Reaction Kinetics --- the Iodination of Acetone
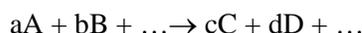## Part I

Introduction:

There are several factors that can influence the rate of a chemical reaction:

        1) the nature of the reaction,

        2) the concentrations of the reactants (& partial pressures of gaseous reactant),

        3) temperature,

        4) presence of catalysts.

For a general reaction,

$$aA + bB + \ldots \rightarrow cC + dD + \ldots$$

its rate law expression has the form

$$Rate = k\,[A]^m\,[B]^n\ldots \qquad\qquad (1)$$

In this equation, [A] and [B] are molar concentrations (moles/Liter), k is referred to as the **rate constant**, which does not depend on the concentrations of reactants and accounts for the other variables — nature of reaction, temperature and the availability of catalysts. The exponents of the concentrations are called the **reaction orders**, which define how the rate is affected by reactant concentrations. In this experiment we will study the reaction between acetone, $CH_3(CO)CH_3$, and iodine, I_2 under acidic condition, which proceeds at a moderate, relatively easily measured rate around room temperature.

$$CH_3\,(CO)\,CH_3\,(aq) + I_2\,(aq) \rightarrow CH_3\,(CO)\,CH_2I\,(aq) + H^+(aq) + I^-\,(aq)$$

The rate of this reaction is found to depend on the concentration of hydrogen ion in the solution as well. Therefore, the rate law of this reaction based on equation 1 is

$$rate = k[acetone]^m[I_2]^n[H^+]^p \qquad\qquad (2)$$

where m, n, and p are the orders of the reaction with respect to acetone, iodine, and hydrogen ion, respectively, and k is the rate constant for the reaction.

The rate of this reaction can be expressed as $\Delta[I_2]$, the change in the concentration of I_2, divided by the time interval Δt required for the change:

$$rate = \frac{-\Delta[I_2]}{\Delta t} \qquad\qquad (3)$$

The minus sign is to make the rate positive ($\Delta[I_2]$ is negative). Ordinarily, since rate varies as the concentrations of the reactants according to Equation 2, the above calculation equation only provides an average rate of the reaction, not the instantaneous rate required. However, the iodination of acetone is a rather atypical reaction, because it really is zero order in I_2 concentration. This means that the rate of the reaction does not depend on $[I_2]$ at all. Therefore, we can study the rate by simply making I_2 the limiting reagent present in a large excess of acetone and H^+ ion. Also, iodine has color, so that one can readily follow changes in iodine concentration visually. Experimentally, the rate of the reaction is measured based on the following equation under this special situation

$$rate = \frac{-\Delta[I_2]}{\Delta t} = \frac{-(0 - [I_2]_0)}{t - 0} = \frac{[I_2]_0}{t} \qquad\qquad (4)$$

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/or H^+ ion. If, for example, we should double the initial concentration of acetone over that in Mixture 1, keeping $[H^+]$ and $[I_2]$ at the same values

they had previously, then the rate of Mixture 2 would, according to Equation 2, be different from that in Mixture 1:

$$\text{rate}_2 = k(2A)^m [I_2]^0 [H^+]^p \qquad (5a)$$
$$\text{rate}_1 = k(A)^m [I_2]^0 [H^+]^p \qquad (5b)$$

Dividing the first equation by the second, we see that the k's cancel, as do the terms in the iodine and hydrogen ion concentrations, since they have the same values in both reactions, and we obtain simply

$$\frac{rate_2}{rate_1} = \frac{(2A)^m}{(A)^m} = (\frac{2A}{A})^m = 2^m, \qquad (5)$$

$$therefore, m = \log(rate_2 / rate_1) / \log(2)$$

By a similar procedure we can measure the order of the reaction with respect to H^+ ion concentration and also confirm the fact that the reaction is zero order with respect to I_2. Having found the order with respect to each reactant, we can then calculate 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 I_2, equals zero, and the calculation of the rate constant k for the reaction at room temperature comprise your assignment in this part of the 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.

Materials:

4 M acetone
1 M HCl
 0.005 M I_2
Disposable pipets
Small test tubes
Sirring Rod

Experimental Procedure:

Obtain 4 disposable pipets, Mark a horizontal line on each pipet using a permanent marker that's about 0.5 cm below the bulb portion of the pipet as shown in the diagram to the right. Make sure that the marks are as close to each other as possible as for them to deliver the same volume of liquids.

Use one of the marked pipets for water, one for the 4M acetone, one for the 1M HCl and one for the 0.005 M I_2 solutions. Label with permanent Marker or other methods so that they will not be mixed up.

Draw 1 dropper to the Mark (this volume quantity will be labeled as a dropper from this point on) of 4 M acetone solution and deliver it into a clean, dry small test tube, to it add 1 dropper of 1 M HCl solution and 2 droppers of water. Mix the solutions well by shaking the test tube sideways or by using a clean, dry stirring rod.

Noting the time on your wristwatch or the wall clock to 1 second (this will mark the starting time of the reaction), add one dropper of the 0.005 M iodine solution into the test tube. Quickly mix the solutions well by using a stirring rod.

The reaction mixture will appear yellow because of the presence of the iodine, and the color will fade slowly as the iodine reacts with the acetone. Fill another test tube to the same height will distilled water. Look down the test tubes (one with reaction mixture, one with distilled water) toward a well-lit piece of white paper, and note the time the color of the iodine just disappears for the reaction mixture. Measure the temperature of the mixture in the test tube using a thermometer at the end of the reaction.

Repeat the experiment, using as a reference the reacted solution instead of distilled water. The amount of time required in the two runs should agree within about 20 seconds.

Pause and examine the situation:

In the experiment that you just did, we obtained 1 dropper of the 4 M acetone solution, 1 dropper of the 1 M HCl solution, 1 dropper of the I_2 and 2 droppers of water. What are the concentrations of the reactants: [acetone], $[H^+]$, $[I_2]$ at the beginning of the reaction?

[acetone]: _____ , $[H^+]$: _____ , $[I_2]$ _____

The rate of the reaction equals the initial concentration of I_2, in the reaction mixture divided by the elapsed time. (This is because the reaction is zero order in I_2, and since both acetone and H^+ ion are present in great excess, the rate is the same throughout the reaction.) What is your calculated rate for reaction above?

Rate =

Continuation of the Experiment:

(starting from this point, you should think of tabulated ways of organizing your lab data so that they are clear and also show relationships among the trials.)

Having found the reaction rate for one composition of the system, it is time to think for a moment about what changes in composition you might make to decrease the time and hence increase the rate of reaction. In particular, how could you change the composition in such a way as to allow you to determine how the rate depends upon acetone concentration? If it is not clear how to proceed, reread the discussion preceding Equation 5. In your new mixture you should keep the total volume at 5 droppers, and be sure that the concentrations of H^+ and I_2 are the same as in the first experiment. Carry out the reaction twice with your new mixture; the times should not differ by more than about 15 seconds. The temperature should be kept within about a degree of that in the initial run. Calculate the rate of the reaction. Compare it with that for the first mixture, and then calculate the order of the reaction with respect to acetone, using a relation similar to Equation 5. First, write an equation like 5a for the second reaction mixture, substituting in the values for the rate as obtained by Equation 4 and the initial concentration of acetone, I_2, and H^+ in the reaction mixture. Then write an equation like 5b for the first reaction mixture, using the observed rate and the initial concentrations in that mixture. Obtain an equation like 5 by dividing Equation 5a by Equation 5b. Solve Equation 5 for the order m of the reaction with respect to acetone.

Again change the composition of the reaction mixture so that this time a measurement of the reaction will give you information about the order of the reaction with respect to H^+. Repeat the experiment with this mixture to establish the time of reaction to within 15 seconds, again making sure that the temperature is within about a degree of that observed previously. From the rate you determine for this mixture find p, the order of the reaction with respect to H^+.

Finally, change the reaction mixture composition in such a way as to allow you to show that the order of the reaction with respect to I_2 is zero. Measure the rate of the reaction twice, and calculate n, the order with respect to I_2.

Having found the order of the reaction for each species on which the rate depends, evaluate k, the rate constant for the reaction, from the rate and concentration data in each of the mixtures you studied. If the temperatures at which the reactions were run are all equal to within a degree or two, k should be about the same for each mixture.

Reaction Kinetics --- the Iodination of Acetone
Part II

Introduction:

The second of the experiment is to first to verify the reaction orders and reaction rate constant obtained in part I and to study the rate of this reaction at different temperatures to find its activation energy. To find the activation energy, the general procedure here would be to study the rate of reaction in one of the mixtures at room temperature and at two other temperatures, one above and one below room temperature. Knowing the rates, and hence the k's, at the three temperatures, you can then find E_a, the energy of activation, for the reaction, by plotting ln k vs. 1/T. The slope of the resultant straight line must be - Ea/R (based on the equation $\ln k = \dfrac{-Ea}{R} \bullet \dfrac{1}{T} + \ln A$).

Experimental procedure:

Make up a mixture using reactant volumes that you did not use in any previous experiments. Using Equation 2, the values of concentrations in the mixtures, the orders, and the rate constant you calculated from your experimental data, predict how long it will take for the I_2 color to disappear from your mixture. Measure the time for the reaction and compare it with your prediction.

Select one of the reaction mixtures you have already used that gave a convenient time, and use that mixture to measure the rate of reaction at about 10 ^{o}C and at about 40 ^{0}C. From the two rates you find, plus the rate at room temperature, calculate the energy of activation for the reaction.