KINETICS OF A PSEUDO FIRST ORDER REACTION BETWEEN ACETONE AND IODINE

THEORY

The rate at which a chemical reaction occurs depends on several factors: the nature of the reaction, the concentrations of the reactants, the temperature, and the presence of possible catalysts. All of these factors can markedly influence the observed rate of reaction.

In this experiment, we will study a reaction which, in the vicinity of room temperature, proceeds at a relatively easily measured rate.

For a given reaction, the rate typically increases with an increase in the concentration of any reactant. For the reaction \( A + B \rightarrow C \) the rate can be expressed by the following equation, which is called the rate law,

\[
rate = k[A]^m[B]^n
\]

where \( m \) and \( n \) are generally, but not always, integers, 0, 1, 2 or possibly 3; \([A]\) and \([B]\) are the initial concentrations of A and B (ordinarily in moles per liter); and \( k \) is the specific rate constant for the reaction. The numbers \( m \) 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, the reaction would be third order overall.

As with the concentration, there is a quantitative relationship between reaction rate and temperature. This relation is based on the idea that in order to react, the reactant species must have a certain minimum amount of energy present at the time the reactants collide in the reaction step. This amount of energy, which is typically furnished by the kinetic energy of the species present, is called the activation energy of the reaction.

The first order reaction equation

\[
Rate = -\frac{d[A]}{dt} = k[A]
\]

is integrated to give:

\[
ln[A] - ln[A]_0 = -kt
\]

The kinetics of a second order reaction is described by the equation

\[
-\frac{d[A]}{dt} = k[A]^2
\]

where \([A]\) is the concentration of the reactant A, or
where [A], [B] are the concentrations of the reactants A and B if we consider the following second-order reaction:

\[ A + B \rightarrow \text{Products} \]

if \([A]_0, [B]_0\) are the initial concentrations of the reactants A and B, \(x\) is the decrease after time \(t\), then

\[
\frac{dx}{dt} = k([A]_0 - x)([B]_0 - x)
\]

integration between the limits 0,\(t\) and 0,\(x\) gives:

\[
\frac{2.303}{([A]_0 - [B]_0)} \cdot \log \frac{[B]_0([A]_0 - x)}{[A]_0([B]_0 - x)} = kt
\]

In a second-order reaction, if one reactant is present in sufficiently large excess, its concentration remains essentially constant and so the second-order reaction then appears to be of first-order. These reactions are known to be PSEUDO FIRST-ORDER. If we assume that \([A]_0\) is present in large excess; \(x\) (indicates \([A]_0\) at time \(t\) as mol/lt) will be too small to be taken into consideration in the calculation, so, \([A]_0 - x\) can be considered as \([A]_0\) only.Since \([A]_0 - x = [A]_0\) and \([B]_0\) is neglected in \([A]_0 - [B]_0\), equation (7) becomes:

\[
\frac{2.303}{([A]_0)} \cdot \log \frac{[B]_0}{([B]_0 - x)} = kt
\]

since \([A]_0\) is constant

\[
k \cdot a = k' = \frac{2.303}{t} \cdot \log \frac{[B]_0}{([B]_0 - x)}
\]

where \([B]_0\) = concentration of B (Iodine in this experiment) initially present, in mol/lt, \([B]_0 - x\) = concentration of B (Iodine in this experiment) at time \(t\) in mol/lt.

The plot of \(\log \frac{[B]_0}{([B]_0 - x)}\) versus time will give the slope, thus the \(k'\) value of the reaction.

In this experiment, we will study the kinetics of the acid-catalyzed reaction between iodine and acetone in aqueous solution:

\[
CH_3COCH_3 + I_2 \xrightarrow{H^+} CH_3COC\text{H}_2I + HI
\]

The rate of this reaction is expected to depend on the concentrations of the two reactants. By Equation 1, the rate law for this reaction is
where m and n are the orders of the reaction with respect to acetone and iodine, respectively, and k is the rate constant for the reaction.

The rate of this reaction can be expressed as the (small) change in the concentration of I$_2$, $\Delta$I$_2$, divided by the time interval, $\Delta$t, required for the change:

$$rate = \frac{\Delta[I_2]}{\Delta t}$$  \hspace{1cm} (11)

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 10, in a rate study it would be necessary to measure (directly or indirectly) the concentration of each reactant as a function of time; the rate would typically vary markedly with time, decreasing to very low values as the concentration of at least one reactant becomes very low.

The iodination of acetone is a reaction in that it can be very easily investigated experimentally. First of all, iodine has color so that one can readily follow changes in iodine concentration visually. A second and very important characteristic of this reaction is that it turns out to be zero-order in I$_2$ concentration. This means (see Equation 10) that the rate of the reaction does not depend on $[I_2]$ at all as $[I_2]_0 = 1$ no matter what the value of $[I_2]$ is as long as it is NOT zero.

Since the rate of reaction does not depend on $[I_2]$, we can study the rate by simply making I$_2$ the limiting reagent present in a large excess of acetone. We then measure the time required for a known initial concentration of I$_2$ to be completely used up. If acetone is present at much higher concentrations than that of I$_2$, its concentration will not change appreciably during the course of the reaction, and the rate will remain, by Equation 10, effectively constant until all the iodine is gone, at which time the reaction will stop. Under such circumstances, if it takes t seconds for the color of a solution having an initial concentration of I$_2$ equal to $[I_2]_0$ to disappear, the rate of reaction, by Equation 11, would be

$$rate = \frac{\Delta[I_2]}{\Delta t} = \frac{[I_2]_0 - 0}{t - 0} = \frac{[I_2]_0}{t}$$  \hspace{1cm} (12)

Hence we can apply the equation (9) to find the rate constant of the reaction between acetone and iodine by plotting $\log \frac{[B]_0}{([B]_0 - x)}$ versus time ($[B]_0$: initial concentration of I$_2$).

**PROCEDURE**

1. Prepare the mixture at 25°C, from solutions in the following order; 25 ml acetone, 140 ml distilled water and 10 ml 1 M H$_2$SO$_4$.
2. Start timing as t=0 with the addition of 25 ml 0.05 M I$_2$ in KI.
3. Remove 10 ml samples every 5 min., and run into about 5 ml 1 M NaAcetate solution (to stop the reaction) and titrate the residual iodine with Na$_2$S$_2$O$_3$ solution, after the addition of 1 ml starch indicator. At the end point the color changes from blue to colorless. Record the volume of Na$_2$S$_2$O$_3$ consumed each time.

4. During the titration of iodine with sodium thiosulphate (Na$_2$S$_2$O$_3$) the following reaction takes place:

$$2Na_2S_2O_3 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

5. To investigate the effects of changing the iodine and Acetone concentrations, keeping the total volume constant [200 ml], prepare two more solutions, varying the iodine concentration in one and the Acetone concentration in the other.

6. For the second solution, mix 25 ml acetone, 130 ml distilled water and 10 ml 1 M H$_2$SO$_4$ and finally 50 ml 0.05 M I$_2$ in KI and repeat the procedure.

7. For the third solution, mix 35 ml acetone, 130 ml distilled water and 10 ml 1 M H$_2$SO$_4$ and finally 25 ml 0.05 M I$_2$ in KI and repeat the procedure but remove 10 ml samples every 2 min this time.

CALCULATIONS

Plot $log \frac{[B]_0}{([B]_0-x)}$ versus t and obtain the k’ value from the slope.

POST-LAB QUESTIONS

Is it possible to find the activation energy of this reaction with the data you have in hand? If it is possible, please explain. If not, which additional data should be collected to calculate the activation energy of this reaction?

DATA SHEET:

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<th>25 mL acetone + 35 mL I$_2$</th>
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<td>$V_{Na2S2O3}$(mL)</td>
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