Kinetics of Hydrolysis of t-Butyl Chloride

Introduction:

When tert-butyl chloride is dissolved in aqueous acetone, it reacts to form tert-butyl alcohol and hydrochloric acid according to the mechanism shown below. Note that the first step (carbocation formation) is rate limiting. This step is unimolecular and therefore first order in regard to tert-butyl chloride concentration.

1. \( \text{CH}_3\text{C-C-CH}_3 \quad \text{Slow} \quad \text{CH}_3\text{C-C-CH}_3 \)

2. \( \text{CH}_3\text{C-C-CH}_3 \quad + \quad \text{O-H} \quad \text{Fast} \quad \text{CH}_3\text{C-C-O-H} \)

3. \( \text{CH}_3\text{C-C-O-H} \quad \text{Fast} \quad \text{CH}_3\text{C-C-O-H} \quad + \quad \text{H}^+ \)

Notice that this reaction releases protons (H⁺) into solution. This release of protons offers a convenient method for monitoring progress via reaction with sodium hydroxide and use of a pH indicator. By using a 2:1 molar ratio of tert-butyl chloride to sodium hydroxide, we will be able observe the passage of one half-life through the color change of the pH indicator. In other words, the indicator will change color when sodium hydroxide is completely consumed and the hydrolysis of tert-butyl chloride has gone half way to completion. Measurement of the half-life will allow us to calculate the rate constant using the equation below.

\[
\frac{t}{2} = \frac{\ln 2}{k} \quad \text{rearrangement to solve for } k \text{ yields: } k = \frac{\ln 2}{\frac{t}{2}}
\]
Procedure:

1. Use the graduated cylinder to measure out 25.0 mL of the water-acetone solution and add the solution to the 125 ml Erlenmeyer flask.
2. Place the magnetic stir bar in the in the 125 ml Erlenmeyer flask, place the flask on the stir plate and stir at a medium rate.
3. Add 2 drops of bromothymol blue to the flask.
4. Use the 1 ml calibrated pipette to measure and add 1.00 ml of 0.100 M NaOH to the flask. Be sure that none of the NaOH solution ends up stuck to the side of the flask.
   • Why is it important to ensure that the NaOH doesn’t stick to the sides of the flask?
5. Note: This step will require you to coordinate with your partner. Use the 2 ml calibrated pipette to measure 2.00 ml of 0.100 M tert-butyl chloride in acetone. Add the 2.00 ml of tert-butyl chloride solution to the flask (be careful none sticks to the sides) while your partner simultaneously starts the stopwatch.
6. The passage of one half-life will be indicated by a color change from blue to yellow. Record the elapsed time in seconds upon color change as precisely as possible.
7. Repeat (1)-(7).

Prelab Questions:
(PL1) Adding 3 elementary steps given in introduction, write the overall equation.
(PL2) Write a rate expression and the rate law for this reaction.
(PL3) What order reaction is this and how does one know it is?
(PL4) If the solution takes 55 seconds to change color, calculate the rate constant.
(PL5) Is the rate constant (k) constant under all conditions?

Analysis
(A1) calculate the rate constant for each trial.
(A2) calculate the average rate constant.

Post Lab Questions:
(Q1) Use the integrated rate law to calculate the concentration of tert-butyl chloride at 1.5 half lives.
(Q2) What factors may have resulted in error? "Human error" is not an acceptable answer you must be more specific!
(Q3) What would happen to the final result if your lab partner didn’t start the stopwatch immediately after addition of the tert-butyl chloride? Be specific.
(Q4) Explain why the rate law cannot be determined simply by examining the balanced equation. Why is experimentation necessary?
(Q5) Propose an experiment to determine the activation energy of this reaction.

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