Kinetics of Solvolysis

**Reference:** “Solvent Effects Experiment” Handout; Chemistry Lessons: SN1 reactions, solvent effects on reaction rate, kinetics; Green Lessons: alternative solvent selection

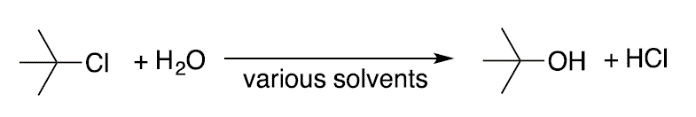
**Purpose:** To measure the kinetics of solvolysis reaction by use of titration and finding the rate constants in solvolysis reactions

**Table of Reagents:**

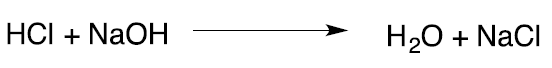
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| --- | --- | --- | --- | --- | --- |
| **Reagents** | **Amount** | **MW** | **BP (°C)** | **MP (°C)** | **Density** |
| Tert-butyl Chloride | Varies | 92.57 g/mol | 50.6 °C | -26.0 °C | 0.9 g/cm3 |
| Acetone | 58.0 g/mol | 56 °C | -95 °C | 0.78 g/cm3 |
| 2-Propanol | 60.1 g/mol | 82.5 °C | -89 °C | 0.786 g/cm3 |
| Water | 18.02 g/mol | 100 °C | 0 °C | 0.997 g/cm3 |

**Balanced Chemical Equation:**

* **Solvolysis Reaction**

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* **Titration Chemical Equation**

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**Safety:**

* Avoid creating flames as Acetone, 2-propanol, and tert-butyl chloride are flammable

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| --- | --- |
| **Experimental Procedures** | **Data & Observations** |
| **Part 1: Reaction**  **1.** Get stopwatch, bromothymol blue indicator solution, and white card |  |
| **2.** Prepare 100 mL of solvent mixture in Erlenmeyer flask. Mix solvents, add stopper, and set aside | *Solvent:* 50/50 🡪 isopropyl/water  *Lab Temperature:* 21 °C |
| **3.** Obtain 250 mL Erlenmeyer Flask. Add 150 mL of 0.04 N NaOH solutions. Fill burette! |  |
| **4.** Obtain 1g of tert-butyl chloride into 100 mL volumetric flask. Dilute with solvent mixture. Add stopper, shake flask, and start timer.  \*\*\*Keep flask stoppered 🡪 prevent evaporation\*\* | *Tert-butyl Chloride:* 1.0033 g |
| **5.**  Make 2 “infinity” time samples   * Add 10 mL of reaction mixture to 2 Erlenmeyer Flask with 10 mL of water. * Stopper flask after for 1 hour   \*\*\*High concentration of water makes reaction go faster; used to determine concentration of HCl\*\*\* | *Samples Prepared:* 15:45 |
| **6.** Remove aliquots from reaction mixture at each time interval depicted. At each time sample, remove 10 mL from sample and add it with 15 mL of acetone. Hydrolysis reaction is slow with acetone; quenches the reaction. Record exact time samples are quenched. |  |
| **7.** Add 3 drops of bromothymol blue indicator to flask and titrate with NaOH solution to blue end point that stays ~20 seconds. Record volume of Na OH needed to reach this point.  \*\*Clean and dry pipette after withdrawing aliquot\*\*  **Data for:**   * 50/50 solvent mixture: collected every 15 min up to 90 min; Final Data Point collected at 115 min * 60/40 solvent mixtures: collected every 20 min up to 120 min | *NaOH Needed:*   1. 6.74 mL NaOH 2. 11.01 mL NaOH 3. 14.98 mL NaOH 4. 17.80 mL NaOH 5. 20.17 mL NaOH 6. 21.49 mL NaOH 7. 26.83 mL NaOH |
| **8.** After collecting data, titrate the 2 “infinity time” samples. Record volume of NaOH needed to reach end point. | *NaOH Needed:*   * Sample 1: 18.88 mL * Sample 2: 21.01 mL |
| **Part 2: Data Analysis**  **9.** Calculate [HCl] from “infinity” time samples |  |
| **10.** Calculate concentration of HCl at each sample time for the aliquots of reaction mixture. |  |
| **11.**  Plot ln([infinity]-[individual]) vs time(t)  \*\*\*Calculate best fit and slope\*\*\*  Calculate rate of reaction from slope |  |

**Post-lab Questions:**

**1. a.**

**b.** We had a solvent mixture of 50:50 2-Propanol:Water, and our calculated rate constant is 0.0153.

**2.**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | **50:50**  **Acetone/H2O** | **60:40**  **Acetone/H2O** | **50:50**  **2-Propanol/H2O** | **60:40**  **2-propanol/H2O** |
| **Result 1** | 0.0066 | 0.0013 | 0.0158 | 0.0012 |
| **Result 2** | 0.0161 | 0.0015 | 0.0341 | 0.0015 |
| **Average** | 0.0114 | 0.0014 | 0.025 | 0.0014 |

**3.** Our rate constant was relatively close with that of our class. The class had an average of 0.025 for their rate value, while our rate value was within +/- 0.01 magnitude off from their value.

**4.** In comparing the solvents with each other, the proposed mechanism for the Sn1 reaction holds true. Solvents with more polar compounds have a faster reaction rate than compounds with more nonpolar compounds. This is mainly due to the transition state being charge-separated in nature and wanting a polar solvent to stabilize it, which results in the activation barrier being lowered, therefore, enhancing the reaction. In our case, the reaction with the 2-Propanol/H2O has more polar compounds which resulted in it having the fastest reaction out of all our other solvents. In addition, the mixture with 60:40 Acetone/H2O holds the most nonpolar compounds and has the slowest reaction rate, which solidifies the proposed mechanism for the Sn1 reaction.

**5.** Tert-butyl ether is formed in the solvolysis of tert-butyl chloride as a result of the reaction happening in an alcohol-water environment, thus creating two products: tert-butyl alcohol and tert-butyl ether. The result of the two products happens during the rate determining step, in which the tert-butyl substrate is stabilized due to formation of the carbocation (this step is slow). When the substrate is stabilized, this is when either nucleophiles: alcohol or water, can now react with the substrate (step is fast). Either products are formed depending on which nucleophile reacts with the substrate. The kinetics of the reaction is affected based on the concentration of the substrate, tert-butyl chloride, as well as the polarity of the solvent.

**6.** Reaction rate is determined by how polar a solvent is, since this will stabilize the substrate better, which results in a faster reaction rate. In our case, we used a 50:50 2-Propanol:Water solvent which resulted in our reaction rate being faster, due to the fact that our activation energy required is lower. In the diagram below, more water means a lower activation energy resulting in a faster reaction, while less water means a higher activation energy resulting in a slower reaction.

