**University of Portland**

**CHM 278 General Chemistry Laboratory II**

**EXPERIMENT 12:**

**The Iodination of Acetone: Determination of Reaction Rate &**

**Energy of Activation**

T

he rate at which a chemical reaction occurs depends on several factors: the nature or mechanism of the reaction, the concentrations of the reactants (and sometimes the products!), the temperature, and the presence of possible catalysts. All of these factors can markedly influence the observed rate of reaction.

Some reactions are very slow indeed; the oxidation of gaseous hydrogen or wood at room temperature would not proceed appreciably in a century. Other reactions are essentially instantaneous; the precipitation of silver chloride when solutions containing silver ions and chloride ions are mixed and the formation of water when acidic and basic solutions are mixed are examples of extremely rapid reactions. In this experiment we will study a reaction that, in the vicinity of room temperature, proceeds at a moderate, relatively easily measured rate.

For a given reaction, the rate typically increases with an increase in the concentration of any reactant. The relation between rate and concentration is a remarkably simple one in many cases, and for the reaction

aA + bB 🡪 cC

the rate can usually be expressed by the equation

rate (Eq. 1)

where *m* and *n* are generally, but not always, integers, 0,1, 2, or possibly 3; [A] and [B] are the concentrations of A and B (ordinarily in moles per liter); and *k* is a constant (the *rate constant* of that chemical reaction) that makes the mathematical relationship in Eq. 1 quantitatively correct. The powers *m* and *n* are called the *orders of the reaction* with respect to A and B. If *m* is 1, the reaction is said to be *first order* with respect to the reactant A. If *n* is 2, the reaction is *second order* with respect to reactant B. The overall order is the sum of *m* and *n*. In this example, if (*m* + *n*) = (1 + 2), the reaction would be *third order* overall.

The rate of a reaction is also significantly dependent on the temperature at which the reaction occurs. An increase in temperature increases the rate, an often-cited rule being that a rise in temperature of 10°C doubles a reaction rate. This rule is only approximately correct; nevertheless, it is clear that a rise of temperature of say 100°C could change the rate of a reaction appreciably.

As with concentration, there is a quantitative relation between reaction rate and temperature, but here the relation is somewhat more complicated. This relation is based on the theory that in order for a molecular collision to lead to bonds made or broken, reactant species must have a minimum amount of kinetic energy at the time of collision. This minimum kinetic energy is called the *activation energy* or Ea for the reaction. The Arrhenius Equation relates the logarithm of the rate constant *k* to the absolute temperature *T* and the activation energy according to Eq. 2:

ln *k* + constant (Eq. 2)

In applying Eq. 2, use a value for *R,* the gas constant, of 8.31 J/mol\*K to give *Ea* in J/mol. By measuring *k* at different temperatures and plotting the logarithm of *k* vs. 1/T, we can determine the activation energy for a given chemical reaction by measuring the slope of a best-fit line and solving for *E*a.

In this experiment, we will study the kinetics of the reaction between iodine and acetone:



Previous investigation of this reaction has revealed dependence of the reaction rate on the concentration of the product hydrogen ion as well as the concentration of the reactant acetone; perhaps surprisingly, the rate does not seem to depend on the concentration of iodine present.

As in Eq.1, the rate expression for this chemical reaction is that shown in Eq.3:

rate (Eq. 3)

In Eq. 3, *m*, *n*, and *p* are the orders of the reaction with respect to acetone (A), iodine and hydrogen ion respectively, and *k* is the rate constant for the reaction. Note: all these values (*k*, *m*, *n*, and *p*) must be determined by experimental observation; these values cannot be derived from the balanced chemical equation for the reaction observed.

The rate of this reaction can be expressed as the incremental (small) change in concentration of I2, Δ(I2), that occurs, divided by the time interval Δ*t* required for the change, as expressed in Eq. 4:

rate (Eq. 4)

Note that the minus sign in Eq. 4 makes the rate expression positive since the reactant iodine disappears as the reaction proceeds; in other words, Δ[I2] is negative because [I2]f is zero and ([I2]f - [I2]o) is less than zero.

The iodination of acetone is an unusual reaction in that it can be easily investigated experimentally by following the disappearance of the brown colored molecular iodine. A second important characteristic of this reaction is the fact that the rate is independent of iodine concentration: in Eq. 3, *n* = 0 and the reaction is zeroth order in I2 concentration. Thus [I2]0 = 1, no matter the value of [I2], as long as the concentration value is not zero.

Because the rate of the reaction does not depend on [I2], we can study the rate of iodination by simply making iodine the limiting reagent present in a large excess of acetone and hydrogen ion. We then measure the time required for a known initial concentration of I2 to be used up completely. If both acetone and H+ are present at much higher concentrations than that of I2, their concentrations will not change appreciably during the course of the reaction, and the rate will remain, according to Eq. 3, effectively constant until all the iodine is consumed, at which time the reaction will cease.

Under these reaction conditions, if it takes *t* seconds for the color of a solution having an initial concentration of I2 equal to [I2]0 to disappear, the rate of the reaction given by Eq. 4, would be reduced to the expression given in Eq. 5:

rate (Eq. 5)

Although the rate of the reaction is constant during its course under the conditions we have set up, we can vary it by changing the initial concentrations of acetone and H+ ion. If, for example, we should *double* the initial concentration of *acetone* over that in Mixture 1, keeping [H+] and [I2] at the *same* values they had previously, then the rates of Mixture 2 and Mixture 1 would be expressed as shown in Eq. 6a and 6b:

rate 2 (Eq. 6a)

rate 1 (Eq. 6b)

Dividing the first equation by the second, we see that the *k*-factors cancel, as do the factors of iodine and hydrogen ion concentrations, since they have the same values in both equations and in Mixtures 2 and 1. Thus the ratio reduces to Eq.7:

(Eq. 7)

Solving Eq. 7 for *m*, either by inspection or by using logarithms, reveals the *order* of the reaction with respect to acetone.

By similar procedures we can measure the order of the reaction with respect to H+ ion concentration (*p*) and also confirm the fact that the reaction is zero order with respect to I2. Having found the order with respect to each reactant, we can then evaluate *k*, the rate constant for the reaction.

The determination of the orders *m* and *p*, the confirmation of the fact that *n*, the order with respect to I2, equals zero, and the evaluation of the rate constant *k* for the reaction at room temperature comprise your main assignment in this experiment. You will be furnished with standard solutions of acetone, iodine, and hydrogen ion, and with the composition of one solution that will give a reasonable rate. The rest of the planning and the execution of the experiment will be your responsibility.

A second part of the experiment is to study the rate of this reaction at different temperatures in order to calculate the activation energy. The general strategy for obtaining Ea involves measurement of the reaction rate at three temperatures and plotting ln *k* vs. 1/*T*; according to Eq. 2, the slope of such a plot must be *–E*a */ R*.

**EXPERIMENTAL METHODS**

With a partner, sign up for one of the three reaction temperature baths: 25°C, 35°C, or 45°C. Record the actual temperature of the bath ±0.1°C. Select three medium test tubes (15x125 mm) that, when filled with water, have identical color and clarity. You will also need two additional, non-matched tubes (to use as storage tubes), a long glass Pasteur pipette and latex bulb, and a digital timer.

This experiment involves four different reaction mixtures. Two identical reactions will be completed for each mixture and the results averaged. Thus you will collect data for eight separate trials.

**Mixture 1**: Prepare reaction, storage, and reference tubes in the following way:

* REACTION TUBE: Using pipet pumps on the appropriate reagent bottles, dispense 1.00 mL of 4.00 M acetone, 1.00 mL of 1.00 M HCl, and 2.00 mL of deionized water into one of the matched test tubes. NOTE: you may also prepare a second reaction tube for the duplicate run and allow it to equilibrate during the first run.
* STORAGE TUBE: Dispense 1.00 mL of 5.00 mM I2 into one of the non-matched tube (this serves as a storage tube during temperature equilibration). NOTE: you may also prepare the second storage tube for the duplicate run and allow it to equilibrate during the first run.
* Loosely stopper the reaction and storage tubes with rubber stoppers, in order to slow evaporation of acetone, and clamp them in the water bath that is maintained at your chosen reaction temperature.
* REFERENCE TUBE: Prepare the remaining matched test tube by adding 5 mL of deionized water to serve as a color reference for the reactions. This single tube is used as a reference for all the kinetic runs.

Allow the test tubes to equilibrate in the water bath for 5 minutes. Remove the stoppers from one reaction tube and one iodine storage tube. Use the Pasteur pipette to pick up all of the iodine solution, then transfer the iodine solution into the reaction tube. **Try to transfer all the iodine with one pass.** Start the timer midway through the addition process. With the timer running, use the Pasteur pipette to mix the solution by **quickly pipetting up and down in the tube for a few seconds.**

The reaction will appear yellow because of the presence of iodine, and the color will fade slowly as the iodine reacts with the acetone to form the colorless product. Use the comparison tube to note the completed disappearance of the yellow color. Record the elapsed time at the moment that the color in the reaction tube disappears. Repeat the experiment with the second set of reaction tubes. The elapsed time should agree within about 10%; if the times do not agree, consider additional reaction runs in order to achieve sufficient precision.

The rate of the reaction equals the initial concentration of I2 *in the reaction mixture* divided by the elapsed time. Since the reaction is zeroth order in I2, and since both acetone and H+ ion are present in great excess, the rate is constant throughout the reaction and the concentrations of both acetone and H+ remain essentially at their initial values in the reaction mixture.

**Mixture 2:** Plan a second composition that has a concentration of acetone twice that of Mixture 1. In the new mixture you should keep the total volume at 5.00 mL and be sure that the concentrations of H+ and I2 are the same as for the first experiment. If in doubt, check your recipe with the instructor.

Prepare new REACTION and STORAGE test tubes in a manner similar to that of the last experiment; of course, these tubes will have different volumes of reactants as laid out in your recipe for Mixture 2. Ensure that the temperature bath is within 1 °C of the previous runs, then execute the experiment in duplicate runs. Elapsed reaction times should agree within 10%.

TO CALCULATE EXPONENT “*m*” (the calculations can be accomplished after all kinetic experiments are performed): Calculate the order of the reaction with respect to acetone, using a relationship similar to Eq. 7. First, write an equation similar to Eq. 6a for this second reaction mixture, substituting the observed value for the reaction rate as well as the initial concentrations of acetone, I2, and H+ in Mixture 2. Then write an equation like Eq. 6b for the first reaction mixture, using the observed rate and the initial concentrations in that mixture. Divide Eq. 6a by Eq. 6b in order to obtain an expression analogous to Eq. 7; solve Eq. 7 for *m*, the order of this reaction with respect to acetone concentration.

**Mixture 3:** For the third set of runs, change the composition of the reaction mixture to allow determination of reaction order with respect to H+; plan a new recipe in which the concentration of H+ is double that of Mixture 1, the other concentrations are the same as Mixture 1, and the total volume is 5.00 mL. Check the bath temperature, then perform the experiment in duplicate runs to establish reaction times that agree within 10%. Using equations analogous to Eq. 6a, 6b, and 7, determine a value for *p*, the order of the reaction with respect to H+.

**Mixture 4:** For the final reaction mixture adjust the concentration of I2 to ensure that the reaction order w/respect to I2 is, in fact, zero. Measure the rate of reaction twice and calculate n. *Hint: Should you double or halve the concentration of I2? Consider the length of the experiment in answering that question.*

**Calculation of the rate constant:** Using the values of *m*, *n*, and *p* that you have determined, evaluate *k*, the rate constant for the reaction, for *each* of the reaction mixtures that you studied. Average the *k*-values and calculate the standard deviation and % variation for your set of *k*-values.

**Calculation of the energy of activation:** Obtain rate data from your classmates and determine the value of *Ea*, the energy of activation, in J/mol, by plotting ln *k* vs. 1/*T* in Excel.

**RESULTS: Data & Calculations for Experiment 12: The Iodination of Acetone**

**TOS**

Your name and that of your lab partner:\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

**A. Reaction Rate Data**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Mixture | Volume (mL) of 4.00 M acetone | Volume (mL) of 1.00 M HCl | Volume (mL) of 0.00500 M Iodine | Volume (mL) of H2O | Time (sec) for 1st run | Time (sec) for 2nd run | Avg. Time, t (sec) | %  Δt  (of the 2 runs) | Bath Temp (±0.0 C) |
| **1** | 1.00 | 1.00 | 1.00 | 2.00 |  |  |  |  |  |
| **2** |  |  |  |  |  |  |  |  |  |
| **3** |  |  |  |  |  |  |  |  |  |
| **4** |  |  |  |  |  |  |  |  |  |

**B. Determination of Reaction Orders with Respect to Acetone, H+ Ion, and I­2.**

rate (Eq. 5)

Enter the *initial* concentrations of acetone, H+ ion, and I2 in each of the mixtures you examined and use Eq. 5 to find the rate of each reaction. Be sure to note the **units**!

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  | Initial Concentrations (M) | | |  | Reaction rate |
| Mixture | [A]o | [H+]o |  | Avg. Time, *t* (s) | rate = |
| **1** | 0.800 M | 0.200 M | 0.00100 M |  |  |
| **2** |  |  |  |  |  |
| **3** |  |  |  |  |  |
| **4** |  |  |  |  |  |

**Sample Calculations (Part B).** Below, show the calculation of the reaction rate of one of the mixtures. Be sure to include the correct units!

Substituting the initial concentrations and the numerical rate value from Table B above, write Eq. 3 as it would apply to reaction Mixture 2:

**TOS**

rate 2 =

Now write Eq. 3 for reaction Mixture 1, substituting concentrations and the calculated rate from the Table B:

rate 1 =

Divide the equation for Mixture 2 by the equation for Mixture 1; the resulting equation should have the ratio of rate 2 to rate 1 on the left side, and a ratio of acetone concentrations raised to the power *m* on the right and should be similar in appearance to Eq. 6. Show your work and write the resulting equation below:

The only unknown in the equation is *m.* Solve for *m. m* = \_\_\_\_\_\_\_\_\_\_\_

Now write Eq. 3 as it would apply to reaction Mixture 3 and also as it would apply to reaction Mixture 4:

rate 3 =

rate 4 =

Using the ratios of the rates of Mixtures 3 and 4 to those of Mixtures 2 **or** 1, find the orders of the reaction with respect to H+ ion and I­2; show your work:

*n* = \_\_\_\_\_\_\_\_\_\_\_

*p* = \_\_\_\_\_\_\_\_\_\_\_

**C. Determination of the Rate Constant *k*.**

**TOS**

Given the values of *m*, *p*, and *n* as determined in Part B, calculate the rate constant *k* for each mixture by simply substituting those orders, the initial concentrations, and the observed rate from the table into Equation 3. Use the correct units!

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Mixture | Rate constant k | Average k | Standard deviation | % Variation |
| **1** |  |  |  |  |
| **2** |  |
| **3** |  |
| **4** |  |

**Sample Calculations (Part C).**

a)Show the calculation of the rate constant, *k*, for one of the mixtures.

b) Show the calculation of the average value of k, the standard deviation, and the % variation.

**D. Determination of the Energy of Activation**

**TOS**

Use shared class data and Excel to plot ln *k* vs 1/*T* where *T* is the absolute temperature in Kelvin units. Organize your data clearly, and include in your notebook a copy of the graph. Be sure to display the equation for the best fit line (linear) for those data and the R2 value for the equation. Make sure the axes are labeled correctly with units and be sure to have a chart title for the graph.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Average k | ln k | Bath temp (oC) | T (K) | 1/T (1/K) |
|  |  |  |  |  |
|  |  |  |  |  |
|  |  |  |  |  |

Line equation:\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

R2  value: \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Slope (include units): \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Calculated Ea (include units): \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Literature value for Ea (include units): \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Percent Error:\_\_\_\_\_\_\_\_\_\_\_\_

**Sample Calculations (Part D).** Show your calculation of the value of the activation energy, *E*a, from the slope of the graph. INCLUDE ALL CORRECT UNITS. (What should the units of the slope be? Recall that the ln k values of the *y*-axis are unitless.) Show your calculation of the percent error of your calculated *E*a relative to a literature value.

**SPECIFIC ITEMS TO INCLUDE IN THE NOTEBOOK**

As noted in Appendix A, be sure to include the Table of Contents (with an entry for this experiment), Title of experiment and Date completed, Objectives, and Experimental Methods. Details on what to include in the other sections are described below.

**DATA & OBSERVATIONS and SAMPLE CALCULATIONS**

Complete the data sheets for Parts A – D of this experiment. This involves filling in tables, writing out requested calculations (including the designated “Sample Calculations” for Parts B, C, and D), and entering requested information. Also include in this section of the notebook, a print copy of the Excel graph used to determine the value of the activation energy for the reaction. The expected format for this graph is described in Part D.

**ANALYSIS & CONCLUSIONS**

1. Restate the objectives of the experiment.
2. Write out the derived rate expression for the iodination of acetone that explicitly shows your values of the exponents *m, n*, and *p*, and the value (with units) you determined for the rate constant, *k*.
3. State the temperature of the water bath used in your experiment. State the average value of the rate constant, *k*, observed at this temperature. Express your rate constant as the average *k* ± standard deviation; be sure to use appropriate units and significant figures.
4. Evaluate the precision of your rate constant, *k*, by considering the standard deviation and % variation.
5. State the value of the activation energy, *E*a, obtained using class data for the values of the rate constant for this reaction at the three different temperatures; use appropriate units and significant figures.
6. Evaluate the accuracy of the calculated value for the activation energy, *E*a. This evaluation requires an accepted (literature) value for the activation energy and calculation of the % error.
7. Identify any errors encountered in determining an experimental value for the activation energy and how they could be minimized in a future experiment.

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**EXPERIMENT 12 ADVANCED STUDY**

Name \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ Date\_\_\_\_\_\_\_\_\_\_\_\_ Section \_\_\_\_\_\_\_\_

1. In a reaction involving the iodination of acetone, the following volumes were used to make up the reaction mixture:

1.00 mL 4.00 M acetone + 1.00 ml 1.00 M HCl + 1.00 mL 0.00500 M I2 + 2.00 mL H20

1. How many moles of acetone were in the reaction mixture? Recall that, for a compo­nent A, no. moles A = MA x V, where MA is the molarity of A and V the volume in liters of the solution of A that was used.

\_\_\_\_\_\_\_\_\_\_\_\_ moles acetone

1. What was the molarity of acetone in the *reaction mixture*? The volume of the *mixture* was 5.00 mL (0.00500 L) and the number of moles of acetone was found in Part a. Recall the definition of molarity:



\_\_\_\_\_\_\_\_\_\_\_\_M acetone

1. Using the same stock solutions, how could you double the molarity of the acetone in the reaction mixture, keep the total volume at 5.00 mL, and keep the same concentrations of H+ ion and I2 as in the original mixture?
2. Using the reaction mixture in Problem 1, a student found that it took 25.0 seconds for the color of the I2 to disappear.
3. What was the rate of the reaction? Hint: First find the initial concentration of I2 in the reaction mixture, [I2]0. Then use Equation 5.

rate =

1. Given the rate from Part a, and the initial concentrations of acetone, H+ ion, and I2 in the reaction mixture, write Equation 3 as it would apply to the mixture.

rate =

1. What are the unknowns that remain in the equation in Part b? \_\_\_\_ \_\_\_\_ \_\_\_\_ \_\_\_\_

**TOS**

1. A second reaction mixture was made up in the following way:

2.00 mL 4.00 M acetone + 1.00 mL 1.00 M HCl + 1.00 mL 0.00500 M I2 + 1.00 mL H2O

1. What were the initial concentrations of acetone, H+ ion, and I2 in the reaction mix­ture? Show your work.

[acetone]o \_\_\_\_\_\_\_\_\_\_\_\_ M [H+]o \_\_\_\_\_\_\_\_\_\_\_\_ M [I2]0 \_\_\_\_\_\_\_\_\_\_\_\_ M

1. It took 12.0 seconds for the I2 color to disappear from the reaction mixture when it occurred at the same temperature as the reaction in Problem 2. What was the rate of the reaction? Show your work.

rate = \_\_\_\_\_\_\_\_\_\_\_\_

Write Equation 3 as it would apply to the second reaction mixture:

rate =

1. Divide the equation in Part b by the equation in Problem 2b. The resulting equation should have the ratio of the two rates on the left side and a ratio of acetone concentra­tions raised to the m power on the right. Write the resulting equation and solve for the value of m, the order of the reaction with respect to acetone. (Round off the value of m to the nearest integer.)

m = \_\_\_\_\_\_\_\_\_\_\_\_

4. A third reaction mixture was made up in the following way:

2.00 mL 4.00 M acetone + 1.00 mL 1.00 M HCl + 2.00 mL 0.00500 M I2

If the reaction is zero order in I2, how long would it take for the I2 color to disappear at the temperature of the reaction mixture in Problem 3? Hint: solve Eq. 5 given the rate calculated in Problem 3b above.

\_\_\_\_\_\_\_\_\_\_\_\_ seconds