KI Kinetics of Acetone/Iodine Reaction KI(order)

Objective
The objective of this experiment is to determine the rate equation (order of reaction with respect to acetone) and rate constant (k) for the reaction of acetone and iodine in aqueous acidic solvent.

Materials

1N HCl (5 ml)	acetone (3 ml)
KI (6 g)	iodine (0.3 g)
distilled water	disposable cuvettes

Equipment and Supplies
100 ml volumetric flasks (6)
pipettes 1ml (3)
uv/vis spectrophotometer

Background
Acetone and iodine react in the presence of acid to form a mono-substituted product plus HI.

$$CH_3\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_3 + I_2 \xrightarrow{\text{acid}} CH_3\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_2\text{–}I + HI$$

The reaction may be followed by measuring the absorbance of the I_2 using a UV/Vis spectrometer. One has for the rate:

$$\text{Rate} = -\, d[I_2]/dt. \qquad (1)$$

It turns out that this reaction depends on the following: (1) the concentration of acetone, (2) the concentration of the acid, and (3) temperature. In other words, the reaction is independent of the concentration of iodine. Hence, one can write for the rate equation

$$\text{Rate} = k\,[\text{Acetone}]^m \qquad (2)$$

where m is the order with respect to acetone and the acid dependence is accounted for in the magnitude of k (i.e.,

$$k = k'\,[H^+]\,). \qquad (3)$$

Since the Absorbance, A, is directly proportional to the concentration, we can use various plots of A versus time to determine the order of the reaction. If the reaction is zeroth order (i.e., m = 0), then a graph of A versus time will be linear. If the reaction is first order (i.e., m = 1), then ln(A) versus time will be linear. If the reaction is second order (i.e., m = 2), then 1/A versus time will be linear. In addition to these three possibilities also determine the appropriate plot for third order by deriving the integrated rate law(m=3) (show this work in report) and include. You will

plot your data based on these four possibilities in order to determine the order of the reaction. Also, from your data you will determine the numerical value for the rate constant, k, at room temperature.

Procedure

Prepare 100mL of an iodine solution by dissolving 0.200g of I_2 and 4.000g of KI in water using a volumetric flask. I_2 by itself does not dissolve in water. However, I_2 is quite soluble in an aqueous solution of KI. Hence, the KI merely helps the I_2 to dissolve; the KI does not play a role in the kinetics of the reaction. Calculate the molarity of the I_2 in the iodine solution.

Prepare 100 mL of acetone solution by dissolving 1 mL of pure acetone in water using a pipet and a volumetric flask. Calculate the molarity of the acetone solution.

Set the spectrometer to 565 nm for all absorbance readings.

When it comes time to prepare the sample for study, you will combine in the cuvette:
1 mL of iodine solution, 1 mL of acetone solution, and 1 mL of 1.0 N HCl .

To initiate the reaction, pipet the following into the cuvette: 1 mL of the acetone solution, 1 mL of the iodine solution, and 1 mL of the HCl solution. Mix the solution by inverting the cell several times.

Vis/UV Spectrometer Instructions

We will perform this experiment at a temperature of 40°C. Prepare the iodine and acetone solutions in 100 mL volumetric flasks, and clamp the flasks in a constant temperature bath set to this temperature. Pour about 10 mL of 1.0 N HCl into another 100 mL volumetric flasks, and clamp it in the water bath as well.

To operate the Cary 100 Bio UV-Vis spectrometer make sure both the computer and the spectrometer are turned on. We will be using the constant-temperature accessory, so make sure it is on as well (it's the unit on the floor under the spectrometer).

Open the Kinetics program. Click on the Setup command. (You will load the sample and reference cells at a later point.)

1. Click on the Cary tab and set Wavelength to 565 nm, Y Max to 0.50, select Simple Collect, and set Stop to 30 min. <u>Set Ave Time (s) to 30 s.</u> (Don't click on OK yet.)
2. Click on the Accessories tab and check the Use Cell Changer box, under Go to Cell select Cell 1, under Temperature check the Automatic Temperature Setting box, change Block to 40°C, under Temperature Display check Block, check the Show Status box.
3. Click on the Analyze tab and check the Auto Calculate box, set Simple Calculate, Stop to 30 min, and Order to First.
4. Click on the Samples tab and set the Number of Samples to 1.

5. Click on the Reports tab, do NOT check the Auto Print box, bud DO check the Include X-Y Pairs Table.
6. Click on the Auto Store tab and set Storage Off.
7. Now click on the OK button. You should see a Status Display window. Move it to a corner of the screen. It should take only a minute or two for the temperature to reach 40°C. The program will not let you continue until the desired temperature is reached.
8. With nothing in either the sample or reference slots, click on Zero.
9. Use disposable cuvettes for both your Sample and Reference. Place the Sample in Cell 1 and the Reference in Cell 7. Make sure they are all the way down.
10. Click on Start. A Loading Guide pops up -- click OK. A Sync Start pops up -- click OK.
11. You should see data collection begin. When data collection is over, print a copy of your graph. The results of the Auto Calculate should appear at the bottom of your print out.
12. Copy/paste the X-Y data pairs into an Excel spread sheet. (See Calculations section below.)
13. Remove the cells. Leave the computer on, but turn off the Cary 100 and the temperature controller.

Calculations

Include only first 24 minutes of data in your data and plots. As reaction reaches equilibrium then the concentration will not change and this should not be included in an analysis of the kinetics. To insure that the reaction is still proceeding the last 6 minutes of data will be discarded. Observe your plot of A versus time and determine if 24 minutes of data to include seems appropriate based on the values remaining constant toward the end of the data set. Include 4 plots and a Table with values of m and r^2 for first, second, third, and fourth order.

Another way to consider the data plots is shown below. You should note that the first order decay for a system approaching equilibrium follows the equation

$$(A_t - A_\infty) = (A_0 - A_\infty) \exp(-k\,t) \qquad (4)$$

where A_t is the absorbance at time t, A_0 the initial absorbance, and A_∞ the absorbance at equilibrium ($t = \infty$).

Do an additional analysis of the data graphically (first order only) to determine if the reaction fits equation above. A graph of $\mathbf{\ln(A_t - A_\infty)}$ as a function of **t** should be linear if this reaction is first order.

Calculate the rate constant, k. Be sure to include correct units for the rate constant. Note: This constant is sometimes referred to as the *pseudo rate constant*, because it does not take into account the effect of the acid, H^+.

Cleaning Up

Dispose of the three solutions by pouring them down the sink. Rinse all glassware and return it to the drawer. Throw the disposable cuvettes you used into a waste basket.