Chemistry HL Investigation

January 2021

An investigation to determine the activation energy of the reaction between iodine (I_2) and acetone (C_3H_6O) in the presence of a hydrochloric acid catalyst through the observation of a loss of color.

1 Introduction

When learning about catalysis, I was particularly intrigued by the specific subset of acid catalysts. Acid catalysts are often regarded as the most important area of catalysis in industry. More specifically, these acids allow for the protonation of a double bonded oxygen group in various carbonyls, including ketones such as acetone. As acetone is a major organic solvent which sees its own applications in industry and personal life, this combination of acid catalysis and organic chemistry is particularly relevant. A common iteration of this mechanism results from the use of iodine (a frequently found halogen in organic chemistry) due to its strong color. Thus, I was drawn to investigating the reaction between acetone and iodine in the presence of a hydrochloric acid catalyst and determining the activation energy (E_a) by looking for the loss of color in the reaction solution.

1.1 Research Question

How does varying temperature affect the rate of reaction between iodine and acetone solution in the presence of a hydrochloric acid catalyst?

This question will be answered through empirical theory and experimentation, and the resulting data will also facilitate the calculation of the activation energy of this general reaction.

2 Background

The stoichiometric reaction being studied in this investigation can be depicted as:

$$CH_3COCH_{3\,(aq)} + I_{2\,(aq)} \xrightarrow{\text{HCl}} CH_3COCH_2I_{(aq)} + HI_{(aq)}$$
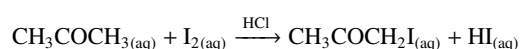
As the iodine is the limiting reagent, it is fully consumed to produce iodoacetone and hydrogen iodide so its brownish-red color slowly disappears from the reactant solution, allowing for the identification of the completion of the reaction. To determine the activation energy of this reaction, the time taken for completion was measured at various temperatures and the Arrhenius equation was then used. However, as the Arrhenius equation is dependent on the rate constant (k), it was first necessary to determine the rate law of the overall reaction.

Additionally, because of the slow nature of this reaction, the *HCl* catalyst was used to provide an alternative pathway with a lower E_a. This allowed for a quicker rate, rendering the reaction feasible for the purpose of this investigation. The basic premise behind the significance of catalysts on lowering the E_a and increasing the rate through kinetics can be seen in Fig. 1.
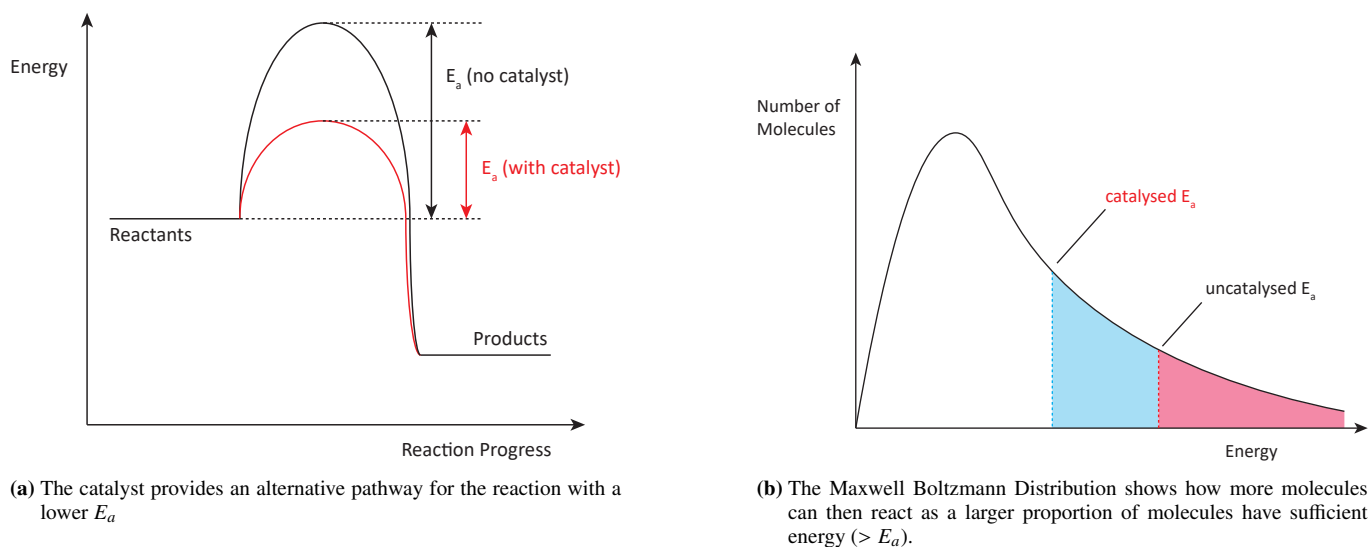

(a) The catalyst provides an alternative pathway for the reaction with a lower E_a

(b) The Maxwell Boltzmann Distribution shows how more molecules can then react as a larger proportion of molecules have sufficient energy ($> E_a$).

Figure 1: Catalyst Function

2.1 Rate Law and Reaction Mechanism

Most reactions involving complex molecules/ions and catalysts rarely occur in a single step identical to the overall reaction, but instead can be further dissolved into multiple steps. This series of reactions is known as a reaction mechanism and plays an instrumental role in determining the rate of a reaction. Of these multiple steps, the slowest is referred to as the rate-determining step as it essentially dictates the rate of the overall reaction. Multiple mechanisms are possible for this reaction (and thus have been proposed), but based on empirical evidence and the rate determined in this experiment, the most likely mechanism is shown in Table 1.

As ketones (specifically acetone) are extremely weak bases, the slowest step in this mechanism would be theorized as the initial one, where the acetone must acquire the donated proton from the acid catalyst. This process is slow even in the presence of a catalyst due to it not being enegetically favorable. Based on this empirical understanding (and the later confirmation via experimentation), this step is the rate-determining step. As the speed of this step is dependent on the concentration of acetone and acid (not the halogen) which both have coefficients of 1, the overall rate law can be theorized as: *rate = k[CH_3COCH_3][HCl]*.

Structural Depiction	Description
	Firstly, protonization of the carbonyl oxygen in acetone occurs as the acid donates its hydrogen ion. This process happens readily, as the highly polar double bond between carbon and oxygen makes the oxygen acquire a high partial negative charge (δ^+). But, as the oxygen must donate both electrons for the electron pair (behave as a nucleophile), it acquires a positive charge. However, this stucture is resonance stabilized, as if the more electronegative oxygen atom takes both electrons in its bond with carbon, the carbon will be left with the positive charge.
	Due to this polarization of the double bond, the α-carbon also becomes more acidic, allowing for easier deprotonation. Thus, as the water molecule approaches, the highly electronegative oxygen with multiple lone pairs attracts a hydrogen molecule from the α-carbon and behaves as a nucleophile. This produces hydronium ion (giving us back the acid catalyst) and the α-carbon can form a double bond with the carbocation, resulting in an electrically neutral enol. These two steps together are referred to as enolization.
	1 of the iodine atoms then behaves as an electrophile (as it is highly electronegative) and the enol becomes a nucleophile, facilitating a S_N2 attack and the heterolyical cleavage of the halogen molecule. The π-bond between the carbon atoms provides the electron pair for the positive iodine, and the oxygen is able to donate its lone pair, creating a dative bond to counteract the resulting positive charge on the carbon atom. This results in the halogenation of the α-carbon and leaves a single iodine ion.
	Due to the resulting positive charge on the oxygen atom, the functional group becomes prime for deprotonization and facilitates the transfer of the hydrogen ion to the highly negative iodine ion. This leaves a double bond between the oxygen and carbon, providing a stable octet configuration for all species involved.

Table 1: Proposed Mechanism

Although a catalyst is utilized for this reaction, it is still generally slow to complete at lower temperatures, making it difficult to perform many trials at lower temperatures.

2.2 Experimental Determination of Rate Law

Although the empirical determination of the rate law can be suggested through the proposed mechanism above, it is still difficult to be fully confident in a rate law without experimental determination. Fortunately, this process is relatively straightforward and relies on basic mathematical principles. The general rate for any reaction can be expressed as a product of powers of the concentrations of all reactants and/or catalysts involved. Thus, for the iodination of acetone, the rate law must be:

$$rate = k[CH_3COCH_3]^p[HCl]^q[I_2]^r$$

where p, q, r are integers greater than or equal to 0. Additionally, k is a constant for the reaction at a fixed temperature. Thus, by altering the concentration of individual reactants while keeping the remaining concentrations the same, different rates can be calculated and the results can be divided to determine the orders (p, q, r). For example, if we double the concentration of acetone while leaving the remaining concentrations untouched, we would have the result:

$$\frac{rate_2}{rate_1} = \frac{k[CH_3COCH_3]^p 2^p[HCl]^q[I_2]^r}{k[CH_3COCH_3]^p[HCl]^q[I_2]^r} = 2^p$$

Then, by taking the logarithm (base 2) of both sides:

$$p = \log_2\left(\frac{rate_2}{rate_1}\right)$$

This process can then be performed for the remaining reactants, allowing for the simple calculation of p, q, r and the final determination/confirmation of the overall rate law.

2.3 Determination of Activation Energy

As mentioned previously, to determine the activation energy of a specific reaction, you must have the value of the rate constant k, which is temperature dependent. By finding/confirming the rate law of $rate = k[CH_3COCH_3][HCl]$, this process becomes straightforward. Because iodine is a limiting reactant, and acetone and acid are used in large excess quantities (keeping their concentration relatively stable), the rate is theorized to remain largely linear for the duration of the reaction. Through this apparatus, the rate can then be defined as $\frac{\Delta[I_2]}{t}$, or the change in concentration of iodine over time. As the loss of color indicates reaction completion (and the total depletion of iodine), this simplifies to $\frac{[I_{2(initial)}]}{t}$. Then, through substitution and rearranging of the above rate equation, we see:

$$k = \frac{[I_{2(initial)}]}{t[CH_3COCH_3][HCl]}$$

This result allows us to experimentally determine the rate constant for various trials of this reaction. After calculating this rate constant at multiple temperatures, the Arrhenius Equation facilitates the determination of activation energy. The Arrhenius Equation highlights the dependence of the rate constant on the absolute temperature as:

$$k = Ae^{\frac{-E_a}{RT}}$$

where A is the steric constant for each chemical reaction, T is the absolute temperature (in Kelvin), and R is the universal gas constant ($8.31 \frac{J}{K \cdot mol}$). Taking the natural log of this entire equation results in the following relationship:

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

Thus, a linear relationship exists between the natural logarithm of the rate constant ($\ln k$) and the inverse of the temperature ($\frac{1}{T}$) with the gradient being $\frac{-E_a}{R}$. As R is a known constant, a plot of the graph between these two variables can be used to find the slope of the line and thus the activation energy (E_a).

3 Hypothesis

Increasing the temperature of the reaction between iodine solution and acetone in the presence of hydrocholoric acid catalyst will directly increase the rate of the reaction.

As discussed earlier, the increase in temperature with the addition of a catalyst allows for a larger proportion of molecules to have sufficient energy greater than the activation energy and induces more frequent successful collisions, resulting in a quicker rate. The exact activation energy will be determined by the experiment and the hypothesis can then simultaneously be confirmed or rejected.

4 Variables

4.1 Rate Law Experiment

Independent Variable: Concentration of reactants ($\frac{mol}{dm^3}$)

It has empirically been confirmed that the rate of a reaction is solely dependent on the rate constant (which is constant at a fixed temperature) and the concentrations of the reactants (and catalysts in the case of specific mechanisms). Thus, to find the rate law for this specific iodination of acetone reaction, a baseline was provided through the initial configuration and then each set of trials manipulated the concentration of a certain reactant (HCl, $Acetone$, or I_2) for the purpose of comparison. This allowed for the determination of the order of each reactant in the rate law through simple proportions. To make this process easy, the baseline configuration used 5 mL of each reactant/catalyst, and the manipulated trials doubled these volumes for each reactant to 10 mL. The total volume was held constant through the addition of water, so this doubling in volume of the reactant meant a direct doubling of that reactant's concentration, and thus the effect on the rate could easily be identified. As the rate law is crucial to the determination of the activation energy in the second part of this investigation, the choice of independent variable is justified.

Dependent Variable: Time taken for solution to lose its color (s)

By using the time for the completion of the reaction (once the iodine color has disappeared) and the initial concentration of iodine, the rate of the reaction can be determined for each chosen configuration of reactants. These rates can then be compared to the baseline provided by the initial configuration for the experiment to identify how the changing of concentrations of each reactant impacts the overall rate. By doing this for each reactant, the rate law for the total reaction can be empirically confirmed/found, allowing us to determine the rate constant in the activation energy experiment. Additionally, as time is also the dependent variable for the activation energy experiment, the trials for the first configuration can then be utilized further. Thus, the time taken for the reaction to lose its color is relevant to the overall investigation.

Unique Control Variable: Temperature (K)

Because the temperature impacts the rate constant (k), it was crucial to maintain a constant temperature for the determination of the rate formula. As the premise of finding the rate law relies on the resultant rate proportions of changing concentrations, a change in k would

introduce a confounding variable and render the results inconclusive. A room temperature of 294.8 K was taken as this constant temperature for all trials conducted as part of the rate law experiment and it was ensured that all reactants were at this fixed temperature prior to the initialization of the reaction through constant temperature checks via thermometer.

4.2 Activation Energy Experiment

Independent Variable: Temperature (K)

As mentioned in the background, the rate constant varies depending on temperature, and the calculation of multiple rate constants at known temperatures can be used to find the activation energy through the Arrhenius equation. The linear relationship between the inverse of the temperature and the natural logarithm of the rate constant allows for simple graphing and gradient calculation which can then be used to find the activation energy, indicating the relevance to the investigation. Because specific temperatures are not required and instead a variety of temperatures are crucial, temperatures in the ranges of $283 - 285$, $293 - 298$ (room temperature in the above experiment), $303 - 308$, and $313 - 318$ K were used to conduct trials and were manipulated through the use of heated or ice-filled water baths. I refrained from adding higher temperatures for fear of partial evaporation of the reactants, as this would impact concentrations, and lead to erroneous calculations with regards to the rate of reaction and rate constant.

Dependent Variable: Time taken for solution to lose its color (s)

This is an easily observable characteristic of the reaction which allows for the determination of the completion of the reaction and thus leads to a straightforward process for quantifying the rate of the reaction (as discussed previously). All times were calculated in seconds (s) for consistency and to maintain the appropriate rates for k for a second order reaction ($\frac{dm^3}{mol \cdot s}$). Because the rate constant can then be used to determine the activation energy of the reaction, this choice of a dependent variable is entirely relevant to the investigation and allows for the answering of the initial research question.

Unique Control Variable: Volumes of reactants (cm^3)

All trials utilized for this experiment had identical volumes of each reactant and identical total volumes leading to the same concentration of each reactant for all trials. These volumes were chosen to make iodine the limiting reactant and provide large excess of HCl and *Acetone*, so as to ensure that all iodine was used up after the reactions completion and prevent large fluctuations in the concentration of the other reactants which could also impact the rate. This was necessary as the experiment was designed to investigate the change of the rate due to temperature alone, and thus the control variable was necessary.

4.3 Universal Controls

Pressure

Large fluctuations in pressure can impact the rate of evaporation of the reactants involved in the experiment which would affect the concentrations and induce erroneous rate calculations. Pressure changes have also been found to impact the kinetics of molecules with regards to aqueous reactants which could have introducing confounding causes for the change in the rate constant with varying temperatures. To control for pressure, all experiments were carried out in a controlled environment and a uniform laboratory at a fixed altitude.

Purity/Molarity of Reactants

As the molarity of the reactants was used to determine their respective concentrations, it was crucial that these molarities were accurately measured and maintained for the duration of all trials. To control, all reactants were properly diluted prior to the beginning of the experiment and sufficient quantities were produced so as to allow for consistent utilization for all trials. The diluted solutions were stored safely to prevent any external contamination or evaporation.

Physical Manipulation of Reaction

Swirling of the reaction mixture is crucial for ensuring that the reactants evenly mix throughout and helps faciliate more frequent collisisons between particles (thereby increasing the rate of the reaction). To ensure that discrepancies in swirling did not account for the various results, all trials were given 30 seconds of swiriling and then allowed to sit to completion. This attempted to control the confounding variable and let the reaction occur naturally after all reactants were adequately mixed.

5 Methodology

5.1 Apparatus

Chemicals	Glassware	Miscellaneous
• 120 cm^3 1M HCl • 120 cm^3 4M *Acetone* • 120 cm^3 .005M I_2 solution • 165 cm^3 Distilled H_2O	• 100 mL Earlenmeyer Flask • 1000 mL Beaker • 10 mL Graduated Cylinder • Test Tube(s)	• Ice • Thermometer • Ring Stand • Poly Water Bath • 2x Beaker Clamp • Water Source

Table 2: Materials

5.2 Experimental Procedure

5.2.1 Rate Law Determination

1. Prepare a water bath at room temperature in a 1000 mL beaker.

2. Clamp a 100 mL earlenmeyer flask and a separate test tube into the water bath.

3. Measure out the appropriate amounts of HCl, $Acetone$, and H_2O (as listed in Table 3) into the 10 mL graduated cylinder and add these substances to the clamped earlenmeyer flask.

4. Measure out the appropriate amount of I_2 (as listed in Table 3) into the 10 mL graduated cylinder and pour into the clamped test tube.

5. Ensure that the the reactants in the test tube and flask are fully immersed in the water bath and allow 5 minutes for temperature equilibrium to be reached.

6. Record the water bath temperature after this period is complete.

7. Remove the test tube containing the iodine solution and immediately add its contents to the flask containing HCl, $Acetone$, and H_2O, starting a timer after the addition.

8. Swirl the reaction mixture by gently swirling the ring and then allow the solution to sit.

9. When the iodine color (brownish-red) has completely disappeared, stop the timer and record the total reaction time (as the reaction is complete).

10. Clean the glassware thoroughly and dry (it is not necessary to clean the test tube as it will always contain iodine solution with a constant concentration).

11. Repeat steps 2-8 two more times for configuration #1 in Table 3.

12. Repeat steps 2-9 for all remaining configurations in Table 3.

13. Thoroughly clean all glassware and dispose of any leftover products/substances safely.

5.2.2 Activation Energy Determination

1. Prepare a water bath at temperature within the range listed in Table 4 either in the Pro Water Bath (for high temperatures) or in a 1000 mL beaker with ice (for the low temperature).

2. Clamp a 100 mL earlenmeyer flask and a separate test tube into the water bath.

3. Measure out the appropriate amounts of HCl, $Acetone$, and H_2O (as listed in Table 4) into the 10 mL graduated cylinder and add these substances to the clamped earlenmeyer flask.

4. Measure out the appropriate amount of I_2 (as listed in Table 4) into the 10 mL graduated cylinder and pour into the clamped test tube.

5. Ensure that the the reactants in the test tube and flask are fully immersed in the water bath and allow 5 minutes for temperature equilibrium to be reached.

6. Record the water bath temperature after this period is complete.

7. Remove the test tube containing the iodine solution and immediately add its contents to the flask containing HCl, $Acetone$, and H_2O, starting a timer after the addition.

8. Swirl the reaction mixture by gently swirling the ring and then allow the solution to sit.

9. When the iodine color (brownish-red) has completely disappeared, stop the timer and record the total reaction time (as the reaction is complete).

10. Clean the glassware thoroughly and dry (it is not necessary to clean the test tube as it will always contain iodine solution with a constant concentration).

11. Repeat steps 2-8 two more times for temperature #1 in Table 4.

12. Repeat steps 2-9 for all remaining temperature ranges in Table 4.

13. Thoroughly clean all glassware and dispose of any leftover products/substances safely.

Table 3: Rate Law Experiment

| Volumes (mL) | | | | |
HCl	$Acetone$	I_2	H_2O	Total
5	5	5	10	25
5	5	10	5	25
5	10	5	5	25
10	5	5	5	25

Table 4: Activation Energy Experiment

| Temperature (°C) | Volumes (mL) | | | | |
	HCl	$Acetone$	I_2	H_2O	Total
$10-15$	5	5	5	10	25
$30-35$	5	5	10	5	25
$40-45$	5	10	5	5	25

Table 5: Experimental Configurations

5.3 Risk Assessment

(a) **Experimental Safety**

   (i) Acetone is highly flammable and can cause moderate irritation on repeated exposure to skin. Hydrochloric acid is corrosive and can lead to severe damage to both the eyes and skin in the case of direct contact. Strong iodine solution is partially corrosive and can cause blistering or necrosis of the skin on direct contact. To counteract these potential concerns, an apron and goggles were worn for the duration of the experiment. All materials were kept at a moderate distance from the body and spills were immediately cleaned.

   (ii) Glassware is relatively fragile and any potential breakage can be harmful to those in the lab, both through glass shards and substance spillage. To remedy, extreme caution is used at all times in the lab, especially when handling glassware. In the case that glass did break, the teacher would immediately assist in disposing of any pieces prior to the resumption of the experiment.

   (iii) Hot water or glassware can cause sudden reactions and burns of the skin. As water was heated and glassware (with various chemicals) were placed in the water baths, tongs were used at all times to handle warm glass. The water was never directly touched and the water bath was kept closed when not in use.

(b) **Environmental Concerns**

All materials were properly stored and disposed of based on lab best practices and teacher advice to prevent any potential environmental contamination. No limited resources were used nor were any harmful byproducts produced.

(c) **Ethical Concerns**

Materials were measured out in small quantities to minimize the potential wastage of any chemicals. No live organisms were employed, so limited ethical concerns were present.
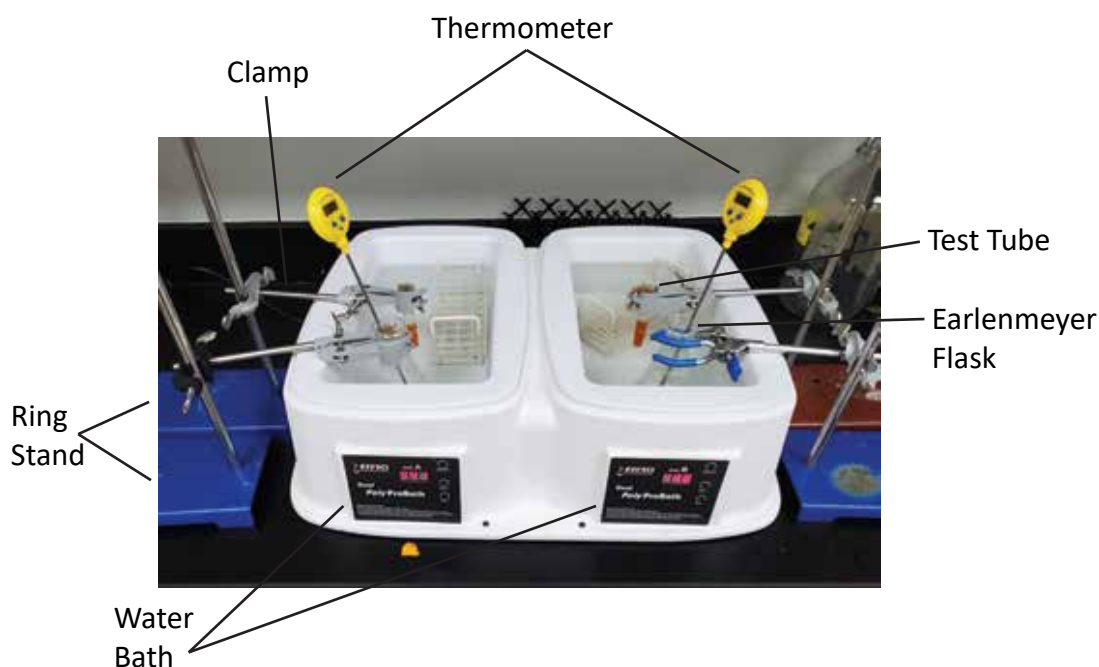

Figure 2: Labelled image depicting the visual setup of the experiment being conducted for two different temperatures.

6 Results

6.1 Raw Data

Setup	Volumes (±.05mL)					Time (±.05s)		
	HCl	Acetone	I_2	H_2O	Total	#1	#2	#3
#1	5	5	5	10	25	342	354	331
#2	5	5	10	5	25	621	682	634
#3	5	10	5	5	25	161	183	164
#4	10	5	5	5	25	152	165	153

Table 6: Rate Law Experiment (all trials performed at 294.8 K)

Temperature (±.05K)	Time (±.05s)		
	#1	#2	#3
287.1	734	725	756
294.8	342	354	331
306.8	134	142	115
317.5	37	42	46

Table 7: Activation Energy Experiment (all trials carried out with volume setup #1 in Table 6)

Table 8: Raw Data

6.2 Qualitative Data

- The iodine solution had a distinctive brownish-red color, similar to that of rust on iron metal.

- A noticeable loss in color could be observed within the first 30 seconds of the reaction, even for trials that took over 10 minutes to come to full completion.

- No observable immediate signs of a vigorous reaction could be observed (outside of the color loss) immediately after the addition of bromine to the remainder of the reactants.

- The acetone had a relatively pungent odor similar to that of nail polish remover.

- The iodine solution seemed to be particularly viscous, especially as opposed to the remainder of the reactants.

6.3 Calculations

6.3.1 Rate Law Experiment

Rationale	Sample Calculation
Firstly, for each volumetric configuration, we must calculate the average time for the three unique trials performed, using the simple arithmetic mean formula: $$\bar{t} = \frac{1}{n} \sum_{i=1}^{n} t_i$$ where n represents the number of trials (3).	Example for Setup #1: $$\bar{t} = \frac{(342 \pm .05) + (354 \pm .05) + (331 \pm .05)}{3}$$ $$= \frac{(1027 \pm .15)}{3}$$ $$= (342.0 \pm 0.5)\,\mathrm{s}$$
Then, we must calculate the concentrations of each reactant based on the total volume and their specific volume using the mole-constant dilution formula: $$M_1 V_1 = M_2 V_2 \text{ or } M_2 = \frac{M_1 V_1}{V_2}$$ where M_1 is the initial molarity of the reactant, V_1 is the initial volume of the reactant, and V_2 is the total volume ($25mL$). We can additionally calculate potential discrepancies for the largest percent uncertainty and then propagate this error for the remaining results.	Example for Setup #1: $$[I_2] = \frac{0.005\,\mathrm{mol\,dm^{-3}} \times (5.0 \pm 0.5)\,\mathrm{mL}}{(25.0 \pm 0.2)\,\mathrm{mL}} = \frac{(.025 + .00025)}{(25 \pm .2)}$$ $$= \frac{(.025 + 1\%)}{(25 \pm .8\%)} = .001 \pm 1.8\%$$ $$= (0.001\,00 \pm 0.000\,18)\,\mathrm{mol\,dm^{-3}}$$ Through an identical process, the final concentrations of $[HCl]$ and $[Acetone]$ can also be determined. Because $[I_2]$ has the smallest quantity, it has the largest percent error of 1.8%, which is carried over for all final concentrations.
Using the two above steps, we can then determine the rate for each individual configuration using the previously discussed equation: $$rate = \frac{[I_2]}{\bar{t}}$$ The same propagation approach is utilized, but the uncertainties are largely irrelevant for the purpose of rate calculation which is predicated on approximation already.	Example for Setup #1: $$rate = \frac{(0.001\,00 \pm 0.000\,18)\,\mathrm{mol\,dm^{-3}}}{(342.0 \pm 0.5)\,\mathrm{s}}$$ $$= \frac{.001 \pm 1.8\%}{342 \pm .01\%} = 2.92 \times 10^{-6} \pm 1.81\%$$ $$= 2.92 \times 10^{-6}\,\mathrm{mol\,dm^{-3}\,s^{-1}}$$
After determining the rates for all trials, we can compare the rates for configurations $2-4$ to the baseline provided by 1 to determine the rate law. As in each of the last 3 trials, the concentration of one reactant was changed while maintaining the total volume, the concentration of that reactant is doubled for that specific trial. Thus, we can calculate our order m by the formula: $$m = \log_2\left(\frac{rate_i}{rate_1}\right)$$ where $rate_i$ is the rate for the given setup and $rate_1$ is the rate for configuration #1. The result must be approximated, as m must be a whole integer $>= 0$.	Example for Setup #4 (compared to the baseline of Setup #1): $$m = \log_2\left(\frac{6.37 \times 10^{-6}}{2.92 \times 10^{-6}}\right) = \log_2 2.18 = 1.12 \approx \mathbf{1}$$ Thus, the concentration of HCl is first order with respect to the overall reaction based on this determination. The remaining orders are also calculated in the same manner.

Table 9: Rate Law Calculations

Using this process for all trials, the order of HCl, $Acetone$, and I_2 are found to be 1, 1, and 0 respectively. This confirms the theorized rate law of $rate = k[HCl][CH_3COCH_3]$ and is further supported by the published literature on this subject. Through this knowledge, we can now determine the activation energy.

6.3.2 Activation Energy Experiment

Rationale	Sample Calculation
The first three steps–calculating the average (mean) time for each temperature, determining diluted concentrations, and finding the rate using those two values–are identical for this section as well, and are thus not included to limit redundancy.	
After these three steps, we must determine the value of the rate constant k, which we can do by utilizing the rate law. As $rate = k[HCl][Acetone]$, we can rearrange to get: $$k = \frac{rate}{[HCl][Acetone]}$$ Furthermore, the concentrations of HCl and $Acetone$ are consistent for all temperatures as identical volumes were chosen to ease calculations and limit confounding variables.	Example for 294.8 K: $$k = \frac{(2.92 \times 10^{-6} \pm 1.9\%)}{(.2 \pm 1.8\%) \times (.8 \pm 1.8\%)}$$ $$= 1.83 \times 10^{-5} \pm 5.5\%$$ $$= (1.83 \pm 0.10) \times 10^{-5}\,\mathrm{dm^3\,mol^{-1}\,s^{-1}}$$
After determining k at each temperature, we will create an Arrhenius graph to determine the activation energy. Taking the natural logarithm of the Arrhenius equation results in: $$\ln k = \left(\frac{-E_a}{R}\right)\frac{1}{T} + \ln A$$ Thus, a linear relationship exists between $\ln k$ and $\frac{1}{T}$, so these values must be determined (along with their uncertainties) for the purpose of graphing.	Example for 294.8 K: $$\frac{1}{T} = \frac{1}{(294.80 \pm 0.05)\,\mathrm{K}} = \frac{1}{(294.8 \pm .017\%)}$$ $$= .00339 \pm .017\% = (3.3900 \pm 0.0058) \times 10^{-3}\,\mathrm{K^{-1}}$$ $$\ln k = \ln\left((1.83 \pm 0.10) \times 10^{-5}\right) = \ln\left(1.83 \times 10^{-5}\right) + \frac{.10}{1.83}$$ $$= -10.91 \pm .05$$

Table 10: Activation Energy Calculations

This process is again carried out for all four temperatures, providing the necessary values for graphing purposes.

6.4 Processed Data

Setup	Avg. Time (± 0.5 s)	Rate (mol dm^{-3} s^{-1})
#1	342	$(2.920 \pm 0.053) \times 10^{-6}$
#2	646	$(3.100 \pm 0.056) \times 10^{-6}$
#3	169	$(5.920 \pm 0.107) \times 10^{-6}$
#4	157	$(6.370 \pm 0.115) \times 10^{-6}$

Table 11: Rate Law Experiment (all trials performed at 294.8 K)

Temperature	k (dm^3 mol^{-1} s^{-1})	$\frac{1}{T}$ ($\pm.17\%$ K^{-1})	$\ln k$ ($\pm.055$)
287.1	$(8.47 \pm 0.47) \times 10^{-6}$	#1	-11.68
294.8	$(1.83 \pm 0.10) \times 10^{-5}$	#2	-10.91
306.8	$(4.81 \pm 0.26) \times 10^{-5}$	#3	-9.94
317.5	$(1.49 \pm 0.08) \times 10^{-4}$	#4	-8.81

Table 12: Activation Energy Experiment (all trials carried out with volume setup #1 in Table 6)

Table 13: Processed Data

As determined already, the rates in the Rate Law Experiment were sufficient for calculating/deriving the rate law of the overall reaction. However, to calculate the activation energy, the values of $\ln k$ and $\frac{1}{T}$ were plotted and a linear regression was utilized to calculate a line of best fit (to allow for the determination of the gradient between the 2 variables). The table, including data points and uncertainties, are depicted in Fig. 3. The initial best fit line (for the entire dataset) had a very high correlation coefficient (R^2) of around 99%, indicating a good fit, however this value was partially misleading. By significantly overshooting the data point at 294.8 K, the regression was able to overcome its slightly lower predictions at the other three temperatures. In fact, this line of best fit was completely outside of the range of uncertainty for the data point at 287.1 K. By removing the outlier at 294.8 K, a new trend line was produced with a R^2 of 99.5% and a much better ability to account for the actual data points. However, both lines seemed to generate similar gradients, thus minimizing the overall impact of the improved regression.

To determine the uncertainty of the coefficients in the regression, the statistical premise of confidence intervals was employed. Using the $\frac{1}{T}$ as the x variable and the $\ln k$ as the y, the following procedure was used for the regression of $y = \beta x + \alpha$.

$$S_x = \sum x_i = 13.28$$

$$S_y = \sum y_i = -41.34$$

$$S_{xx} = \sum x_i^2 = 44.15$$

$$S_{yy} = \sum y_i^2 = 431.87$$

$$S_{xy} = \sum x_i y_i = -137.79$$

$$\hat{\beta} = \frac{nS_{xy} - S_x S_y}{nS_{xx} - S_x^2} = -8.54$$

$$\hat{\alpha} = \frac{1}{n}S_y - \hat{\beta}\frac{1}{n}S_x = 18.02$$

$$s_\epsilon^2 = \frac{1}{n(n-2)}\left[nS_{yy} - S_y^2 - \hat{\beta}^2(nS_{xx} - S_x^2)\right] = .01005$$

$$s_{\hat{\beta}}^2 = \frac{ns_\epsilon^2}{nS_{xx} - S_x^2} = .160$$

$$\beta \in [\hat{\beta} \mp t_2^* s_{\hat{\beta}}] = \mathbf{-8.54 \pm 1.72}$$

Thus, the gradient (β) is -8.54 ± 1.72, which can be equated to the slope of the relationship in the Arrhenius equation ($\frac{-E_a}{R}$) to determine the activation energy (using the universal gas constant R). The factor of 10^3 is also reincorporated, as the inverse temperature values had been normalized by factoring out 10^{-3} for improved graphing:

$$E_a = (-8.54 \pm 1.72)\,\text{K}^{-1} \times -8.3145\,\text{J mol}^{-1}\,\text{K}^{-1} \times 10^3 = (-8.54 \pm 20.1\%) \times -8.3145 \times 10^3 = 71005.83 \pm 20.1\% = (71.01 \pm 14.27)\,\text{kJ mol}^{-1}$$

Using the literature value of $86.60\,\text{kJ mol}^{-1}$, the percent error can also be determined:

$$Total\ Percent\ Error = \left| \frac{Literature\ Value - Experimental\ Value}{Literature\ Value} \right| \times 100 = \left| \frac{86.60 - 71.01}{86.60} \right| \times 100 = 18.0\%$$
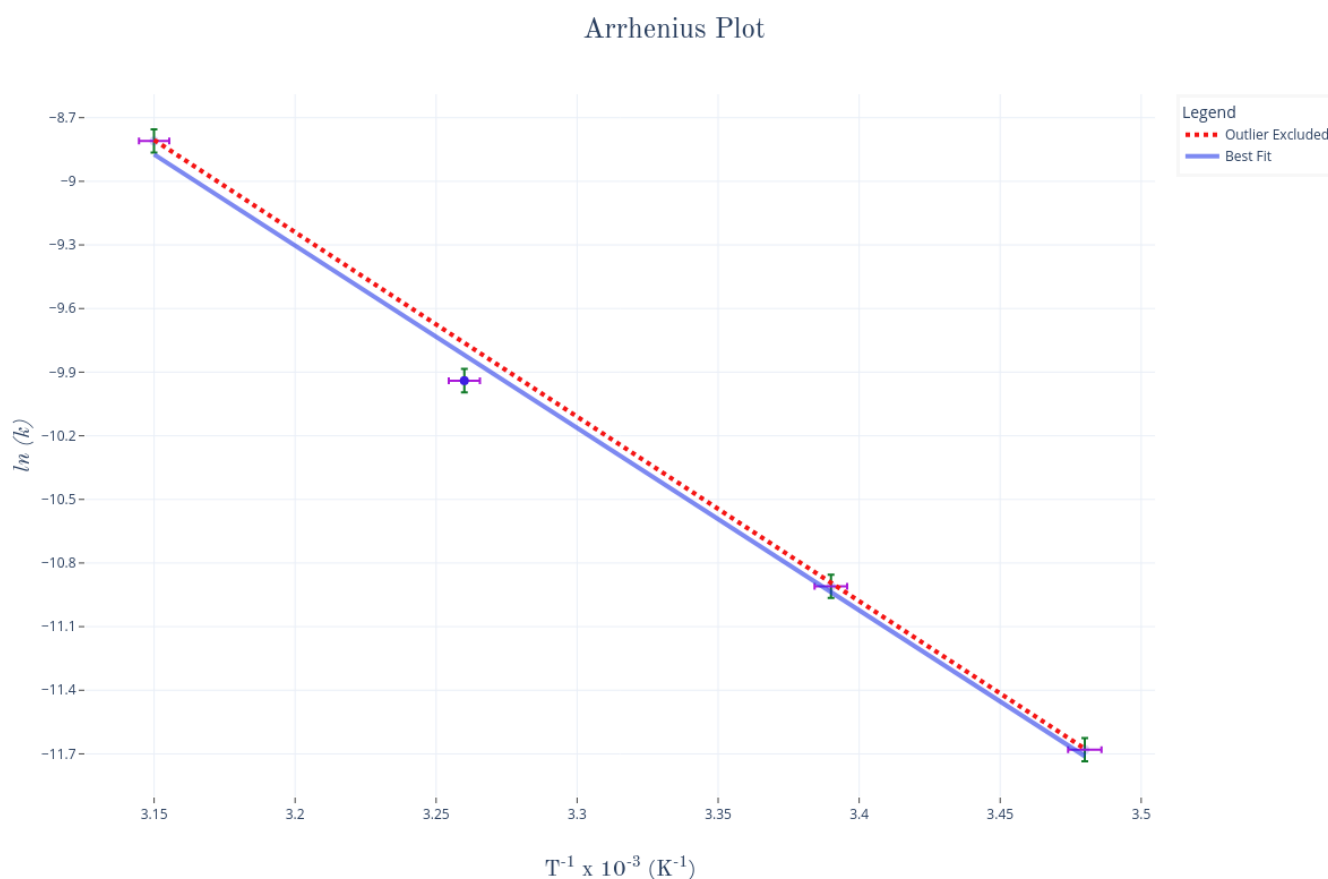

Figure 3: Arrhenius plot of $\ln k$ versus $\frac{1}{T}$ (scaled by 10^3), including a best fit line for the general data and an improved trendline with the outlier removed.