Chemical Kinetics: a Clock Reaction

Chemistry 102

Abstract

In this experiment, iodine clock reaction was performed to represent a chemical kinetic scheme. Different concentration of I^-, $BrO_3^{-,}$ and H^+ were primary reactants by using thiosulfate's consumption in reaction to iodine, which then reacted with starch to show an appearance of blue coloration as representation of the reaction. Based on this color changes, time was recorded, then the rate of reaction was calculated based on given concentration. Furthermore, temperature range of 0 °C to 40 °C and the presence of catalyst by use of ammonium molybdate was also observed. Based on these findings, the order was determined for I^-, BrO_3^-, and H^+ as 1, 1, and 2, respectively, the rate constant k_{avg} 36.0 $M^{-3}S^{-1}$ was obtained, and the activation energy 45 kJ/mol, was calculated. The most important finding in this experiment was upon proposed theory of chemical kinetics; it showed clear numerical and graphical correlations.

Introduction

Chemical kinetics is a study of reaction rates based on conditions of molecule at which the nature of the reactants, the concentration of the reactant, the temperature, and the catalyst dictate a speed of reaction. The knowledge of combination of these conditions are important tools in various manufacturing industries and chemistry laboratories. Along with these conditions, reacting molecules must also collide at right orientation to yield a higher frequency factor, leading higher a chance to overcome given activation energy, which then leads to a final product. Reactants need to have the certain amount of energy to overcome the repulsive forces between approaching molecules and to break the existing bonds in the reacting molecules.

The rate constant, k, concentration of reactants and the rate order of the reaction are the factors that affect the reaction rate and can be expressed by a rate law:

$$\text{Rate}= k[A]^x[B]^y[C]^z\ldots \qquad \textbf{[1]}$$

The purpose of this experiment in part 1 is to determine the values of x, y, and z using the method of initial rates. The k value and the rate order can only be determined experimentally.

To find the rate law, two colorless solutions are mixed and, after a period of time, the solution suddenly turns from colorless to colored and it is represented by the following chemical equation:

$$6I^- (aq) + BrO_3^- (aq) + 6H^+ (aq) \rightarrow 3I_2 (aq) + Br^- (aq) + 3H_2O (l) \quad (slow) \quad \textbf{[2]}$$

The reaction between bromate and iodide ions [2] is the one we will be focusing in this experiment since the reaction [3] is only used to delay the reaction between iodine and starch by creating a clock reaction. The solution turns blue when combined with the starch only after all of the $S_2O_3^{2-}$ in [3] has been used up the iodine.

$$I_2 (aq) + 2S_2O_3^{2-} (aq) \rightarrow 2I^- (aq) + S_4O_6^{2-} (aq) \quad (fast) \quad \textbf{[3]}$$

Since we calculate the rate of reaction based on the appearance or disappearance of color involved in the reaction, the change in the concentration of BrO_3^- over time is our rate of reaction:

$$\text{Rate of reaction} = -\left(\frac{\Delta[\mathrm{Br}O_3{}^-]}{\Delta t}\right) \quad \textbf{[4]}$$

By having thiosulfate ion to consume completely with the given amount of I_2 and with the mixture of starch, the blue color was formed post-mix with bromate ion. To relate the rate of change of the $S_2O_3^{2-}$ concentration to that of the BrO_3^-, the stoichiometry of equation [2] and [3] was used:

3 mol I_2 / 1 mol BrO_3^- * 2 mol $S_2O_3^{2-}$ / 1 mol I_2 accounts for $-\left(\frac{\Delta[\mathrm{Br}O_3{}^-]}{\Delta t}\right)=\left(\frac{1}{6}\right)\left(\frac{\Delta[S_2O_3{}^{2-}]}{\Delta t}\right)$ **[5]**

The purpose of this experiment in part 2 is to investigate the rate of a reaction as a function of temperature in order to determine the activation energy, Ea using the Arrhenius equation, where A is the frequency constant, R is the universal gas constant, and T is the temperature in K:

$$k = Ae^{-Ea/RT}$$ **[6]**

The equation is rearranged to be able to use in this experiment and the following equation is represented:

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln A$$ **[7]**

By examining the trend line based on ln k vs. 1/T graph plot, y= mx + b relationship can be used for m= -Ea/R, helps to find a value of activation energy through the four different sets of temperatures.

The final purpose of this experiment in part 3 is to observe the rate of reaction in the presence of a catalyst if this speeds up the reaction. When catalyst is used in the reaction, the pathway is changed and the right orientation favorably affects the rate of the chemical reaction. Generally, the catalyst involved reaction have a lower activation energy than no catalyst involved reaction. So the rate of the catalyzed reaction will be faster.

Experimental

In the first part of the experiment, two different reactant flasks were set up individually to make five different reaction mixes. The total of 10 flasks were prepared to become a combination of five flasks, represented as mixture #1 to mixture #5. As two different flasks were combined and gently swirled, the time was recorded at t=0 and t_f, when the blue coloration first appeared. The setup at the room temperature was prepared as Table 1.

Table 1: Reaction Flask 1 & 2 Data

	Reaction Flask 1 (250 mL)			Reaction Flask 2 (125 mL)		
Mix	.01 M KI	.001 M $Na_2S_2O_3$	H_2O	.04 M $KBrO_3$	.10 M HCl	Starch
1	10 mL	10 mL	10 mL	10 mL	10 mL	3 drops

2	20 mL	10 mL	0 mL	10 mL	10 mL	3 drops
3	10 mL	10 mL	0 mL	20 mL	10 mL	3 drops
4	10 mL	10 mL	0 mL	10 mL	20 mL	3 drops
5	8 mL	10 mL	12 mL	5 mL	15 mL	3 drops

For the second part of the experiment, a same reagents setup as the mixture #1 was conducted at four different temperatures of 39.5 °C, 10.0 °C, 1.0 °C, and 22.5 °C. Timer was started as the two solutions mixed and the time of the first appearance of blue color was noted.

In the last part of the experiment, a same mixture #1 at a room temperature was set up along with a drop of ammonium molybdate, 0.5 M $(NH4)_2MoO_4$, in the flask 2 as the catalyst. Swirled flask 2 was combined with flask 1 and the time was recorded when the blue color was first observed.

Results and discussion

In the first part of the experiment, concentrations of each reactant were obtained by moles which have been used per solution used in the mixtures to find a new molarity. These molarities and rate of reaction were then compared to find order for each reactant as well as overall order by using Equation Rate1/ Rate2 = $k\,[I^-]^x[BrO_3^-]^y[H^+]^z / k\,[I^-]^x\,[BrO_3^-]^y[H^+]^{z.}$ In the Table 2, the comparison between mixture #1 and mixture #2 shows that both iodine and rate of reaction double, which indicates that order is 1 for x. The comparison between mixture #4 and mixture #1 shows that rate of reaction quadruples when H^+ doubles, indicating that order could be 2 for z. The comparison between mixture #3 and mixture #1 shows that rate of reaction nearly doubles whereas BrO_3^- doubles, indicating that the order is 1 for y. In all five mixes, the coloration changes were similar. The reaction rate with different reactant concentration are generated as in Table 2.

Table 2. Dependence of Reaction Rate on Concentration

Mix	Time (s)	Rate (M/s)	$[I^-]$	$[BrO_3^-]$	$[H^+]$	Temp (°C)
1	135.78	$2.45*10^{-7}$	.0020	.008	.02	22.5
2	67.47	$4.94*10^{-7}$	.0040	.008	.02	21.8
3	82.00	$4.06*10^{-7}$	.0020	.016	.02	21.9
4	36.93	$9.02*10^{-7}$	.0020	.008	.04	21.6
5	178.66	$1.86*10^{-7}$	.0016	.004	.03	21.6

The individual value for *k* was first found by plugging in the data from Table 2 into [1], and the average value of *k* was determined. The unit for *k* was determined to be $M^{-3}s^{-1}$ since the overall reaction order was found to be four. The individual k value and the average k value are demonstrated in Table 3:

Table 3: Individual *k* and k_{avg}

Reaction Mixture	Value of *k* (M^{-3} s^{-1})
1	38.28
2	38.59
3	31.72
4	35.23
	k_{avg} = 36.00

In the preceding experiment, same mixture #1 was used to make concentration constant; only temperature was the variable. One can note that higher the temperature, the faster the reaction occurs. In theory, molecules collide more often due to increased thermal energy, and comparison of all 4 mixtures support this theory. According to Table 3 as seen in comparison between mixture #1A and mixture #1D, the time it reacted increased by approximately three folds, while the rates decreased by approximately three folds as well. Comparison between mixture #1A and

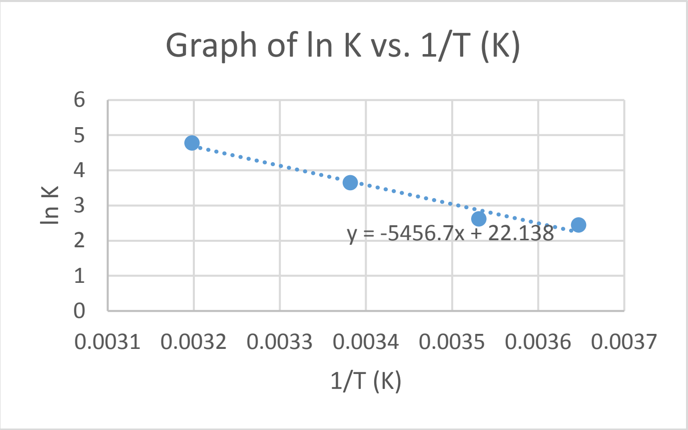
#1C, the change of temperature is by -40K, giving almost 10 folds in time difference and almost 10 folds' difference in reaction rate. Hence, this clearly shows the dramatic relationship between heat which is indicated by temperature, and faster and more collision of molecules as indicated by rate of reaction. These relationship is supported by the following data in Table 4:

Table 4: Dependence of Reaction Rate on Temperature

Mix	Time (s)	Rate (M/s)	Temp (K)	Calculated k ($M^{-3}s^{-1}$)
1A	43.82	$7.60*10^{-7}$	312.7	118.75
1B	379.91	$8.76*10^{-8}$	283.2	13.69
1C	452.65	$7.36*10^{-8}$	274.2	11.50
1D	135.78	$2.45*10^{-7}$	295.7	38.28

The temperature and constant (k) relationship, shown linearly in Figure 1, indicates k increases with the temperature. The slope (m) is -5456.7 and the activation energy derived from this equation y=-5456.7x + 22.138 is 45 kJ/mol. According to online research, Ea for the iodine clock reaction is 53kJ/mol, which is quite higher than 45 kJ/mol from this experiment. Only four temperature settings are not enough to get exact Ea for iodine clock reaction. So by conducting with more temperature settings, a more accurate Ea could be derived. However, it still shows correlation to what was obtained in the experiment calculation. Therefore, this experiment well demonstrated the strong relationship between constant, k, and temperature as well as behaviors seen in the Arrhenius equation and plots.

Figure 1: Graph of ln k vs. 1/T (K)



In the last part of the lab, only one drop of catalyst made a tremendous difference in reaction time. Same mixture #1 was used for control and experiment at constant temperature. The reaction with catalyst took 135.78 s while one with catalyst decreased time by approximately 27 folds at 5s. This result indicates that catalyst take different mechanism pathway to get to product by lowering Ea.

(see attached for calculation)

Conclusion

The three components of this experiment adequately demonstrated the theory of chemical kinetics, more particularly its concept on the iodine clock reaction rates. The experiment proves that more reactant concentration, higher temperature, and the presence of catalyst all lead to react in shorter length of time. This correlates back to the theory that a higher temperature setting allows for the higher energy collisions to occur increasingly. This correlates back to the theory that a catalyst lowers the activation energy and therefore increases the frequency of collisions between the reactants. The catalyst either changes the orientation of the reactants to speed up the collisions or provides an alternate reaction mechanism for the reaction.

It also proved that by performing such simple set up of apparatus, a crude phenomenon such as rate constant and Ea value for iodine clock reaction can be obtained. Though the resulting Ea and k value were slightly deviated from the true value, its significance in correlation to the true value is absolutely phenomenal. The result of this experiment indicates, the overall order of the reaction to be four, the rate law of $k\ [I^-]\ [BrO_3^-]\ [H^+]^2$, the rate constant k_{avg} at 36 $M^{-3}S^{-1}$, and the activation energy of 45 kJ/mol.