Kinetics

In this experiment you will determine the order of a reaction with respect to the two reactants, *p*-nitrophenyl acetate and hydroxide. You will also determine the rate constant for this reaction.

CHEMICALS

18.1 mg of *p*-nitrophenyl acetate, 65 mL of methanol, 13.9 mg of *p*-nitrophenol, 6.7 g of KCl.

EQUIPMENT NEEDED

2-250 mL Erlenmeyer flasks, 2-100 mL volumetric flasks, 1-glass funnel, several Pasteur pipettes, 1-cuvette, 3-25 mL burettes, 4 small Erlenmeyer flasks, parafilm, weigh boats, a 50 mL graduated cylinder, 8 large test tubes, 2 small test tubes, 2 graduated pipettes, 1 10.00 mL volumetric pipette, 3 1.00 mL volumetric pipettes, 1 pipette bulb, Kimwipes, Q-tips, 1 Spectrometer 200.

WASTE DISPOSAL

Put all methanol in the methanol waste container. Put any solution containing p-nitrophenyl acetate of p-nitrophenol in the organic waste container in the hood.

SAFETY

Goggles and gloves should be worn for the entire experiment. Methanol is toxic if ingested or inhaled. Methanol is very flammable, keep it away from all sources of ignition.

PROCEDURE

SOLUTION PREPARATION – PART 1

MAKE SURE ALL GLASSWARE YOU USE IS CLEAN!

p-NITROPHENYL ACETATE (NPA)

Using a balance that is precise to 4 places past the decimal, weigh around 18.1 mg (0.0181 g) of NPA into a tared 250 mL Erlenmeyer flask. Record the actual mass in your data table. Add 30.0 mL of methanol to the flask with a graduated cylinder and swirl to dissolve. Transfer all of the solution to a 100.0 mL volumetric flask that is labeled “NPA” using a glass funnel. Rinse the Erlenmeyer flask with D.I. water and transfer the washing to the 100.0 mL volumetric flask. Bring the total volume in the volumetric flask to 100.0 mL with D.I. water. Put the stopper on the flask and invert to mix.

Rinse a 25-mL burette with a small amount of this solution and fill the burette a little less than halfway with the NPA solution.

Rinse another 25-mL burette with D.I. water and fill it with D.I.

Label a small Erlenmeyer flask as “NPA” and add around 1.0 mL of the NPA solution from the burette to the flask. Record the actual volume delivered to 2 places past the decimal in your data table. From the D.I. burette add around 9.0 mL of D.I. to the same flask, recording the actual amount of D.I. delivered to 2 places past the decimal in your data table.

Immediately cover the Erlenmeyer flask with parafilm and swirl to mix.

***p*-NITROPHENOL (NP)**

Using a balance that is precise to 4 places past the decimal, weigh around 13.9 mg (0.0139 g) of NP into a tared 250 mL Erlenmeyer flask. Record the actual mass in your data table. Add 30.0 mL of methanol with a graduated cylinder to the flask and swirl to dissolve. Transfer all of the solution to a 100.0 mL volumetric flask that is labeled “NP” using a glass funnel. Rinse the Erlenmeyer flask with D.I. water and transfer the washing to the 100.0 mL volumetric flask. Bring the total volume in the volumetric flask to 100.0 mL with D.I. water. Put the stopper on the flask and invert to mix.

Rinse a 25-mL burette with a small amount of this solution and fill the burette a little less than halfway with the NP solution.

Label a small Erlenmeyer flask as “NP” and add around 5.0 mL of the NP solution from the burette to the flask. Record the actual volume delivered to 2 places past the decimal in your data table. From the D.I. burette add around 45.0 mL of D.I. to the same flask, recording the actual amount of D.I. delivered to 2 places past the decimal in your data table.

Immediately cover the Erlenmeyer flask with parafilm and swirl to mix.

AQUEOUS METHANOL

In a 150 mL beaker (labeled as "Methanol") add 3.0 mL of methanol with a graduated cylinder. Add 97.0 mL of D.I. water with a graduated cylinder and swirl to mix. Cover immediately with parafilm.

SODIUM HYDROXIDE SOLUTION

Label a small Erlenmeyer flask as "NaOH". Using a 10.00 mL volumetric pipette add 10.00 mL of the standardized sodium hydroxide solution to a small Erlenmeyer flask. Record the molarity of the standardized solution in your data table. Add about 20 mL of D.I. water with you D.I. burette to the Erlenmeyer flask. Record the volume of D.I. added to 2 places past the decimal. Cover the flask with parafilm and swirl to mix.

POTASSIUM CHLORIDE SOLUTION

Label a small Erlenmeyer flask as "KCl". Weigh out about 11.2 g of KCl into a tared weigh boat and record the mass in your data table. Add the KCl to the Erlenmeyer flask and add 50 mL of D.I. water from a graduated cylinder. Swirl to dissolve.

MOLAR EXTINCTION COEFFICIENT DETERMINATION – PART 2

Label 8 test tubes as 1, 2, 3, 4, 5, 6, 7, & 8. Prepare the following mixtures:

<u>Test Tube #1</u>

4.00 mL KCl solution (use a graduated pipette)

4.00 mL NP solution (use the NP burette)

4.00 mL standardized NaOH (use graduated pipette)

Test Tube #2

4.00 mL KCl solution (use a graduated pipette)

3.00 mL NP solution (use the NP burette)

4.00 mL standardized NaOH (use graduated pipette)

1.00 mL D.I. water (use D.I. burette)

Test Tube #3

4.00 mL KCl solution (use a graduated pipette)

2.00 mL NP solution (use the NP burette)

4.00 mL standardized NaOH (use graduated pipette)

2.00 mL D.I. water (use D.I. burette)

Test Tube #4

4.00 mL KCl solution (use a graduated pipette)

1.00 mL NP solution (use the NP burette)

4.00 mL standardized NaOH (use graduated pipette)

3.00 mL D.I. water (use D.I. burette)

For **test tubes 5 – 8** repeat the above procedure but replace the standardized NaOH with your diluted NaOH.

Prepare two blank solutions in small test tubes. Label these test tubes #9 and #10.

To test tube #9 add 3.00 mL of the KCl solution with a graduated pipette, 3.00 mL of the standardized NaOH with a graduated pipette, and 3.00 mL of the aqueous methanol solution with a graduated pipette. Mix well.

To test tube #10 add 3.00 mL of the KCl solution with a graduated pipette, 3.00 mL of the diluted NaOH with a graduated pipette, and 3.00 mL of the aqueous methanol solution with a graduated pipette. Mix well.

Zero the spectrometer using test tube #9 at 405 nm, then measure the absorbance of each of test tubes 1-4 recording each absorbance in your data table.

Use the same cuvette for all measurements. After each measurement dry the test tube out using a Kimwipe and a Q-tip.

Zero the spectrometer using test tube #10 at 405 nm, then measure the absorbance of each of test tubes 5-8 recording each absorbance in your data table.

Use the same cuvette for all measurements. After each measurement dry the test tube out using a Kimwipe and a Q-tip.

REACTION ORDER – PART 3

Zero the spectrometer with the blank from test tube #9 at 405 nm. Clean and dry the cuvette as above.

Using volumetric pipettes add 1.00 mL of the KCl solution and 1.00 mL of the standardized NaOH solution to the cuvette.

Clean the outside of the cuvette with a Kimwipe and place it in the spectrometer.

Add 1.00 mL of the NPA solution using a clean and dry volumetric pipette and **IMMEDIATELY** close the lid and start recording the absorbance.

Record the absorbance every 10 seconds for 360 seconds in your data table.

Zero the spectrometer with the blank from test tube #10 at 405 nm. Clean and dry the cuvette as above.

Using volumetric pipettes add 1.00 mL of the KCl solution and 1.00 mL of the diluted NaOH solution to the cuvette.

Clean the outside of the cuvette with a Kimwipe and place it in the spectrometer.

Add 1.00 mL of the NPA solution using a volumetric pipette and **IMMEDIATELY** close the lid and start recording the absorbance.

Record the absorbance every 10 seconds for 360 seconds in your data table.

CALCULATIONS

Molar Extinction Coefficient

-Calculate the [NPA] in the NPA solution. The molar mass of NPA is 181.1 g/mol. Enter this in your table of constants.

-Calculate the [NP] in the NP solution. The molar mass of NP is 139.11 g/mol. Enter this in your table of constants.

-Calculate the [NP] in test tubes 1-4.

-Using Excel plot the absorbance (y-axis) vs. the [NP] (x-axis). Have Excel plot the best fit straight line and get the equation of this line.

-Repeat for test tubes 5-8.

The slope is εl in the equation $A= \varepsilon lc$ (Beer's law). Here A is the measured absorbance, ε is called the molar extinction coefficient, l is the path length (the distance the light travels through the solution) and c is the [NP]. Obtain the y-intercept and εl for the two different concentrations of NaOH.

Reaction Order

-Calculate the initial [NPA] for each of the two reactions performed in the cuvette.

-For each of the two reactions calculate the [NP] at each absorbance reading using Beer's law ($A= \varepsilon lc$).

-For each of the two reactions calculate the [NPA] using the fact that $[NPA]_t=[NPA]_{t=0} - [NP]_t$. This is true because the mole to mole ration in the balanced equation for this reaction between NPA and NP is 1:1.

-Using Excel make 3 graphs for the first reaction. Plot: [NPA] vs. time; ln([NPA]) vs. time; and 1/[NPA] vs. time. Whichever appears to be a straight line, have Excel draw the best fit straight line and get the equation of the line.

-The slope of this line is a pseudo rate constant, $k'=k[OH^-]^y$. This is because the $[OH^-]$ in the first reaction is so much greater than the [NPA] that it essentially remains constant.

-Find the order of the reaction with respect to OH^- by solving the following equation:

$$\frac{k_1'}{k_2'} = \frac{k[\mathrm{OH}^-]_1^y}{k[\mathrm{OH}^-]_2^y} = \left(\frac{[\mathrm{OH}^-]_1}{[\mathrm{OH}^-]_2}\right)^y$$

Plug in the pseudo rate constant you got for the first reaction as k_1'. Whichever graph gave you the straight line, make the same sort of graph ([NPA], ln([NPA]), or 1/[NPA] vs. time) for the second reaction. Get the equation of the best fit straight line. The slope of this line is k_2'.

Now you know the order of the reaction with respect to both NPA and OH^-.

-To get the rate constant, k, solve the equation $k' = k[OH^-]^y$ for k using data from either the first or second reaction.

CONCLUSION

Report the rate law as rate = $k[NPA]^x[OH]^y$ with the values you got for k, x, and y.

List at least two possible sources of error, the effect they would have on your result (be very specific) and why they would have that result.