Scientific research consists in seeing what everyone else has seen, but thinking what no one else has thought.--A. Szent-Gyorgyi

The Rate of Iodination of 2-propanone

For a given reaction, the rate typically increases with an increase in the concentration of any reactant. In many cases the relationship between rate and concentration is a simple one, and for the general reaction:

$$aA + bB \rightarrow cC$$

the rate can often be expressed by the equation

$$\text{rate} = k\,[A]^m[B]^n$$

where **m** and **n** are sometimes, but not always, integers from 0 through 2; **k** is a constant called the rate constant of the reaction, which makes the equation quantitatively correct at different temperatures. The numbers **m** and **n** are 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 A. If n is 2, the reaction is said to be *second order* with respect to B. Clearly the rate is dependent on the concentrations of A and B.

The rate is also significantly dependent on the temperature at which the reaction occurs. An increase in temperature increases the rate. As with concentration, there is a quantitative relationship between reaction rate and temperature, but it is somewhat more complicated. It is based on the concept of *activation energy*--the sufficient energy needed for an effective collision which can initiate reaction. The equation relating the rate constant **k** to the kelvin temperature **T** and the activation energy $\mathbf{E_a}$ is

$$\ln\ k = \frac{-E_a}{R}\ \frac{1}{T} + \text{constant}$$

$$y \;=\; m \quad x \;+\; b$$

where **R** is the gas constant, 8.31 J/mol·K. This equation is in the form of a straight line where *y* is the natural log of k (ln k) and *x* is 1/T. The slope is thus interpreted as $-E_a/R$. By measuring k at different temperatures we can graphically determine the activation energy. The constant is, of course, the y-intercept, and is specific for a particular reaction. It is known as the Arrhenius Constant.

Adapted from: An Investigation of the Rate of the Reaction Between Iodine and Acetone in Aqueous Solution, *Chemistry, Student's Book II, Topics 13-19, Nuffield Advanced Science*, The Nuffield Foundation, 1970

In this experiment you will study the kinetics of the reaction between 2-propanone (acetone) and iodine:

$$CH_3COCH_3(aq) + I_2(aq) \rightarrow CH_3COCH_2I(aq) + H^+(aq) + I^-(aq)$$

The rate of this reaction is found to be dependent on the concentration of hydrogen ion in solution as well as presumably the concentrations of the two reactants. Hydrogen ion could be thought of as a kind of "auto-catalyst". The rate law might thus be:

$$\text{rate} = k\,[CH_3COCH_3]^m[I_2]^n[H^+]^p$$

where m, n and p are the orders of the reaction with respect to 2-propanone, iodine and hydrogen ion respectively, and k is the rate constant for this reaction.

A convenient way to measure the rate for this reaction is in terms of the disappearance of I_2:

$$\text{rate} = \frac{-\Delta[I_2]}{\Delta t}$$

This expression alone will be sufficient since the reaction turns out to be zero order with respect to iodine concentration (i.e., n = 0). Thus the rate of the reaction does not depend on I_2 and we can study the rate by making iodine the limiting reagent, having the 2-propanone and hydrogen ion present in large excesses so that their concentrations do not change appreciably by the time all the iodine is gone and therefore the rate remains fairly constant. Under such circumstances, if it takes **t** seconds for the color of the I_2 to disappear, the rate would be:

$$\text{rate} = \frac{[I_2]_o}{t}$$

where $[I_2]_o$ is the initial iodine concentration in the mixture. Since I_2 is colored in aqueous solution (reddish brown I_3^-), the rate can be determined by measuring the time it takes for the color of a solution with a known amount of I_2 to fade.

In principle this could be done simply by looking at the solution, comparing it to water. There are a couple of problems with this approach. As the reaction approaches completion, the color fades rather rapidly, becoming pale yellow. It is difficult to distinguish just when the color is gone. Also, the final mixture is not perfectly clear like water. Therefore we will employ the colorimeter used before to determine the concentration of the "Blu" solution.

You may recall from an earlier experiment the expression which relates Absorbance to concentration. In this experiment we don't really need to worry about that because all we care about is how long it takes for the absorbance to fall from some starting value to zero (when all the colored I_2 is gone). Since the CBL unit displays % transmittance rather than absorbance, we will be measuring the time it takes for the %T to become 100%. If the time is measured from the moment the solutions are mixed, it is not even important to have the sample in the colorimeter immediately, so long as it is in place before the %T becomes 100%.

Preparing to experiment

You will be provided with the following materials:

1. four 1 mL calibrated beral pipets
2. 2.0 M 2-propanone solution
3. 0.010 M I_2 solution
4. 6.0 M HCl solution
5. a colorimeter
6. a cuvette
7. timer
8. two small test tubes
9. standard thermometer
10. ice

Design an experiment to determine the orders of 2-propanone and HCl in the reaction, and confirm the order (0) of I_2 using BLUE light.

Design an experiment to determine the activation energy for the reaction.

[*hint*: The table below gives a suggested scheme for accomplishing the objectives listed above, but other combinations may be used]

2-propanone	I_2	HCl	H_2O	Temperature
mL	mL	mL	mL	^oC
0.5	0.5	0.5	1.0	room
1.0	0.5	0.5	0.5	room
0.5	0.25	0.5	1.25	room
0.5	0.5	1.0	0.5	room
1.5	0.5	0.5	0.0	about 10
1.0	0.5	0.25	0.75	about 30

BE SURE TO BRING YOUR TI-83/84 CALCULATOR TO CLASS FOR THIS EXPERIMENT. YOU WILL ALSO NEED A COPY OF THE HCHEM.83G FILES IN YOUR CALCULATOR MEMORY.

Technique

1. Preparing a "blank"

For many experiments the "blank" used to set 100% T is simply distilled water. In this case, water is not an adequate reference since the mixture at the end of the reaction is not completely clear and not completely colorless. Therefore, a reacting solution will be prepared before you come into lab. You should use this solution to set up your colorimeter.

2. Timing a reaction using the CBL

There are some limitations in using the CBL for kinetics experiments. One is the fact that readings do not commence as soon as you send the instructions to the CBL. You may have noticed this. If you select a 10 second interval for taking readings, the first measurement may be recorded as late as 10 seconds after you press [ENTER]. Because of this it is more accurate to use a stopwatch to measure the time and set up the CBL to read %T continuously. Just be sure to start timing as soon as the solutions are mixed, not when the cuvette is finally placed in the colorimeter. An efficient sequence of events might go something like this:

a. measure out all ingredients except 2-propanone into a 50 mL beaker
b. draw up desired amount of 2-propanone into pipet
c. start the stopwatch as you quickly squirt the 2-propanone into the mixture in the beaker; swirl or stir to mix
d. pour the mixture into a cuvette and place in the colorimeter to measure until %T until it reaches 100%; stop the stopwatch

3. Measuring temperature

Since thermometers do not allow light to pass through them you cannot measure the temperature of the mixture in the cuvette while you measure the %T (there is also the problem of the lid on the colorimeter...). For the mixtures which are run below room temperature and above room temperature the best "guesstimate" of the temperature for the reaction is arrived at by measuring the temperature of the solutions *before* mixing and then again after the %T is 100%. The average of these temperatures may be taken as the temperature of the reaction.

The CBL may be used to measure *both* %T and temperature at the same time. You simply specify 2 probes at the beginning of the program and then proceed through the probe selection one channel at a time. **However, the high concentration of 2-propanone in the mixtures has the potential to weaken the seal around the measuring end of the thermometer. For that reason we will be using standard thermometers in this experiment.**

4. Running the reaction at hot/cold temperatures

The easiest way to set this up is to place all of the ingredients except the 2-propanone into a small test tube and the 2-propanone into a second tube. Place both in a beaker containing either hot or cold water. Put the thermometer into the test tube with the mixture and when the temperature is reached, pour both solutions into a small beaker, mix and place in the cuvette.

The chemicals

None of the chemicals in this experiment is new to you but a word needs to be said about I_2. Working with large amounts of solution which end up mainly in the trough sinks is a problem because iodine vapors are very irritating to the eyes. However, iodine is readily contained if the solutions are poured into water in a large waste beaker that is kept covered with a watch glass. Therefore you will be provided with a large covered beaker of water. ALL of your discards should go into this beaker and not into the sink. You will be grateful for the enhanced comfort this precaution should ensure.

Analysis

1. Use the volumes and concentrations of the solutions to calculate the *diluted initial* concentrations of the 2-propanone, I_2 and HCl in each mixture [note that each mixture in the suggested table has a total volume of 2.5 mL, including the water------recall $V_1M_1 = V_2M_2$].

2. Use the results from #1 above and the time for each reaction to determine the rate of each reaction (as shown in the introduction).

3. If you compare the concentration of 2-propanone in the first two mixtures, you will see that the second mixture contains twice a much as the first (see portion of mixture table below). All other substances remain the same. So any effect on the rate will be due to the fact that 2-propanone has been doubled.

2-propanone	I_2	HCl	H_2O	Temperature	**Rate**
mL	mL	mL	mL	^oC	
0.5	0.5	0.5	1.0	room	?
1.0	0.5	0.5	0.5	room	?

Having calculated the rates already, you can examine the effect on the rate when 2-propanone doubles. Although your data may be a little rough, it is important to remember here that the orders in this rate law are all *integers*, so you should round accordingly.

By a similar procedure, using the first and third mixtures, the order of iodine (0) can be confirmed. And by using the first and fourth mixtures, the order of hydrogen ion can be determined.

4. Write the rate law for the reaction based on your results.

5. Use your rate law and each rate to determine a value for k, the rate constant, in each reaction. Average the values for the room temperature runs. Since you had limited time in the experiment, two additional values are given below:

k	^oC
7.1×10^{-6}	5.0
3.2×10^{-5}	25.0

6. Use the five values of k to determine E_a by plotting the information as described in the introduction.