0$$

The titration data can be used to determine whether or not the rate of solvolysis of t -BuCl is proportional to the concentration of unreacted t -BuCl. If the original assumption that the reaction is first order in t -BuCl and zero order in nucleophile is correct, the plot of $\ln(1 - V/V_{\infty})$ versus t will be a straight line with slope $-k$ and a y intercept of zero, as shown in Figure 3.

Equipment

600-mL beaker*
50-mL buret
125-mL Erlenmeyer flask,
with stopper

10-mL graduated cylinder
50-mL graduated cylinder
hot plate
stop watch[†]

*for water bath

†or watch with second hand

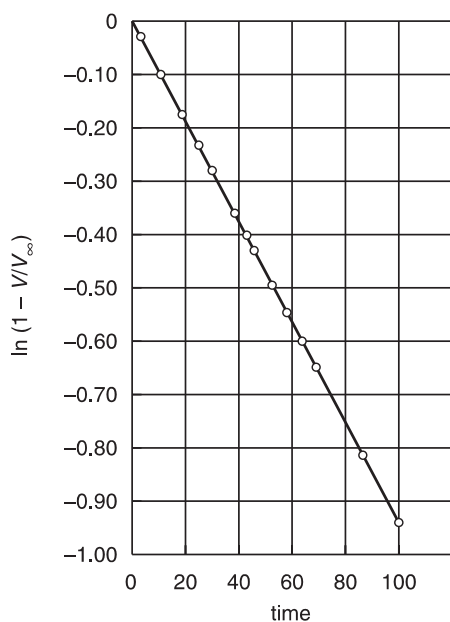


Figure 3 The relationship between $\ln(1 - V/V_{\infty})$ and elapsed t for the solvolysis of 2-chloro-2-methylpropane in a 2-propanol-water mixture

Reagents and Properties

| <i>substance</i> | <i>quantity</i> | <i>molar mass</i> (g/mol) | <i>bp</i> (°C) | <i>density</i> (g/mL) |
|---|-----------------|------------------------------|-------------------|--------------------------|
| 2-chloro-2-methylpropane | 1.00 mL | 92.57 | 51–52 | 0.851 |
| phenolphthalein, 1% | 2–3 drops | | | |
| 2-propanol–water (1:1) | 50 mL | | | |
| sodium hydroxide, 0.350M in 2-propanol–water (1:1) | 70 mL | | | |

Preview

- Add the 2-propanol–water mixture and phenolphthalein to a flask
- Rinse a buret with distilled water, then with 0.350M NaOH
- Fill the buret with NaOH solution and read the initial volume
- Add 1.00 mL of 2-chloro-2-methylpropane to the reaction mixture and start the timer
- Add 1–2 mL of NaOH solution to make the mixture pink
- Note the time when the color disappears; read the buret volume
- Repeat NaOH solution additions, noting time of color disappearance and buret volume until reaction is 75% complete
- Place reaction mixture in a 60–65 °C water bath for 15 min to complete the reaction
- Cool the reaction mixture to room temperature
- Titrate the mixture to phenolphthalein end point with NaOH solution and record the final buret reading

PROCEDURE **Caution:** Wear departmentally approved safety goggles at all times while in the chemistry laboratory.

Always use caution in the laboratory. Many chemicals are potentially harmful. Follow safety precautions given for all reagents used in this experiment. Prevent contact with your eyes, skin, and clothing. Avoid ingesting any of the reagents.

1. Setting Up the Experiment **Caution:** 2-Chloro-2-methylpropane and 2-propanol–water are flammable. Keep away from flames or other heat sources. Phenolphthalein is irritating. 0.350M Sodium hydroxide (NaOH) is corrosive and toxic.

Transfer 50 mL of the 2-propanol–water mixture supplied by your laboratory instructor to a clean, dry 125-mL Erlenmeyer flask equipped with a tight-fitting stopper. Add 2–3 drops of phenolphthalein indicator and mix thoroughly. Stopper the flask. [NOTE 1]

NOTE 1: The stopper prevents the diffusion of carbon dioxide from the air into the reaction mixture. Carbon dioxide dissolves in water to become carbonic acid, which reacts with the NaOH.

Rinse a clean 50 mL-buret with 10 mL of distilled or deionized water. Then rise the buret with two 10-mL portions of the standard NaOH solution supplied by your laboratory instructor. Discard the NaOH rinses into the collection container designated by your laboratory instructor.

Fill the buret with the standard NaOH solution. Read the buret to the nearest 0.02 mL and record this initial volume. Also record the exact concentration of the NaOH solution.

2. **Conducting the Reaction** To start the reaction, add 1.00 mL of 2-chloro-2-methylpropane into the Erlenmeyer flask containing the 2-propanol–water mixture. Start the timer and record the exact time (t_0) of this addition. Swirl the flask to thoroughly mix the solution.

Immediately after you have mixed the solution, add 1–2 mL of NaOH solution from the buret. Swirl the flask to mix thoroughly. If the mixture does not turn pink, continue adding NaOH solution until it just does turn pink. Stopper the flask. Then carefully observe the solution in the flask and note the exact time (t_1) at which the pink color fades completely. Record this time and the corresponding buret reading.

Remove the stopper from the flask and *immediately* add another 1–2 mL of NaOH solution until the mixture again turns pink. Swirl the flask. Restopper the flask. Again note the exact time at which the pink color fades. Record this time and the corresponding buret reading.

Continue adding 1–2 mL portions of NaOH solution and recording exact time and buret readings as frequently as possible, but without undue hurry. If you miss the time at which a particular fading of the pink occurs, add more NaOH solution, mix, and observe the next fading. Be certain to stopper the flask between NaOH additions. Continue in this manner until the reaction is approximately 75% complete. [NOTE 2]

NOTE 2: The calculation of Pre-Laboratory Assignment 2(d) gives the volume of 0.350M NaOH needed for 75% completion.

Place 400 mL of water in a 600-mL beaker. Use a hot plate to heat the water to 60–65°C. Then, loosen the stopper and place the Erlenmeyer flask in the water bath for 15 min to bring the reaction to 100% completion. [NOTE 3]

NOTE 3: Never heat a closed container.

Cool the solution to room temperature. *Carefully* titrate the remaining HCl with NaOH solution to a phenolphthalein end point at which the faint pink color persists for 30 s. Record the final buret reading.

3. **Cleaning Up** Place your recovered materials in the appropriate labeled collection containers as directed by your laboratory instructor. Clean your glassware with soap or detergent.

Caution: Wash your hands thoroughly with soap or detergent before leaving the laboratory.

Post-Laboratory Questions

- From the experimental data, prepare a table of the following values. Record all calculated results to three significant figures. Note that V and V_∞ are the volumes of NaOH solution delivered; they are not buret readings, unless, of course, your initial buret reading was 0.00 mL. Time, t , is the elapsed time in min.

$$t(\text{min}) \quad V(\text{mL}) \quad V/V_\infty \quad (1 - V/V_\infty) \quad k$$

- Prepare a graph of $\ln(1 - V/V_\infty)$ versus time, t , and draw the best straight line through its points. Do the data support the S_N1 mechanism? Briefly explain.
- Calculate the value of k from the slope of the line from the graph in 2.
- Using Equation 10, calculate a value of k for each value of t . Using these values, calculate the average value of k , and estimate its uncertainty. One way to estimate its uncertainty is to (1) calculate an average value of k , (2) calculate the absolute value of the deviation of each value from the average value, and then (3) calculate the average of these deviations.

(c) the volume in milliliters of 0.350M NaOH required to neutralize the HCl produced by complete solvolysis of 1.00 mL of *t*-BuCl.

(d) the volume in milliliters of 0.350M NaOH required to neutralize the HCl produced when solvolysis of 1.00 mL of *t*-BuCl is 75% complete.