

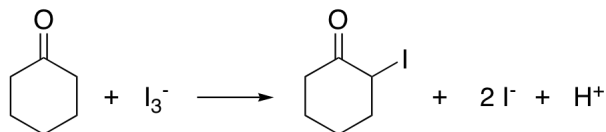
Chemical Kinetics: The Iodination of Cyclohexanone

Lab #5, Chem 36

Spring 2009

Introduction

In this experiment the kinetics of the reaction between triiodide and cyclohexanone ($C_6H_{10}O$) will be studied.



Although we expect the rate of this reaction to be dependent upon the concentrations of cyclohexanone and triiodide present in the solution, in somewhat of a surprise it is also dependent upon the hydrogen ion concentration. The general rate law for this reaction is:

$$rate = k[C_6H_{10}O]^a [I_3^-]^b [H^+]^c$$

where a, b and c (generally integers) are the orders of the reaction with respect to cyclohexanone, triiodide, and hydrogen ion, respectively, and k is the rate constant for the reaction.

For a particular set of conditions, the experimental rate of this reaction can be expressed as the change in the concentration of I_3^- , $\Delta[I_3^-]$, divided by the time interval, Δt ,

$$rate = \frac{\Delta[I_3^-]}{\Delta t}$$

The average rate or velocity of a car to a given location is the distance traveled divided by time. The amount of I_3^- consumed is analogous to the distance traveled by the car; both quantities, when divided by elapsed time, give rates. The rate is generally not constant, but varies with time because the concentrations of the reactants decrease as they are consumed during the reaction. This complication normally makes the study of reaction rates rather complex. However, in the reaction between triiodide and cyclohexanone, the triiodide reacts or is "consumed", after the rate determining step. This

permits us to relate the rate of reaction to the disappearance of triiodide. Triiodide is a brown colored liquid, and the reaction is considered to be over when the brown color just disappears.

If a series of reactions is run in which the concentration of only one of the reactants is changed at a time, then the order of reaction with respect to that reactant can be determined. As an example, the order with respect to cyclohexanone can be determined by examining the rates of two different trials. In both trials the triiodide and hydrogen ion concentrations are held constant and only the cyclohexanone concentration is varied. Thus, any change in the rate is due to the change in the cyclohexanone concentration. If one now compares the rate of trial II with trial I the following expression results:

$$\frac{rate_{II}}{rate_I} = \frac{k[C_6H_{11}O]_{II}^a [I_3^-]^b [H^+]^c}{k[C_6H_{11}O]_I^a [I_3^-]^b [H^+]^c}$$

Since the triiodide and hydrogen ion concentrations are being held constant the equation reduces to:

$$\frac{rate_{II}}{rate_I} = \frac{k[C_6H_{11}O]_{II}^a}{k[C_6H_{11}O]_I^a}$$

By taking logs of both sides of the equation the order of reaction with respect to cyclohexanone can be determined by:

$$\log\left(\frac{rate_{II}}{rate_I}\right) = \log\left(\frac{[C_6H_{11}O]_{II}^a}{[C_6H_{11}O]_I^a}\right) = a \log\left(\frac{[C_6H_{11}O]_{II}}{[C_6H_{11}O]_I}\right)$$

rearranging

$$a = \frac{\log\left(\frac{rate_{II}}{rate_I}\right)}{\log\left(\frac{[C_6H_{11}O]_{II}}{[C_6H_{11}O]_I}\right)}$$

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A similar procedure enables one to measure the order of the reaction with respect to hydrogen ion and to confirm the fact that the reactions order is zero with respect to triiodide. Once the order of reaction with respect to each reactant is known, the rate constant, k , for the reaction can be evaluated.

In the second part of this experiment the energy of activation, E_a , will be evaluated by studying the rate of the reaction at two additional temperatures. The procedure will be to inspect the rate of reaction of the fastest trial mixture at a lower temperature and the slowest trial mixture at a higher temperature. Using these rates and calculating the rate constants at each of the three temperatures permits one to estimate the energy of activation. The relationship between the rate constant, temperature, and the energy of activation is given by the Arrhenius Equation:

$$\ln k = -\frac{E_a}{RT} + \text{constant}$$

To find the energy of activation, $\ln k$ is plotted against $1/T$. The slope is equal to $-E_a/R$. R is the gas constant, $8.314 \text{ J/mol}\cdot\text{K}$.

Experimental

Part I. Determination of Reaction Orders.

1. Select two 18 x 150 mm test tubes and fill them about three-quarters full with distilled water. Both tubes must be filled to the same height. Hold the two tubes beside each other, place a sheet of white paper under them and look down through the two tubes. If the colors appear the same in both tubes then the pair can be used to observe the color change due to the loss of the I_3^- . If the colors are different then select another tube and re-do the comparison test. These tubes will be used for all of the following trials.
2. In a clean, dry Erlenmeyer flask obtain approximately 75 mL of 0.50 M $\text{C}_6\text{H}_{10}\text{O}$ (cyclohexanone), and 75 mL of 1.0 M HCl. In a third flask obtain 50 mL of 0.020 M I_3^- . Keep the flasks containing the I_3^- and $\text{C}_6\text{H}_{10}\text{O}$ covered to prevent evaporation of the cyclohexanone and triiodide.
3. Preparation of a blank: Using graduated pipettes, transfer 6 mL of the 0.50 M $\text{C}_6\text{H}_{10}\text{O}$ solution, 6 mL of the 1.0 M HCl solution, and 5 mL of distilled water into an Erlenmeyer flask. Separate pipettes should be used with each solution. Lastly pipette 3 mL of the 0.020 M I_3^- into the flask, and swirl it to mix the reagents. Let this mixture stand for 10 minutes and then fill one of the test tubes from A-1. This test tube will be used as a comparison to determine when each of the of the following trials has fully reacted.
4. Use the graduated pipettes to transfer 6 mL of the 0.50 M $\text{C}_6\text{H}_{10}\text{O}$ solution, 6 mL of the 1.0 M HCl solution, and 10 mL of distilled water into an Erlenmeyer flask. Lastly pipette 3 mL of the 0.020 M I_3^- into the flask, and swirl it to mix the reagents. Since the reaction begins the instant the triiodide is added it is important to record the time that the reagents are mixed to the second. Transfer this solution to the second test tube until it is at the same height as the solution in the test tube being used as the blank. The brownish color of the solution is due to I_3^- . As the I_3^- is consumed by the reaction the color will fade. Keep looking down the two test tubes toward a piece of white paper and note the time at which the colors in the tubes are the same. Do a second trial. The time required for the two trials should agree within 10%. If the difference in the time for the two trials is greater than 10%, a third trial should be performed.
5. If the concentration of one of the other components is changed while keeping the concentration of the other two components constant, the dependence of the reaction upon that component can be determined. Start by doubling the volume of $\text{C}_6\text{H}_{10}\text{O}$ used. The amount of distilled water used will have to be decreased, as the total volume of the reaction mixture should always be 25 mL. Remember the $[\text{H}^+]$ and $[\text{I}_3^-]$ must be the same as in the initial trials. Only one reactant concentration should be changed in each new mixture tested. Perform

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two trials at the new cyclohexanone concentration. Do a third trial if the rates vary by more than 10%.

- In the next series of trials double the $[H^+]$, while returning the $C_6H_{10}O$ concentration to that of the original mixture. Do two trials at this H^+ concentration. Do a third trial if the rates vary by more than 10%.
- Finally, reduce or increase the $[I_3^-]$ so that the time it takes for the triiodide to disappear is reasonable. The $[H^+]$ and the $[C_6H_{10}O]$ should be the same as the original mixture. Perform two trials on this mixture. Do a third trial if the rates vary by more than 10%.
- Record the temperature of the mixture from one of the trials. As all the bottles have been stored in the same room it safe to assume that this is the temperature of all the solutions.

Energy of Activation.

The energy of activation, E_a , can be determined by measuring the rate constant, k , at two different temperatures and then plotting the $\ln k$ against $1/T$.

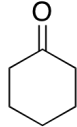
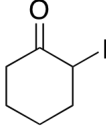
- Select the reaction mixture that took the longest time and measure the rate of this reaction in the hotter water bath, at about $33^\circ C$. Be sure to use the solutions of $C_6H_{10}O$, H^+ , I_3^- and distilled water that are suspended in the water bath to perform these trials. Do two trials. Do a third trial if the rates vary by more than 10%.
- Take the reaction mixture that took the shortest time and measure the rate of this mixture in a cold water bath, at about $16^\circ C$. Do two trials using the solutions suspended in this water bath. Do a third trial if the rates vary by more than 10%.

Waste

Pour the left over solution into the appropriately labeled bottle in the hood.

Calculations

- From the data in the first part of this experiment, determine:
 - The new concentrations of all reagents after mixing.
 - The average rate for each of the mixtures.
 - The order of reaction for $C_6H_{10}O$, H^+ and I_3^- , by comparing the various trials to one another.
 - The rate constant, k , for each trial and then the average rate constant.
- From the data in the second part of the experiment; determine
 - The average rate for the trials at the high and low temperatures.
 - The rate constant, k , for the trials at these temperatures.
 - The energy of activation, E_a , by plotting $\ln k$ vs. $1/T$.
- Given the following heats of formation:

| compound | ΔH_f° (kJ/mol) |
|---|-----------------------------|
|  | -165 |
|  | -159 |
| I_3^- (aq) | -60.3 |
| H^+ (aq) | 0.00 |
| I^- | -56.0 |

- Calculate the heat of reaction for the iodination of cyclohexanone.
- Construct an energy vs. reaction pathway diagram (plot) showing the relative energy of the starting materials, the products and the activation energy.
- In the reaction mechanism shown below, the second step is the slow step. Show that this corresponds to the rate law determined in lab.

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