EXPERIMENT 2
THE HYDROLYSIS OF t-BUTYL CHLORIDE

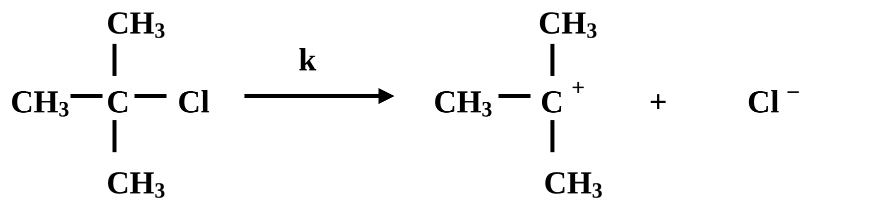
PURPOSE:

To verify a proposed mechanism for the hydrolysis of t-Butyl Chloride.

PRINCIPLES:

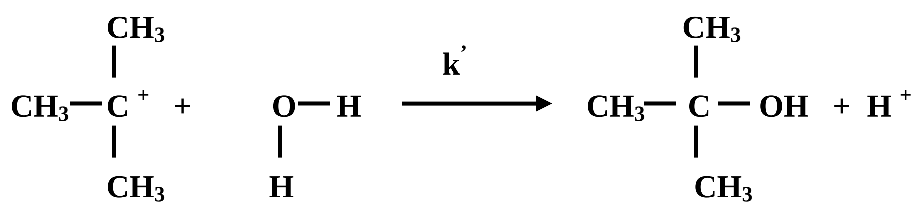
Once the Rate Law for a reaction has been experimentally established the next step is its explanation in terms of a **Reaction Mechanism.** This is a sequence of elementary steps, which describe in detail the actual interactions among the atoms and the molecules during the reaction which would lead to the observed rate law.
In this experiment, you will verify a proposed mechanism for the hydrolysis ("water breaking") of t-butyl chloride by determining the rate law of the slower step involved in the mechanism. The reaction of t-butyl chloride with water proceeds as shown in the two step reaction below:

STEP ONE: SLOW



t-butyl chloride — carbonium ion — chloride ion

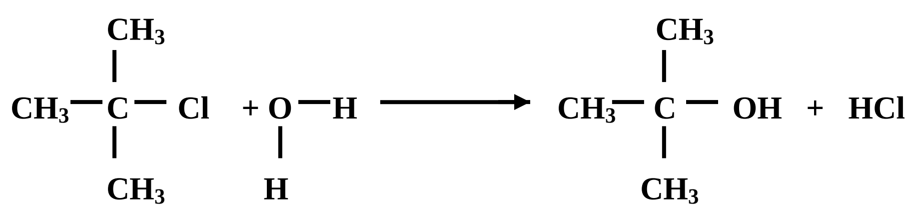
STEP TWO: FAST



carbonium ion — water — t-butyl alcohol

In the overall reaction (obtained by simply adding Steps One and Two), t-butyl alcohol and hydrochloric acid are the two products:

OVERALL:



t-butyl chloride — water — t-butyl alcohol — hydrochloric acid

or simply: $\boxed{\mathbf{RCl} \quad + \quad \mathbf{H_2O} \longrightarrow \mathbf{ROH} \quad + \quad \mathbf{HCl}}$

where **R** is an abbreviation for the $\mathbf{(CH_3)_3C}$ (t-butyl group).

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The commonly accepted mechanism suggests that the **first step is the slower step** and therefore determines the overall rate of reaction. One of the most important pieces of evidence in favor of this reaction mechanism is the kinetic rate law that this reaction follows.
If the first step in the reaction sequence is indeed **the rate determining step**, than:
The Rate of Overall Reaction = Rate of Slower Step = Rate of Step 1
Since Step 1 is a **unimolecular reaction**, it follows that:
Rate of Overall reaction = Rate of Step 1 = Rate of disappearance of t-butyl chloride (RCl)

$$\text{Rate} = -\frac{\Delta\,[\text{RCl}]}{\Delta\,t} = k\,[\text{RCl}] \qquad \text{Equation 1}$$

where: [RCl] = is the Concentration of t-butyl chlorides in moles per liter
k = Rate Constant

If: n_{RCl} = number of moles of t-butyl chloride
V = the volume of the solution in liters

Then: $$[\text{RCl}] = \frac{n_{RCl}}{V} \qquad \text{Equation 2}$$

During the very short time required for RCl to change by Δ [RCl], the volume of the solution remains constant.
If we substitute Equation 2 into Equation 1, we get:

$$\text{Rate} = -\frac{\frac{\Delta\,n_{RCl}}{V}}{\Delta\,t} = -\frac{1}{V}\,\frac{\Delta\,n_{RCl}}{\Delta\,t} = k\,n_{RCl}\left(\frac{1}{V}\right) \qquad \text{Equation 3}$$

Dividing both sides of Equation 3 by (1/V), we obtain the Rate Law in a form more convenient for our purposes:

$$-\frac{\Delta\,n_{RCl}}{\Delta\,t} = k\,n_{RCl} \quad \text{or} \quad \boxed{\frac{\Delta\,\mathbf{n_{RCl}}}{\mathbf{n_{RCl}}} = -\,\mathbf{k}\,\Delta\,\mathbf{t}} \qquad \textbf{Equation 4}$$

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If the initial number of moles of t-butyl chloride at **time 0** is $\mathbf{n^0_{RCl}}$ and the number of moles at time t is $\mathbf{n_{RCl}}$, integration of Equation 4 between these limits gives:

$$\boxed{\frac{\Delta n_{RCl}}{n_{RCl}} = -k\,\Delta t} \longleftarrow \textbf{Equation 4}$$

$$\boxed{\ln\left(\frac{n_{RCl}}{n^0_{RCl}}\right) = -k\,t} \qquad \textbf{and} \qquad \boxed{\ln(n_{RCl}) = -k\,t + \ln(n^0_{RCl})}$$

Equation 5a Equation 5b

Respectively:

$$\boxed{\log\left(\frac{n_{RCl}}{n^0_{RCl}}\right) = \frac{-k\,t}{2.303}} \qquad \textbf{and} \qquad \boxed{\log(n_{RCl}) = \frac{-\,kt}{2.303} + \log(n^0_{RCl})}$$

Equation 6a Equation 6b

Equations 5b and 6b are similar to the equation of a straight line (**y = b + mx**)

$$\boxed{\log(n_{RCl})} = \boxed{\frac{-k}{2.303}}\; t \quad + \quad \log(n^0_{RCl}) \qquad \textbf{Equation 6b}$$

$$\begin{array}{ccccccc} \mathbf{y} & = & \mathbf{m} & \mathbf{x} & + & \mathbf{b} \\ \textbf{(vertical coordinate} & & \textbf{(slope)} & \textbf{(horizontal coordinate)} & & \textbf{(Intercept)} \end{array}$$

Equation 6b predicts that if the reaction rate is correctly given by Equation 1 (Rate = k[RCl]), a plot of $\mathbf{\log(n_{RCl})}$ versus "**t**" should be linear with **slope = m = – k/2.303**

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In this experiment the study of the hydrolysis of t-butyl chloride will be carried out in a 50-50 mixture (by volume) of isopropyl alcohol and water.
The reason for studying the reaction in this solvent, rather than in pure water, is twofold:

1. t-butyl chloride is not very soluble in pure water, and
2. the hydrolysis reaction in pure water proceeds too rapidly to be followed conveniently.

The progress of the reaction may be followed by following the production of the H^+ ion;

$$\boxed{\mathbf{RCl} \quad + \quad \mathbf{H_2O} \longrightarrow \mathbf{ROH} \; + \; \mathbf{H^+} + \; \mathbf{Cl^-}}$$

Note that for every mole of t-butyl chloride (RCl) consumed in the overall reaction 1 mole of HCl (and therefore 1 mole of H^+ and 1 mole of Cl^-) is produced. Therefore the number of moles of HCl produced during the course of the reaction is a measure of the number of moles of t-butyl chloride (RCl) reacting.
Furthermore, the number of moles of unreacted t-butyl chloride is equal to the total number of moles of t-butyl chloride (RCl) initially present (n^0_{RCl}) minus the number of moles of HCl produced. Summarizing:

$$\mathbf{n_{HCl\ produced} = n_{RCl\ reacted}}$$

$$\mathbf{n_{RCl\ unreacted} = n^0_{RCl} - n_{HCl\ produced}}$$

The rate of production of HCl can be tracked by determining the volume of standard NaOH solution required for the neutralization of the H^+.
This is done by adding a few drops of phenolphthalein indicator to the t-butyl chloride solution at the start of the experiment. An amount of NaOH solution will then be added so that the total number of moles of OH^-, n_{OH}, is initially in excess of the number of moles of H^+, n_{H^+}, thus far produced.
As the reaction proceeds the amount of H^+ ion produced increases. After some time"**t**" the amount of H^+ produced will be just sufficient to react completely with the amount of OH^- ion added to the solution. At this time, the phenolphthalein indicator will change from pink to colorless.
Recall that he reaction between H^+ ion and OH^- ion in solution is: $\mathbf{H^+ \; + \; OH^- \longrightarrow H_2O}$
Hence, at the time "t" at which the indicator changes color:

$$\boxed{\mathbf{n_{RCl\ reacted} = n_{H^+} = n_{OH^-}}} \quad \text{and} \quad \boxed{\mathbf{n_{RCl\ unreacted} = n^0_{RCl} - n_{H^+} = n^0_{RCl} - n_{OH^-}}}$$

Equation 7

After the first color change has been observed, sufficient NaOH solution is added to the t-butyl chloride solution to return the pink color of the solution, and the observation of the time at which the indicator turns from pink to colorless is repeated. In this way, a large amount of data giving the number of moles oft-butyl chloride remaining in the solution at various times may be collected.

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In order to calculate the number of moles of t-butyl chloride remaining at time "**t**" ($\mathbf{n_{RCl}}$) , it is necessary to know the number of moles of t-butyl chloride present at the start of the reaction ($\mathbf{n^0_{RCl}}$) :

$$\boxed{\mathbf{n_{RCl\ remaining} = n^0_{RCl} - n_{HCl\ produced}}}$$

The number of moles of t-butyl chloride present at the start of the reaction ($\mathbf{n^0_{RCl}}$) is determined by titrating the reaction mixture with the standard NaOH solution after a sufficient lapse of time so that practically all of the t-butyl chloride (RCl) has had time to react.

PROCEDURE:

1. Obtain in a clean, dry beaker approximately 60 mL of 0.250 M NaOH in 50-50 isopropyl alcohol – water solution.
2. Rinse your buret twice with 3 – 4 mL portion of the isopropyl alcohol – water solution.
3. Fill your buret completely with the NaOH solution, making sure that no bubbles are trapped in the buret tip.
4. Clamp the buret in a vertical position and read and record the initial solution level to the nearest 0.01 mL. The buret should then be capped with a loose fitting test tube or small beaker to prevent the evaporation of the alcohol from the NaOH solution and the absorption of CO_2 from the air.
5. In your graduated cylinder, measure out 100 mL of 50-50 isopropyl alcohol – water solution and empty this into a **clean**, **dry** 250 mL Erlenmeyer flask. Add five drops of phenolphthalein indicator solution to the flask.
6. Add approximately 1 mL of t-butyl chloride to the flask and swirl immediately to dissolve t-butyl chloride (RCl) in the solvent mixture.
   The t-butyl chloride reagent will be provided with a Pasteur pipet which will be marked to indicate the level of liquid corresponding to about 1 mL of t-butyl chloride.
   Start the stop watch at the very same instant at which the t-butyl chloride is added to the solvent mixture.

IMPORTANT!

Do not stop the stop watch until you finished taking all the required readings!

7. **Immediately** return to your bench and add to the flask about 1 mL of NaOH solution from the buret. Swirl to mix. If the solution does not turn pink, add a second milliliter of NaOH solution. **Record the buret reading**
   Watch the t-butyl chloride solution closely and note and record the time (nearest second) at which the pink color of the solution disappears.
   Record the time in minutes and seconds (no fraction of seconds)
8. Add another 1-mL portion of NaOH, swirl to mix, and record the new buret reading and the time at which the pink color disappears again from the solution.
9. Repeat step 8 until a total of 16, 1-mL additions of NaOH solution have been made, and the corresponding times of color discharge have been recorded.
   If you should miss noting the time of any color change, simply ignore this data point, add another increment of NaOH solution, and continue with the experiment.
10. Measure and record the solution temperature.

YOU MAY STOP THE STOP WATCH AT THIS POINT!

11. Fill a large 600-mL beaker half-full of water and heat the water to about 40^0C.
    Measure out about 50 mL of this warm water in your graduated cylinder, add it to the t-butyl chloride solution in the flask and swirl to mix. Then stopper the flask and immerse it in the large beaker of warm water.
    Allow the flask to remain in the beaker for about 1 hour, turning it occasionally and periodically. Warm the water with a hot plate or a Bunsen so as to keep the temperature between 35^0C and 45^0C. **Do not overheat**.
    The addition of the extra water and the increase in temperature speed up the hydrolysis of t-butyl chloride (RCl) so that at the end of 1 hour, virtually all of the t-butyl chloride has reacted.
12. Remove the flask from the beaker of warm water, unstopper it, and titrate the solution with the standard NaoH to a faint pink end point. **Record the final buret reading**
    Be careful not to overshoot the endpoint in this final titration, since the accuracy of all your calculations depends on the accuracy of this titration.

CALCULATIONS:

1. Convert all your time readings in seconds "**t elapsed**" since the t-butyl chloride was first added to the solvent mixture.
   For example:
   Recorded elapsed time in minutes and seconds = **14:11**
   Corresponding elapsed time in seconds = (14 minutes) x (60 seconds/minute) + 11 seconds
   = 840 seconds + 11 seconds = **851 seconds**
2. From your buret reading and the molarity of the NaOH solution, calculate **the total number of moles of NaOH**, ($\mathbf{n_{OH^-}}$) that had been added to the solution for each time "**t**" at which the color discharge was observed.
3. From the result of the final titration, calculate the number of moles of t-butyl chloride (RCl) which were initially present ($\mathbf{n^0_{RCl}}$)
4. From Equation 7, calculate the number of moles of t-butyl chloride remaining in the solution ($\mathbf{n_{RCl}}$) at each time "**t**".
5. Plot **log** $\mathbf{n_{RCl}}$ versus "**t**"
6. From the slope of the curve "**m**" and Equation 6b determine the rate constant "**k**" and the half-life "$\mathbf{t_{1/2}}$" for the reaction
7. Answer Question 4 on the Report Form

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Name: ________________________
Partner: ________________________

REPORT FORM

Concentration of NaOH: ____________ M   Average temperature: ____________ ^{0}C

DATA TABLE

Time elapsed t (minutes and seconds)	Time elapsed t (seconds)	Buret reading (mL)	Total mL of NaOH added	Total number of moles NaOH added (n_{OH})	Number of moles of RCl remaining (n_{RCl})	log n_{RCl} (3 decimals)
	0	0.00	0.00	0	0	

Final titration: ________________ mL NaOH

Total Number of moles of NaOH added: ________________ moles
Show calculations below:

Number of moles of $(CH_3)_3Cl$ initially present (n^0_{RCl}): ________________ moles

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1. Plot **log n_{RCl}** versus **t(seconds)** on graph paper provided. Attach the graph to your report.
   In the upper-right hand side of the graph provide a table that includes he data being plotted.
   Recall that every graph must have a title.
   Draw the best straight line through the experimental points
   Find the slope of the line.
   Show calculations for the slope <u>on the graph</u> and include units.

   Slope = m =

2. Calculate the Rate Constant,"**k**" for the Hydrolysis of t-Butyl Chloride from your experimental data. Include units.
   Show calculations below:

   k =

3. Calculate the Half-Life ($t_{1/2}$) for the Hydrolysis of t-Butyl Chloride.
   Show calculations below. Include units.

   $t_{1/2}$ =

4. From your experimental data, calculate the time in hours which would have been required for 99.9 % of the t-butyl chloride to hydrolyze, if the reaction had been allowed to proceed without the addition of extra water or heating.