Reaction Kinetics: The Bromination of Acetone

**Objective:** The purpose of this experiment is to determine the rate law and the rate constant for the bromination of acetone.

**Introduction—** Chemical Kinetics is the study of rates (or speeds) of chemical reactions and the mechanisms (sequence of steps) by which they occur. The rate of a reaction tells us how quickly reactants are used up and products are formed. To be useful, chemical reactions must occur at reasonable rates. The Haber process is an important industrial process used to produce millions of tons of ammonia each year.

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g) \]  
(Haber process)

Many fertilizers, explosives, dyes, plastics, and synthetic fibers are then synthesized from the ammonia. At 25 °C, the reaction occurs too slowly to make it economically useful. However, the speed of the reaction can be increased significantly if it is run at high temperatures and pressures with an iron oxide catalyst (usually 450 °C and 200 atmospheres).

The aim of this experiment is to determine the rate law for the reaction

\[(\text{CH}_3)_2\text{CO(aq)} + \text{Br}_2(aq) \xrightarrow{\text{H}^+} \text{BrCH}_2\text{COCH}_3(aq) + \text{HBr(aq)}\]

(\(\text{CH}_3\text{CO})\) is called acetone. We don’t need to worry about its structure or about the organic product \(\text{BrCH}_2\text{COCH}_3\) (bromoacetone). The reaction is replacing one of the hydrogens on acetone with a bromine—hence it is called a bromination reaction. The bromination of acetone in acid solution proceeds according to

\[\text{CH}_3\text{C(O)CH}_3 + \text{Br}_2 \xrightarrow{\text{H}^+} \text{CH}_3\text{C(O)CH}_2\text{Br} + \text{Br}^- + \text{H}^+ \quad [1.]\]

The reaction is catalyzed by hydrogen ion. The rate law is assumed to be of the form

\[\text{rate} = -\frac{d[\text{acetone}]}{dt} = -\frac{d[\text{Br}_2]}{dt} = k[\text{acetone}]^x[\text{Br}_2]^y[\text{H}^+]^z\quad [2.]\]

where \(k\) is the rate constant and \([A]\) represents concentration of \(A\) in moles per liter. The exponents \(p, q,\) and \(r\) indicate the order of the reaction with respect to acetone, bromine, and hydrogen ion, respectively.

The rate law of a reaction shows a relationship between the rate constant and the concentrations of the reactants involved raised to their respective reaction orders. The rate law of the above reaction can be written as:

\[\text{rate} = k[\text{acetone}]^x[\text{Br}_2]^y[\text{H}^+]^z\]

Where \(k\) is the rate constant and \(x, y,\) and \(z\) are the reaction orders. To determine the rate law, we will have to determine the values of \(k, x, y,\) and \(z.\) Unfortunately, these values CANNOT be determined from the stoichiometric equation. However, they can be determined experimentally. If we determine how fast a reactant is being consumed in the reaction process or how fast a product is formed, then we can generate some useful data that can help us determine the unknown values \((k, x, y, \text{and } z).\) Our strategy will be to change the concentration of one reactant at a time, while keeping the other reactant concentrations constant. This will definitely change the reaction rate, however, the rate constant and the reaction orders will remain the same irrespective of how we change the reactant concentrations.
In this experiment you will set up a reaction at known concentrations and time until completion as demonstrated by a color change. The other experiments will involve the doubling of the concentration of one reactant and measuring the change in rate. The most likely effects of doubling a concentration are:

1. rate is the same, takes the same time, then it's a zero order.
2. rate also double, takes half the time, then it's a first order
3. rate increases by four, takes one quarter the time, then it's second order.

This laboratory exercise will focus on how changing concentration affects how long to complete a reaction.

Materials:
This exercise will require the use of the following glassware and hardware:
- 6 small test tubes and stopper
- Thermometer
- Auto-pipetters
- A piece of white paper

This exercise will use the following chemicals:
- Acetone solution
- Bromine solution
- Hydrochloric acid solution

Procedure: This exercise will contain four parts. Each part has a separate page of instructions and a data sheet in Excel to enter collected data and make calculations. The spreadsheet should be down loaded to the laboratory computer and opened from its hard drive during the experiment. The four parts to the experiment are:

1. Determination of the reaction rate at set concentrations.
2. Double one concentration and determine the new rate.
3. Double a different concentration and determine the new rate.
4. Calculate the orders of the reagents.

Download kineticsdatapage Spreadsheet.

- CAUTION: The solutions used are corrosive and hazardous!

To obtain a stopwatch on line go to: http://www.online-stopwatch.com/
If you want to run more than one reaction at a time, open multiple stopwatch windows on your computer.

Mixture 1:

1. Fill a test tube 10 ml of water. This is a reference.
2. Prepare a mixture of 2.0 ml of 4.0 M acetone, 2.0 ml of 1.0 M hydrochloric acid and 4.0 ml of water in a test tube.
3. Record the temperature of the mixture on the data page.
4. Measure of 2.0 ml of 0.020 M bromine solution into a second test tube. One partner will add this to the other solution, stopper and shake.
5. The initial time is when the bromine solution has been added and the other partner should record this on the data page.
6. Looking down from the top to the bottom of the test tubes, with the mixture and water
against a white background. Watch until all the color in the mixture has disappeared. This is the end of the reaction. Record this as the final time.

7. Repeat steps 1 through 6 two more times. Average the final results.

**Mixture 2:**

1. Prepare a mixture of 4.0 ml of 4.0 M acetone, 2.0 ml of 1.0 M hydrochloric acid and 2.0 ml of water in a test tube.
2. Record the temperature of the mixture on the data page.
3. Measure of 2.0 ml of 0.020 M bromine solution into a second test tube. One partner will add this to the other solution, stopper and shake.
4. The initial time is when the bromine solution has been added and the other partner should record this on the data page.
5. Looking down from the top to the bottom of the test tubes, with the mixture and water against a white background. Watch until all the color in the mixture has disappeared. This is the end of the reaction. Record this as the final time.
6. Repeat steps 1 through 5 two more times. Average the final results.

**Mixture 3:**

1. Prepare a mixture of 2.0 ml of 4.0 M acetone, 4.0 ml of 1.0 M hydrochloric acid and 2.0 ml of water in a test tube.
2. Record the temperature of the mixture on the data page.
3. Measure of 2.0 ml of 0.020 M bromine solution into a second test tube. One partner will add this to the other solution, stopper and shake.
4. The initial time is when the bromine solution has been added and the other partner should record this on the data page.
5. Looking down from the top to the bottom of the test tubes, with the mixture and water against a white background. Watch until all the color in the mixture has disappeared. This is the end of the reaction. Record this as the final time.
6. Repeat steps 1 through 5 two more times. Average the final results.

**Calculations:** The order of the reagents can be determined by first determining the ratio of the rate of disappearance of bromine.

\[
\frac{-\Delta [Br_2]}{\Delta t} = \frac{-0.020 [Br_2]_{initial}}{t_{final} - t_{initial}}
\]

Don’t forget to calculation the concentrations of each reagent used for the experiment.

Based on the change in the rate for experiments 2 and 3 resulting from the doubling of concentration fill in the data table for them in the spreadsheet. Remember:

Doubling the concentration of a zero order reagent, the rate stays the same.
Doubling the concentration of a first order reagent causes the rate to double.
Doubling the concentration of a second order reagent causes the rate to become 4 times greater.

**Optional Mathematical approach:** The algebraic method is especially useful for rate laws which have fractional exponents. First, write the general form of rate law, for example rate = \( k[NO]^x[H_2]^y \). Now, write the ratio of rates for experiments 1 and 3 in which \([H_2]\) remains constant and \([NO]\) changes.
Now add in numbers from your data table and then solve for x:

\[
\frac{1.23 \times 10^{-3}}{4.92 \times 10^{-3}} = \frac{(0.10)^x}{(0.20)^x}
\]

This simplifies to

\[
\frac{1.00}{4.00} = \left(\frac{1.0}{2.0}\right)^x
\]

Taking the log of both sides,

\[
\log \frac{1.00}{4.00} = x \log \left(\frac{1.0}{2.0}\right)
\]

- 0.602 = x(-0.30)

x = 2.0 exponent for [NO]

2.0 is now the order for the rate law equation.

**Laboratory Report:** Make sure you explain all of the calculations performed in the lab.