SASTA OLIPHANT SCIENCE AWARDS

Prize Winner

Scientific Inquiry

Year 11-12

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Research Question:
How does the proportion of water and ethanol in the solvent, and thus polarity of the solvent, influence the rate of the S_N1 reaction between a hydroxide nucleophile ($OH^-_{(aq)}$) and 2-chloro-2-methylpropane ($(CH_3)_3CCl_{(l)}$), as measured by the time taken (s) to turn phenolphthalein indicator colourless due to OH^-displacing the Cl^-?

Introduction:
150.00mm^3 of pure 2-chloro-2-methylpropane will be added to solvents containing varying ratios of ethanol to distilled water, along with 100.00mm^3 of 0.100 mol dm^{-3} sodium hydroxide and 3 drops of phenolphthalein indicator. Using different ratios of ethanol and distilled water allows solvents of differing polarity to be created, as water has a greater relative polarity index of 10.2 than ethanol of 4.3 (Fisher Scientific, n.d.). Thus, solvent mixtures containing greater proportions of water will be more polar. Initially, the solution will be basic due to OH^- ions from sodium hydroxide, thus the solution will appear pink following addition of phenolphthalein indicator. However, as the S_N1 reaction progresses, OH^- ions in solution displace the Cl^- in the halogenoalkane, decreasing the concentration of OH^-, and thus basicity of solution. This causes the solution to gradually turn colourless as pH decreases. This colour change from pink to colourless will be the predetermined end point of this reaction. Consequently, the rate of this reaction (s^{-1}) in solvents of different polarity can be determined from the time taken (s) for this end point to be reached when reacted in solvents mixtures containing differing ratios of ethanol to water. This experiment will be repeated 5 times with 10 different ratios of ethanol to water (cm^3): 0.00:10.00, 1.00:9.00, 2.00:8.00, 3.00:7.00, 4.00:6.00, 6.00:4.00, 7.00:3.00, 8.00:2.00, 9.00:1.00 and 10.00:0.00.

Background Information:
Polarity is a measure of the distribution of electrical charge between the two atoms in a covalent bond (Brown & Ford, 2014), and is determined by the difference in electronegativity of the atoms. Electronegativity is the ability of an atom to attract a shared pair of electrons towards itself in a covalent bond (Key & Ball, n.d.), generally increasing across a period and up a group of the periodic table (Gordon, 2023).

A bond is defined as polar when the difference in electronegativity of two covalently bonded atoms is between 0.4 and 1.8 (Wittman, 2022), as this means the more electronegative atom will exert a greater pulling power on the shared pair of electrons, pulling the electrons closer towards itself and thus becoming partially negatively charged (δ^-). Consequently, the less electronegative atom will become partially positively charged (δ^+), as it has a lower electron density and weaker share of the electrons, which are now further away. This dipole moment makes the bond unsymmetrical with respect to electron distribution, thus is said to be polar (Brown & Ford, 2014).

A polar molecule differs from a polar bond in that it occurs when there is an unsymmetrical distribution of charge not just between a pair of covalently bonded atoms, but around the whole molecule (Dillon, n.d.). This could be due to the molecule containing different bonds of unequal polarity, the central atom containing lone pairs of non-bonding electrons, and/or its bonds being asymmetrically arranged around the central atom. As the dipoles will not cancel out, this causes a net dipole moment, thus the molecule is said to be polar, making one side of the molecule δ^- while the other side becomes δ^+.

The relative polarity of a molecule can be determined by its polarity index, with molecules with a higher polarity index being more polar. For example, as mentioned above, ethanol has a relative polarity index of 4.3, whereas water has a polarity index of 10.2 (Fisher Scientific, n.d.). The high polarity of water can be explained by the large electronegativity difference between the two oxygen and hydrogen bonds in the molecule of 1.2 (IB Chemistry data booklet, 2016). This causes the oxygen atom to attract the shared pair of electrons closer towards itself, as oxygen has a greater effective nuclear charge than hydrogen. In addition, the two lone pairs of non-bonding electrons surrounding the central oxygen atom repel each other as well as the bonding electrons, thus giving the molecule an asymmetrical bent structure, which prevents the two polar bonds from cancelling each other out. The oxygen-hydrogen bond in ethanol also has an

electronegativity difference of 1.2 and an asymmetrical structure, however it only has one of these polar hydrogen bonds, and is counteracted slightly by the non-polar hydrocarbon tail, thus ethanol is less polar than water (ECHEMI, 2024).

A nucleophilic substitution reaction occurs when a nucleophile, which is an electron rich molecule that acts as a Lewis base (UCLA, n.d.), attacks the carbon-halogen bond in a halogenoalkane, resulting in the replacement of the halogen with the nucleophile. This is due to the polar carbon-halogen bond which makes the carbon atom electron deficient. This carbon-halogen bond then undergoes heterolytic fission to release the halogen leaving group as a halide ion (Brown & Ford, 2014).

There are two different types of nucleophilic substitution reactions: one is unimolecular and the other is bimolecular. The unimolecular S_N1 reaction between the 2-chloro-2-methylpropane halogenoalkane and a hydroxide nucleophile will be explored in this investigation (see below):

$$(CH_3)_3CCl_{(l)} + OH^-_{(aq)} \rightarrow (CH_3)_3COH_{(l)} + Cl^-_{(aq)}$$

An S_N1 reaction occurs via two steps in the presence of a tertiary halogenoalkane (a halogenoalkane with three alkyl groups attached to the central carbon containing the carbon-halogen bond), and a given nucleophile (Brown & Ford, 2014). It may also occur with some secondary halogenoalkanes. The first step of an S_N1 reaction involves the ionisation of the halogenoalkane by the heterolytic fission of the carbon-halogen bond to form a temporary carbocation intermediate and a halide anion. The carbocation is stabilised by the methyl groups, as indicated by the arrows. This is the slow, rate determining step of the reaction (see Figure 1)

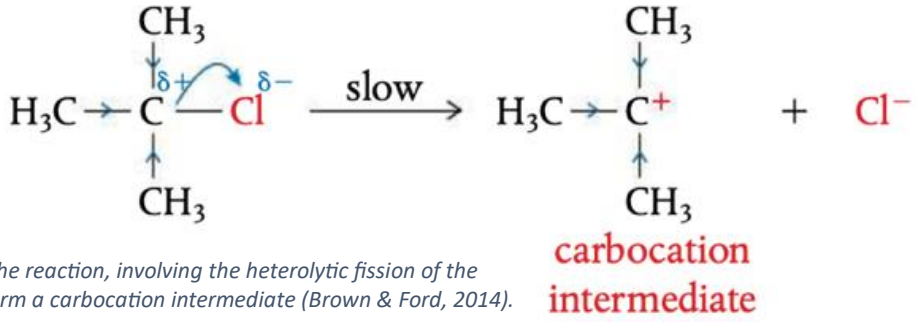


Figure 1: The first step of the reaction, involving the heterolytic fission of the carbon-chloride bond to form a carbocation intermediate (Brown & Ford, 2014).

The second step of the reaction involves the attacking of the planar carbocation intermediate by the nucleophile, leading to the formation of a new bond (see Figure 2). This is the fast step of the reaction.
Thus, because the slow rate determining step of this reaction is only impacted by the concentration of the halogenoalkane, this is a unimolecular reaction (Brown & Ford, 2014).

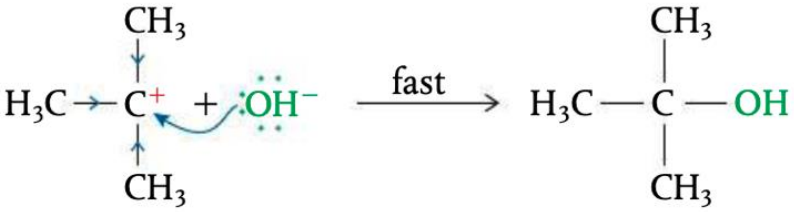


Figure 2: The second step of the SN1 reaction, involving the attacking of the carbocation intermediate by an OH- nucleophile (Brown & Ford, 2014)

A number of factors may affect the rate of this reaction, and more specifically the first step. One such factor is the type of solvent used, with polar protic solvents generally being favoured in an S_N1 reaction (Liu, 2021). This is because these solvents have a net-dipole moment, as well as the ability to form hydrogen bonds. This allows them to better solvate both the carbocation and halide anion formed (via ion-dipole interactions), which lowers the energy of the transition state that leads to the carbocation (see Figure 3). This solvation increases the stability of the carbocation intermediate and halide anion, thus encouraging their formation and increasing the rate of reaction of the rate determining step.

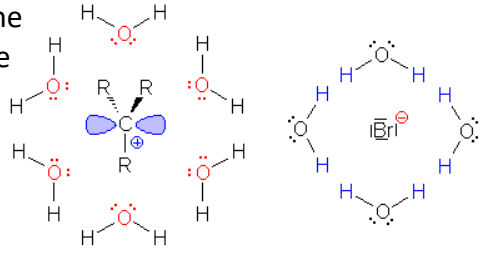


Figure 3: The stabilising impacts of the solvent via ion-dipole interactions between the solvent and both the carbocation and leaving group and the hydrogen atoms (ChemistryScore, 2024)

In this investigation, both water and ethanol will be used as solvents. Both are polar protic, so will encourage the S_N1

reaction, however as aforementioned, differ in polarity, so should have differing effects on the rate of the S_N1 reaction. One method of measuring the rate of this reaction is by measuring the change in pH of the solution over time using an acid-base indicator, as OH^-, the strongest nucleophile involved in this reaction, is a Lewis base that is removed from solution as the reaction progresses, and Cl^- is produced from the substitution reaction to form NaCl, thus lowering the pH of the solution. Phenolphthalein indicator will be used due to its suitable pH range for colour change, with the time taken (s) for the solution to change colour from pink to colourless being the predetermined end point used to mark the completion of the reaction.

Initial Trials

Initial trials were conducted to determine the most suitable volume and concentration of $NaOH_{(aq)}$ to add, as well as the most suitable volume of 2-chloro-2-methylpropane to use in each trial (due to limited halogenoalkane available), for the reaction to reach the predetermined endpoint within a reasonable time frame. This is because with a constant volume of halogenoalkane, increasing the volume and concentration of sodium hydroxide added will increase the time taken to reach the endpoint, as the starting point will be more basic, thus more nucleophilic substitutions need to take place. $150\mu L$ of 2-chloro-2-methylpropane was used in each trial due to limited quantities of the halogenoalkane being available, and volumes and concentrations of sodium hydroxide were then adjusted accordingly from there. All initial trials were conducted in a solvent made up of 100% ethanol, as the rate of reaction was expected to be slowest in the least polar solvent. This ensured the slowest reaction reached completion after around 5 minutes, allowing data to be collected within the allocated time frame. See Appendix A for full data collected during initial trials.

Aim

To determine the impacts of the solvent polarity on the rate of the S_N1 reaction of 2-chloro-2-methylpropane.

Hypothesis

If the ratio of ethanol decreases, then the rate of the S_N1 reaction of 2-chloro-2-methylpropane will increase, as S_N1 reactions are favoured by a polar protic solvent, and ethanol has a lower polarity index than water, so the reaction will take place at a faster rate in higher ratios of water.

Variables

Independent Variable

The ratio of ethanol to distilled water in the solvent mixture. Each solvent mixture was the same total volume of 10.00cm^3, however contained differing ratios of ethanol to water (in cm^3) of 0.00:10.00, 1.00:9.00, 2.00:8.00, 3.00:7.00, 4.00:6.00, 6.00:4.00, 7.00:3.00, 8.00:2.00, 9.00:1.00 and 10.00:0.00.

Dependent Variable

The time taken (s) for the SN1 reaction to reach a predetermined endpoint when using solvents of a different polarity. The selected endpoint was a colour change of the solution from pink to colourless, which indicates the solution has reached a pH below 8.3 (Petrusevski, 2007), as the phenolphthalein indicator used changes colour at this specific pH. This colour change is due to the substitution of hydroxide ions in place of the chlorine ions in the halogenoalkane (2-chloro-2-methylpropane), which decreases the basicity of the solution, thus lowering pH.

Controlled Variables

Volume (mm^3) and concentration (mol dm^{-3}) of $NaOH_{(aq)}$ added. 100.00mm^3 of 0.100 mol dm^{-3} $NaOH_{(aq)}$ was measured using a micropipette and added to each solvent mixture for each reaction. This ensures the number of moles of $NaOH_{(aq)}$ required to be removed via nucleophilic substitution to change the colour of the solution from pink to colourless remains constant throughout the experiment, thus maintaining a consistent endpoint, as the starting point will also be constant.

The same halogenoalkane, 2-chloro-2-methylpropane ($(CH_3)_3CCl_{(l)}$) was used each time. This is because the structure, leaving group, and length of carbon chain of the halogenoalkane all may affect the rate of the

S_N1 reaction (Brown & Ford, 2014). A different structure, i.e., primary, secondary, or tertiary halogenoalkane, and a carbon chain of a differing length, both impact the amount of steric hindrance around the central carbon atom, which may impact both the rate of reaction and the reaction mechanism. Additionally, using halogenoalkanes with a different halogen leaving group would also likely cause a differing rate of reaction, as decreasing electronegativity of the leaving group decreases the strength of the carbon-halogen bond, thus increasing the rate at which substitution by the nucleophile may occur. Furthermore, the halogenoalkane used was of 99% purity and extracted from the same bottle from the same source (Sigma-Aldrich) each time to minimise random errors.

Volume (mm^3) of halogenoalkane used. 150.00mm^3 of 2-chloro-2-methylpropane ($(CH_3)_3CCl_{(l)}$) of 99% purity was used each time. This was controlled, as a differing halogenoalkane volume would impact the number and frequency of successful collisions, thus impacting the rate of reaction (s^{-1}).

The rate of stirring of the conical flask was kept constant at 950rpm using a magnetic stirrer throughout the experiment. This was because differing rates of stirring may influence the level of interaction between the particles and hence the frequency of collisions and rate of reaction (s^{-1}).

Uncontrolled Variables

The temperature (°C) that the S_N1 reactions occurred at likely differed slightly over the several days of data collection, as room temperature was difficult to control. This may have impacted both the energy and frequency of collisions, and thus rate of reaction (s^{-1}).

Risk Assessment

Safety considerations

Table 1: Table of safety concerns

What	Hazard	Minimising Risk
Use of organic compounds	Organic compounds i.e. ethanol and halogenoalkanes are highly flammable, and 2-chloro-2-methylpropane may cause eye, skin and/or respiratory tract irritation if ingested.	Safety equipment worn when handling organic compounds, with first aid equipment nearby if needed. Furthermore, the experiment was performed in a fume hood in a well-ventilated lab to minimise fire hazards.
Use of glassware	Risk of laceration if equipment breaks	All apparatus was handled carefully and stored securely when not in use. Safety equipment such as gloves, glasses and a lab coat were worn.
Production of hydrochloric acid	Is corrosive to eyes and skin and toxic to inhale and ingest.	Hands were washed immediately after each trial, safety equipment was worn at all times, and first aid equipment was nearby if needed.
Use of sodium hydroxide	May cause skin irritation/corrosion, is toxic if inhaled	Hands were washed immediately after each trial, safety equipment was worn at all times, and first aid equipment was nearby if needed.

Ethical considerations

There were no ethical considerations throughout the experiment

Environmental considerations

All organic compounds were stored in a fume hood to minimise exposure to toxic vapours. After each trial, organic compounds were disposed of appropriately in a brown halogenated organic waste container to avoid harm to the environment and contamination of waterways.

Apparatus/Materials

2 x 10.00cm^3 graduated pipettes ($\pm 0.05 cm^3$)
1 x Conical flask (100.00cm^3)
1 x 1000.00mm^3 micropipette ($\pm$0.16%)
1 x 1000.00mm^3 micropipette Tips (x2)
500.00cm^3 100% Ethanol
500.00cm^3 Distilled water

20.00cm^3 Phenolphthalein indicator
5.00 cm^3 0.100 mol dm^{-3} $NaOH_{(aq)}$
1 x Magnetic Stirrer
1 x Magnetic Stirring Bar
1 x stopwatch ($\pm 0.01s$)
1 x Magnetic Stirring Bar retriever
1 x sheet of white paper
7.50cm^3 2-chloro-2-methylpropane$_{(l)}$

Methodology:

1. A 100.00cm^3 conical flask was placed in a fume hood on a sheet of white paper on a magnetic stirrer.
2. 5.00cm^3 of 100% ethanol and 5.00cm^3 of distilled water was measured out using separate graduated pipettes after being rinsed with the respective liquid that it was to carry, before being added to the conical flask to make a 5.00:5.00 ratio of ethanol to water. The magnetic stirrer was set to 950rpm.
3. 100.00mm^3 of 0.100 mol dm^{-3} $NaOH_{(aq)}$was added to the flask using a 1000.00mm^3 micropipette before 3 drops of phenolphthalein indicator were added to the solution.
4. A separate micropipette tip was then used to add 150.00mm^3 of pure 2-chloro-2-methylpropane to the conical flask, and a stopwatch was immediately started.
5. The stopwatch was stopped as soon as the solution turned completely colourless.
6. Steps 1-5 were repeated 2 more times for this same ratio of ethanol to water.
7. Steps 1-6 were repeated for 0.00:10.00, 1.00:9.00, 2.00:8.00, 3.00:7.00, 4.00:6.00, 6.00:4.00, 7.00:3.00, 8.00:2.00, 9.00:1.00 and 10.00:0.00 ratios of 100% ethanol to distilled water respectively, ensuring to keep the total volume of solution constant at 10.00cm^3.

Results

Qualitative Data

Observation	Evidence
During initial trials, it was observed that colour of solutions containing higher ratios of ethanol after adding phenolphthalein appeared a comparatively paler pink than solutions with lower percentage concentrations of ethanol	Figure 4. This was accounted for by adding more phenolphthalein (3 drops instead of 1), making solutions containing 0% ethanol appear a comparatively more vibrant pink colour (Figure 5). This pink colour of the solution after adding phenolphthalein indicates the solution is basic, as phenolphthalein turns pink at pH > 8.3. The solution becoming colourless over time suggests that the pH is decreasing as the reaction progresses (Figure 6).
As the reaction progressed, temperature of solution increased	This was likely due to heat generated by the magnetic stirrer, and occurred over each of the days data was collected.

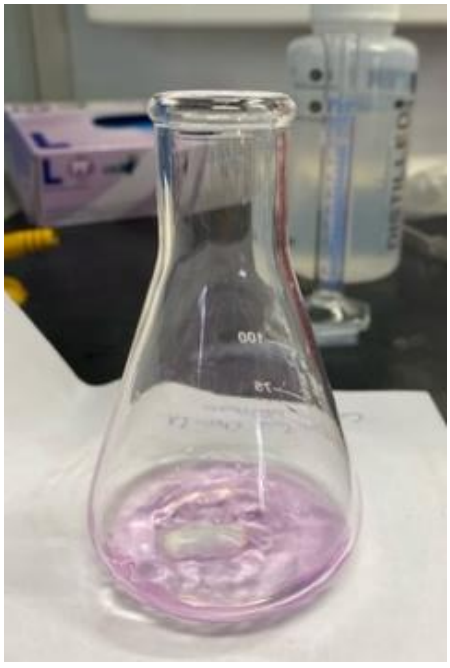


Figure 3: Colour of 100% ethanol solution before adding 2-chloro-2-methylpropane

Figure 4: Colour of 0% ethanol solution before adding 2-chloro-2-methylpropane

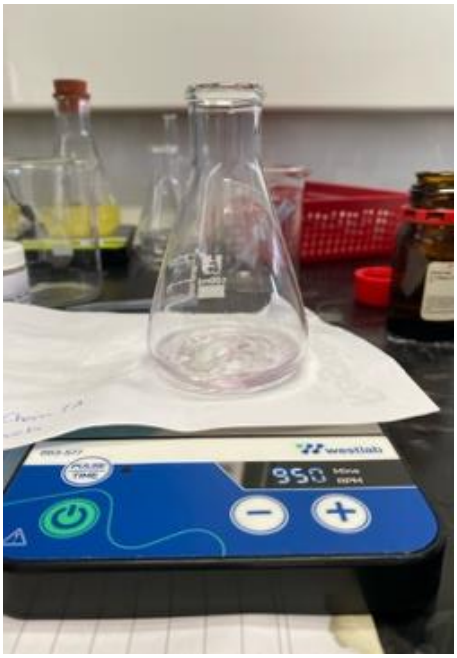


Figure 5: Colour of 50% ethanol solution in the process of changing colour

Quantitative Data

Raw Data

Table 2: Time taken (s) for the predetermined endpoint of the S_N1 reaction to be reached in solvents containing differing percentages of ethanol.

		Time Taken (s) for colour change ($\pm 0.01s$)		
		Trial 1	Trial 2	Trial 3
Volume of ethanol in 10cm^3 of solvent (cm^3) ($\pm 0.1cm^3$)	0.00	24.48	26.23	22.59
	1.00	32.58	30.03	28.18
	2.00	52.33	51.60	53.62
	3.00	65.48	63.78	70.11
	4.00	86.13	81.28	85.32
	5.00	87.32	82.63	81.23
	6.00	147.54	133.98	142.48
	7.00	253.39	248.57	231.78
	8.00	262.21	273.63	260.45
	9.00	273.63	237.72	236.21
	10.00	272.90	318.37	295.13

Calculations

Example calculation for average time taken (s) for trials conducted in 0.00cm^3 of ethanol:

$$\overline{x} = \frac{\sum fx}{n}$$

$$mean = \frac{24.48 + 26.23 + 22.59}{3}$$

$$= 24.43$$

Example calculation for standard deviation of time taken (s) for trials conducted in 0.00cm^3 of ethanol:

$$\sigma = \frac{\sqrt{\sum (x - \overline{x})^2}}{n}$$

$$= \frac{\sqrt{(24.48 - 24.43)^2 + (26.23 - 24.43)^2 + (22.59 - 24.43)^2}}{3}$$

$$= 1.82$$

Example calculation for mean rate of reaction (s^{-1}) of trials conducted in 0.00cm^3 of ethanol:

$$rate = \frac{1}{time\ taken}$$

$$= \frac{1}{24.43}$$

$$= 0.0409s^{-1}$$

Example calculation for relative rate of reaction for trials conducted in 0.00cm^3 of ethanol:

$$relative\ rate = \frac{measured\ rate}{base\ rate}$$

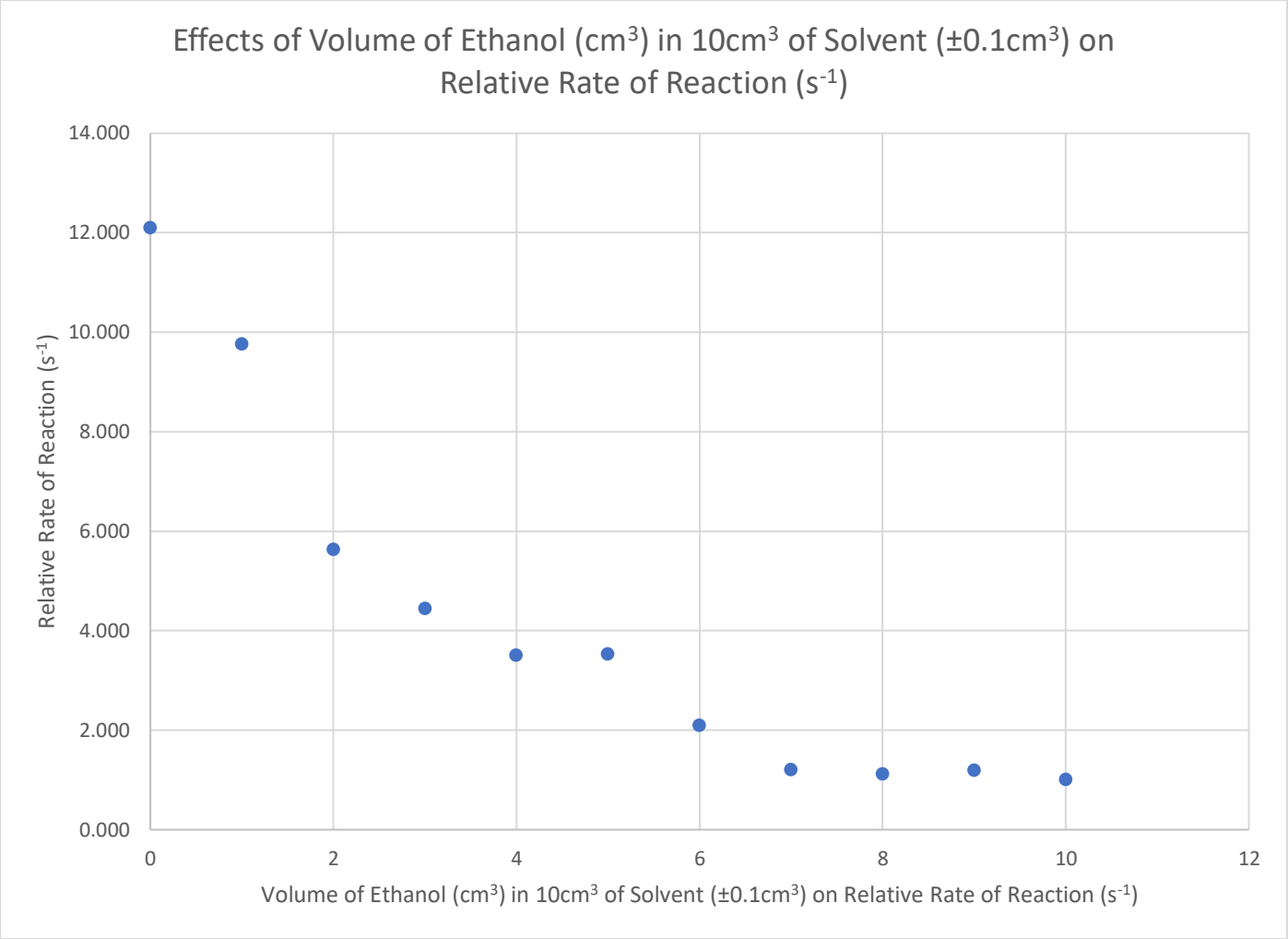
$$= \frac{0.0409}{0.0034}$$

$$= 12.093$$

Processed Data

Table 3: Processed data table displaying rate of reaction, standard deviation, and relative rate of reaction in each solvent mixture.

Volume of ethanol in 10cm^3 of solvent (cm^3) ($\pm 0.1cm^3$)	Average Time Taken (s) ($\pm 0.01s$)	Standard Deviation of Average Time Taken (s) ($\pm 0.01s$)	Rate of Reaction (s^{-1})	Relative Rate of Reaction (3 d.p.)
0.00	24.43	1.82	0.0409	12.093
1.00	30.26	2.21	0.0330	9.763
2.00	52.52	1.02	0.0190	5.626
3.00	66.44	3.28	0.0151	4.447
4.00	84.24	2.60	0.0119	3.507
5.00	83.73	3.19	0.0119	3.529
6.00	141.33	6.85	0.0071	2.091
7.00	244.58	11.34	0.0041	1.208
8.00	265.43	7.16	0.0038	1.113
9.00	249.19	21.18	0.0040	1.186
10.00	295.47	22.74	0.0034	1.000



Graph 1: The relationship between volume of ethanol (cm^3) in 10cm^3 of solvent (±0.1cm^3) and the relative rate of the S_N1 reaction (s^{-1})

Propagation of Uncertainties

The percentage uncertainty of the volume of water and ethanol used in the solvent, the time taken for the reaction to reach the end point, and the uncertainty of the volume of $NaOH_{(aq)}$ and $(CH_3)_3CCl_{(l)}$ added to the solution were determined by the following formula: $\frac{uncertainty\ of\ apparatus}{measured\ value\ using\ the\ apparatus} \times 100$

Example calculations for total uncertainty (%) for a solvent containing 1.00cm^3 ethanol and 9.00cm^3 water:

Uncertainty (%) of 10 cm^3 Graduated Pipette for water ($\pm 0.05cm^3$): $\frac{0.05}{1} \times 100 = 5.00$

Uncertainty (%) of 10 cm^3 Graduated Pipette for ethanol ($\pm 0.05cm^3$): $\frac{0.05}{9} \times 100 = 0.56$

Uncertainty (%) of Stopwatch ($\pm 0.01s$): $\frac{0.01}{30.45} \times 100 = 0.03$

Uncertainty (%) of Micropipette for $NaOH_{(aq)}$ ($\pm 0.16\%$): 0.16

Uncertainty (%) of Micropipette for 2-chloro-2-methylpropane$_{(l)}$ ($\pm 0.16\%$): 0.16

Total Uncertainty (%): $5.00 + 0.56 + 0.03 + 0.16 + 0.16 = 5.91$

This was repeated for each of the other percentage ratios of ethanol to water, and the total uncertainty (%) for each solvent ratio was averaged to determine the average uncertainty (%) of the investigation:

Average Uncertainty (%): $0.85 + 5.91 + 3.48 + 2.73 + 2.42 + 2.34 + 2.41 + 2.71 + 3.45 + 5.88 + 0.82 = 3.00$

Table 4: Table of Uncertainties for the Experiment

Volume of ethanol in 10cm³ of solvent (cm³) ($\pm 0.1 cm^3$)	Uncertainty of 10 cm³ Graduated Pipette (%) for water ($\pm 0.05 cm^3$)	Uncertainty of 10 cm³ Graduated Pipette (%) for ethanol ($\pm 0.05 cm^3$)	Uncertainty (%) of Stopwatch ($\pm 0.01 s$)	*Uncertainty (%) of Micropipette for $NaOH_{aq}$ ($\pm 0.16\%$)	*Uncertainty (%) of Micropipette for $(CH_3)_3CCl_{(l)}$ ($\pm 0.16\%$)	Total Uncertainty (%)	Average Uncertainty (%)
0.00	0.00	0.50	0.03	0.16	0.16	0.85	3.00
1.00	5.00	0.56	0.03	0.16	0.16	5.91	
2.00	2.50	0.63	0.03	0.16	0.16	3.48	
3.00	1.67	0.71	0.03	0.16	0.16	2.73	
4.00	1.25	0.83	0.02	0.16	0.16	2.42	
5.00	1.00	1.00	0.02	0.16	0.16	2.34	
6.00	0.83	1.25	0.01	0.16	0.16	2.41	
7.00	0.71	1.67	0.01	0.16	0.16	2.71	
8.00	0.63	2.50	0.00	0.16	0.16	3.45	
9.00	0.56	5.00	0.00	0.16	0.16	5.88	
10.00	0.50	0.00	0.00	0.16	0.16	0.82	

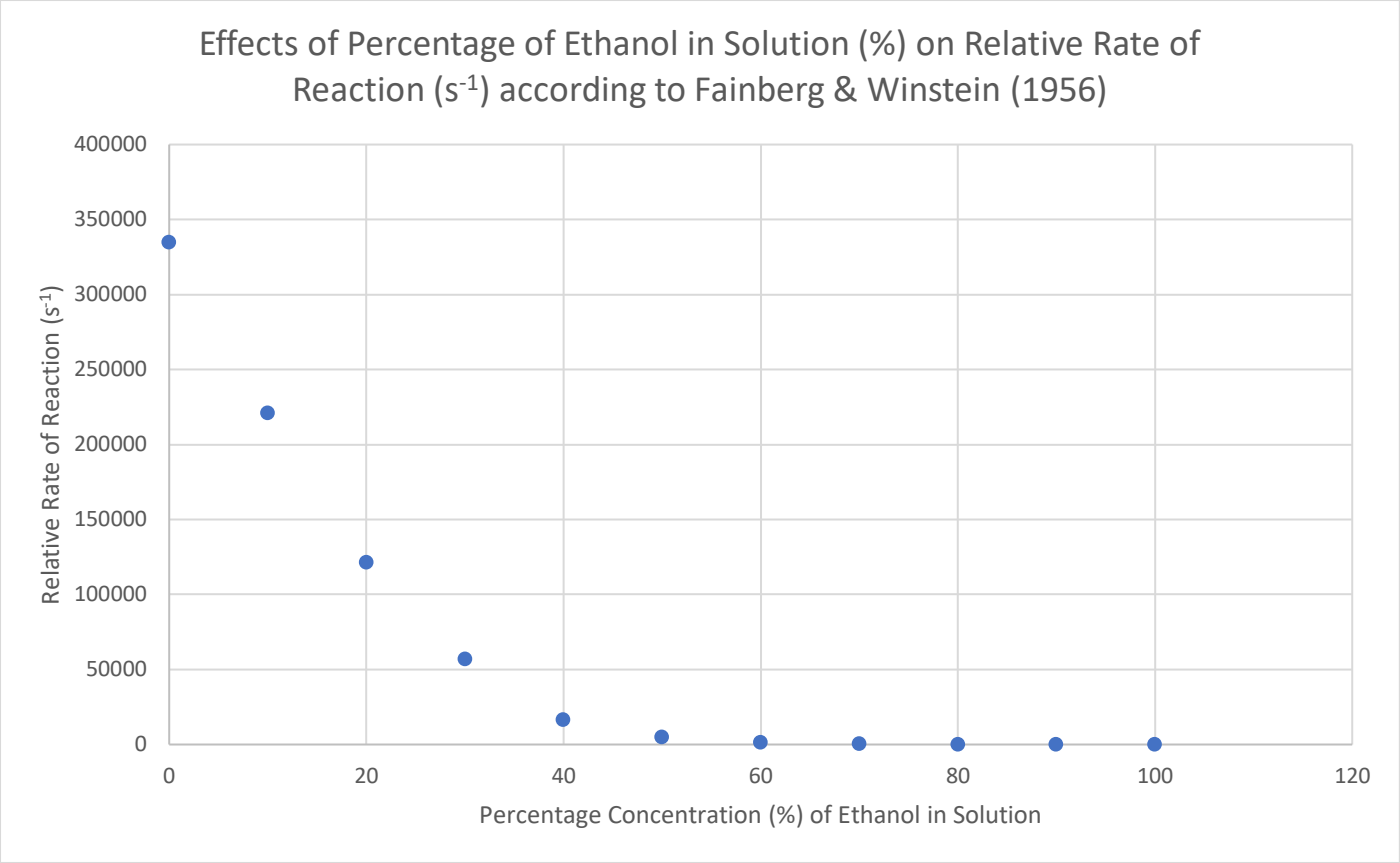
*The uncertainty of the micropipette was determined according to the manufacturer's claim

Comparison to Literature

Specific literature values could not be obtained for the exact method used, however values could be found for a similar experiment (see Table 5). This compares the measured relative rate of reaction data obtained for the S_N1 solvolysis of 2-chloro-2-methylpropane compared to a literature value obtained by Fainberg & Winstein (1956) when in different solvent mixtures made up of various percentage ratios of ethanol to water. However, a direct comparison cannot be made between the datasets, as Fainberg & Winstein's experiment carried out the SN1 reaction to completion, whereas this experiment, due to time restraints, only found the time taken (s) for the reaction to reach a predetermined endpoint. These values would differ, because as the reaction progresses and reactants are used up, the frequency of successful collisions would decrease, thus rate of reaction would also be slower the longer the reaction goes on. Therefore, the literature value is a measure of average rate of reaction, as it goes to completion, whereas this experiment was more of a measurement of instantaneous rate of reaction, as it only measures a small portion of the overall reaction. However, a similar trend can nevertheless be observed between obtained values and literature (see Graph 2), indicating if the SN1 reaction was carried out to completion, it could display a relative rate comparable to the literature value. However, exact percentage error of the overall experiment could not be ascertained.

Table 5: Comparison of obtained relative rate of reaction data for each solvent mixture to a literature value from a similar experiment.

Volume of ethanol in 10cm³ of solvent (cm³) ($\pm 0.1 cm^3$)	Relative Rate of Reaction	
	Measured Value ($\pm 3.00\%$) (4 s.f.)	Literature Value (4 s.f.)
0.00	12.093	334900
1.00	9.763	221100
2.00	5.626	121300
3.00	4.447	56740
4.00	3.507	16400
5.00	3.529	4698
6.00	2.091	1433
7.00	1.208	424.4
8.00	1.113	107.7
9.00	1.186	19.30
10.00	1.000	1.000



Graph 2: Relationship between the percentage concentration of ethanol (%) in the solvent mixture and the relative rate of the S_N1 reaction according to Fainberg & Winstein (1956) when carried out to completion

Graph 2 depicts the expected relationship between percentage of ethanol in the solvent mixture and the relative rate of the SN1 reaction when carried out to completion based on literature values obtained by Fainberg & Winstein (1956). Despite the age of Fainberg & Winstein's study, the publication location of this study from The University of California at Los Angeles and the use of this data in several studies indicates its reliability.

Analysis

According to Graph 1, there is a strong negative correlation between the percentage concentration of ethanol in the solvent and the rate of the S_N1 reaction with 2-chloro-2-methylpropane. This implies that increasing the polarity of the solvent increases the rate of reaction, as solvent mixtures containing lower percentage ratios of ethanol generally cause a faster rate of reaction. Rate of reaction appears to plateau when conducted in solvent mixtures composed of greater than 70% ethanol.

A linear trend line was not fitted to the data, as this would suggest at a certain polarity, the rate of reaction would equal $0s^{-1}$. However, as evidenced by the relative rate of reaction data obtained for 70%, 80%, 90% and 100% ethanol solvent mixtures of 1.208, 1.113, 1.186 and 1.000 respectively, and corroborated by the graph of ethanol percentage compared to time taken (s) (see Appendix B) as well as the expected literature value if carried out to completion, the relationship between solvent polarity and rate of reaction is likely non-linear. Therefore, a Pearson's correlation coefficient could not be applied.

Most data points followed the expected trend of increasing in rate of reaction as the solvent polarity increases. Despite the relatively low percentage uncertainty of 3.00%, a specific literature value for the relative rate of reaction was not obtained, so it could not be determined whether there was greater prevalence of systematic or random errors in the experiment.

Evaluation

Strengths

Table 6: Table of strengths of the methodology

What	Why
Time length over which each reaction took to reach completion.	Long enough to minimise random errors of the stopwatch, while being fast enough to fit within time restraints of data collection. Additionally, data collection was relatively simple and easy, allowing for 5 repeats to be conducted for each solvent mixture, decreasing impacts of random errors, thus improving precision.
High precision equipment used in the experiment, such as the micropipette and graduated pipettes.	Meant there was relatively low random error, as seen in the average percentage uncertainty of equipment of 3.00%. Furthermore, a separate graduated pipette was used for measuring volume of ethanol and water added, as well as a separate micropipette tip for sodium hydroxide and 2-chloro-2-methylpropane. This minimises the potential of cross contamination of reactants and unnecessary mixing of solvents, increasing accuracy of results.
Placing a white sheet of paper under the conical flask whilst the reaction was taking place (see Figures 4, 5 and 6).	Allowed the colour change to be better distinguished as it created more contrast. This improved consistency of the predetermined end point. Furthermore, paper was used instead of a white tile as initial trials revealed a ceramic tile may disrupt the magnetic stirrer's effectiveness.

Weaknesses

Table 7: Table of weaknesses of the methodology

Error	Evidence	Impact on Results	Improvement
Heat was produced by the magnetic stirrer whilst the reaction was taking place.	See qualitative data.	This meant that later repetitions conducted on the same day likely had a faster rate of reaction than expected as the surface of the magnetic stirrer heated up. This is because at higher temperatures, reactants have an increased average kinetic energy, thus there is a greater frequency of successful collisions. This systematic error likely had a relatively significant impact on the accuracy of the results, as although the quantity of heat produced by the magnetic stirrer was not measured, it was quite substantial, making rates of reaction faster than expected.	Use several different magnetic stirrers in rotation to allow them to cool down to room temperature after use.
Subjective endpoint	See Figures 4, 5 and 6. the colour change of solution from pink to colourless was unclear and potentially subject to mis-interpretation.	This could make the measured values for rate of reaction either faster or slower than expected, and by different amounts each time. However, this likely only had a minor impact on the precision of the results, as although the measured rate of reaction would vary from being faster or slower than the expected rate of reaction, it would only vary slightly each trial. Furthermore, the presence of repeats helps to minimise the impacts of this random error.	Conduct this experiment using a spectrophotometer to detect a quantitative colour change rather than a qualitative colour change.

Collection of excess halogenoalkane and sodium hydroxide on the micropipette tip	When extracting both sodium hydroxide and 2-chloro-2-methylpropane using the micropipette, a small amount of liquid would often collect on the outside of the micropipette tip	This increased volume of either sodium hydroxide or 2-chloro-2-methylpropane added, but by different amounts each time. This systematic error had a relatively significant impact on the accuracy of the results, as only small volumes of sodium hydroxide and 2-chloro-2-methylpropane respectively were added, so even small variations in volume added could have significant impacts. If excess sodium hydroxide was added this would decrease the rate of reaction, as it would take longer to reach the endpoint. In comparison, if excess 2-chloro-2-methylpropane was added, this would increase rate of reaction, as there would be a greater concentration of reactants, thus increasing the frequency of collisions.	Wipe excess liquid that has collected on the micropipette tip after extracting each solution prior to adding to the conical flask using a paper towel. However, this could potentially lead to loss of solution from inside the tip.

Limitations

Table 8: Table of limitations of the methodology

What	Why
No literature value for this specific methodology with (same endpoint) was found.	This limited the strength of conclusions made, as the results could not be directly compared to other studies – trends could only be observed.
The halogenoalkane used (2-chloro-2-methylpropane) was immiscible in water, as it could not form hydrogen bonds with the water molecules to replace the hydrogen bonds between the water molecules themselves.	This could have potentially interfered with the S_N1 reaction taking place, particularly at higher concentrations of water, as this may have reduced the extent of interaction between 2-chloro-2-methylpropane and the solvent. For example, the S_N1 reaction may have only taken place where the two layers of the halogenoalkane and the solvent met. This systematic error means measured rates of reaction for solvent mixtures with higher concentrations of water would be slower than expected, however significance of this error on accuracy of results is unknown.

Conclusion

From the results obtained, it was concluded that the order of rate of reaction in each solvent mixture was: 10.00% > 0.00% > 20.00% > 30.00% > 40.00% > 50.00% > 60.00% > 70.00% > 80.00% and 90.00% > 100.00%

This loosely follows the order of decreasing solvent polarity and suggests the SN1 reaction between 2-chloro-2-methylpropane and the nucleophile in solution occurred at the fastest rate when in a solvent made up of 10% ethanol and 90% water, and the slowest rate when in pure ethanol. This mostly supported the hypothesis, which stated that as the percentage concentration of ethanol in the solvent decreases, and thus the solvent becomes less polar, then the rate of the reaction would increase, as S_N1 reactions are favoured by a polar protic solvent. There was also a somewhat similar trend between the obtained relative rate of reaction data for each percentage ethanol concentration to the literature value, although it is to be noted that the two experiments differ slightly in methodological approach, therefore cannot be directly compared.

However, unexpectedly, the reaction occurred at a faster rate in 10% ethanol than 0% ethanol, despite being slightly less polar. A possible explanation for this could be due to the immiscibility of 2-chloro-2-methylpropane in pure 100% water, limiting the level of interaction between the halogenoalkane and both the solvent and the nucleophile, and thus stability of the carbocation intermediate. However, the addition of ethanol to the solvent, despite decreasing the polarity of the solvent, allows for more interaction between the solvent and the halogenoalkane, which consequently leads to a faster overall rate of reaction.

Extension

A potential extension could be to test the impacts of a solvent mixture with a polarity outside of the range tested. This is because this experiment only investigated a solvent polarity between that of 100% water and 100% ethanol (polarity index of 10.2 and 4.3). The experimentally determined rate of reaction appears to plateau in percentage concentrations of ethanol greater than 80%, however this cannot be sufficiently concluded from the results due to the high standard deviation of these values. If propan-2-ol, which has a relative polarity index of 3.9 (Fisher Scientific), is used in the solvent mixture instead of ethanol, for example, then it could be ascertained whether the rate of this S_N1 reaction actually plateaus after a certain solvent polarity, and if the obtained relationship between ethanol percentage and rate of reaction translates to other similar polar protic solvents.

Word Count: 2198

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Appendices

Appendix A

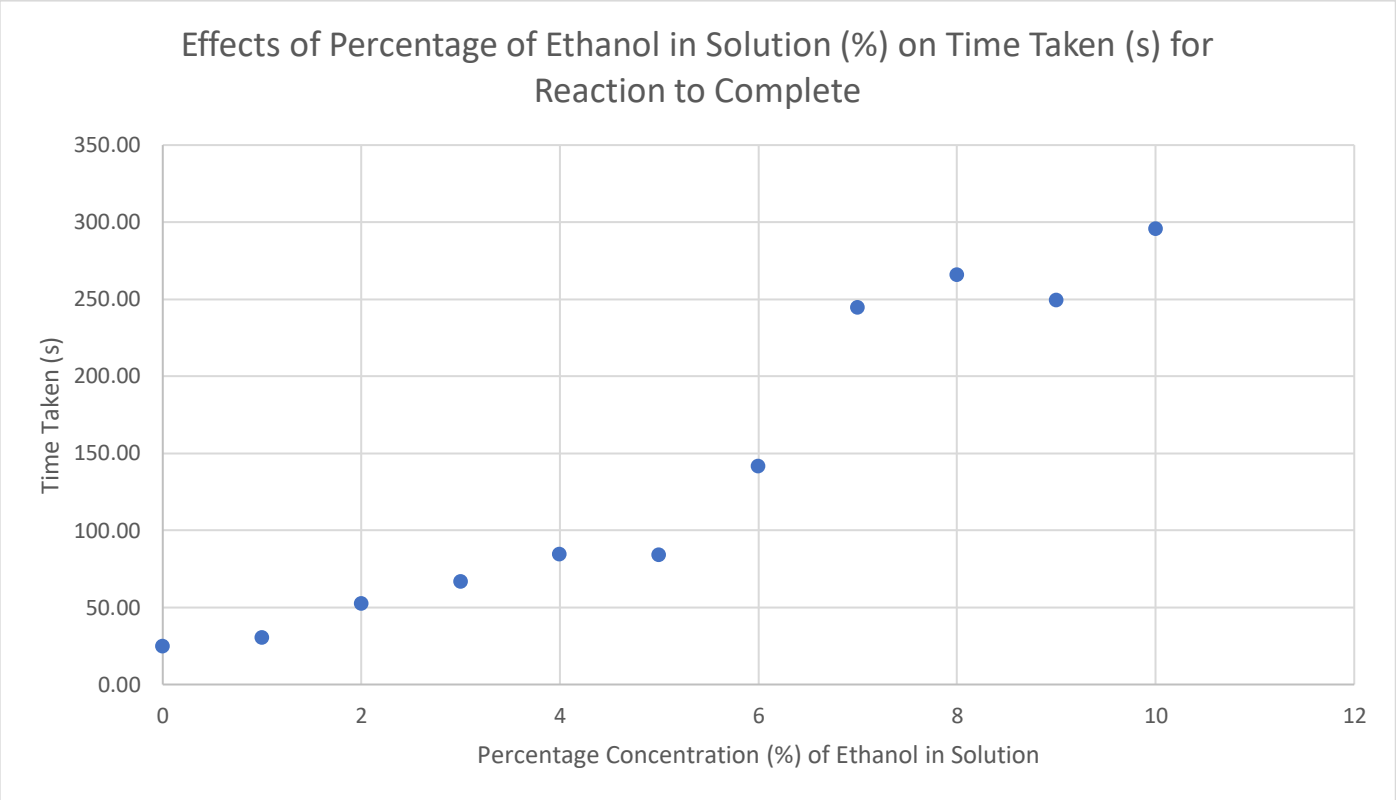
Data from initial trials illustrating time taken for reaction to reach completion when using different volumes and concentrations of $NaOH_{(aq)}$ when in 100% ethanol with 100μL of pure 2-chloro-2-methylpropane added

Table 9: Table of data from initial trials used to determine suitable volumes (cm^3) and concentrations (mol dm^{-3}) of sodium hydroxide to add

Halogenoalkane Volume (mm^3) ($\pm 0.16\%$)	$NaOH_{(aq)}$ concentration (mol dm^{-3})	$NaOH_{(aq)}$ Volume (mm^3) ($\pm 0.16\%$)	Time Taken (s) ($\pm 0.01s$)
150.00	1.000	1000.00	N/A**
150.00	1.000	750.00	N/A**
150.00	1.000	500.00	N/A**
150.00	1.000	200.00	1200.09
150.00	1.000	150.00	1167.68
150.00	1.000	100.00	1142.47
150.00	0.100	350.00	808.35
150.00	0.100	280.00	613.28
150.00	0.100	270.00	589.01
150.00	0.100	250.00	536.98
150.00	0.100	225.00	502.47
150.00	0.100	200.00	475.31
150.00	0.100	150.00	392.48
150.00	0.100	100.00	301.72
150.00	0.100	100.00	272.65
150.00	0.100	100.00	289.21

**Results marked N/A displayed no evidence of a colour change after 30 minutes

Appendix B



Graph 2: The relationship between percentage concentration of ethanol (%) in the solvent mixture and the time taken (s) for the colour change

Chemistry IA Logbook

23/4/24

We have just started our organic chemistry topic, which I am really enjoying.

29/4/24

I have decided to write chemistry IA (internal assessment) on how solvent mixtures of differing polarities may affect the rate of an S_N1 reaction, as I have been intrigued by how minor differences in the reactants involved can cause a completely different reaction mechanism to take place.

30/4/24

Risk assessment form has been submitted to the laboratory technicians at my school. Following some prior research, I have decided to use phenolphthalein indicator and sodium hydroxide to mark the endpoint of the reaction, as it will provide a consistent end point that is relatively cheap and easy to run trials of. Upon speaking to the lab techs, I have decided to use 2-chloro-2-methylpropane as the halogenoalkane involved in the reaction, due to its availability at school, and also it's relatively simple molecular structure. Water and ethanol will be used in the solvent mixtures, also due to their convenience and availability.

2/5/24

Today I began running initial trials of my experiment. Very frustrating day today has been, as no reactions have occurred yet, and I am not sure why, or if this reaction is even possible with the equipment being used.

3/5/24

Tried using a different halogenoalkane, 2-iodo-2-methylpropane, which theoretically should have a faster rate of reaction due to having a larger leaving group, with no luck. I may need to scrap this idea if I can't get the reaction to work.

4/5/24

Upon consultation with my teacher it appears the concentrations and volumes of sodium hydroxide that I am using are way too large for the reaction to occur in a suitable time frame. I was previously using 1 mol dm^{-3} sodium hydroxide solution. Using the same volume of 0.1 mol dm^{-3} solution today with identical volumes yielded an almost instantaneous colour change when the halogenoalkane is added. Next week I will work on finetuning my concentrations of halogenoalkane and sodium hydroxide added to ensure I do not run out of 2-chloro-2-methylpropane, whilst limiting presence of random errors.

8/5/24

I am beginning to finetune my methodology to increase the precision of my results. I used graduated pipettes instead of measuring cylinders to measure volume of water and ethanol, as it has a much lower uncertainty. Similarly, micropippetes will be used to measure volume of sodium hydroxide and 2-chloro-2-methylpropane added, as such small volumes are being handled. Currently, my theoretically slowest reaction (in 100% ethanol solvent) is taking about 20 minutes. I need to change my concentrations of reactants to get that down to

about 5-8 minutes tomorrow. Definitely should start data collection soon though, otherwise I may run out of time.

9/5/24
Finally have gotten my reaction to consistently reach the endpoint after approximately 5 minutes at the slowest. Today I began official data collection. Results are looking reasonably consistent so far, and appear to have a strong negative linear correlation.

12/5/24
Data collection has been completed. Very repetitive process, but also reasonably efficient thanks to extensive initial trials. Trends in rate of reaction actually appears more exponential rather than linear, which is not what I was expecting. Although, upon reflection, if the trend was linear, this would seem to suggest that in a solvent mixture of a certain polarity, the rate of reaction would be 0, ie it would not react, however I don't think this is the case, therefore I think the results actually seem reasonable.

16/5/24
After days of extensive research I have finally found literature values for somewhat of a similar experiment to the one I conducted. I was not expecting this to be so difficult. Very few extensive experiments appear to have been done on the exact chemicals I am using, and the paper I found is from 1956, and a bit difficult to understand, but it is the closest match to my experiment that I have found. However, they seem to have a relative rate of reaction significantly faster than mine.

17/5/24
I think the differences in the literature value and my experimentally obtained results are mainly due to their reactions being carried out to completion, and mine only reaching a predetermined endpoint. This would make a lot more sense. I am starting to realise that I could have yielded much more valid results had I used a digital pH meter and monitored the change in pH over time, rather than just observing a colour change. However, with the limited volumes of sodium hydroxide and 2-chloro-2-methylpropane I used, this would have been difficult I think.

24/5/24
Evaluation of methodology has been written. I had quite a lot of strengths to talk about, which I think can be attributed to the extensive planning and initial trials I undertook prior to officially collecting data. I have been struggling with presenting my uncertainties.

27/5/24
Finally have cut down all of my words. Lots of my introduction had to go unfortunately due to not being entirely relevant.

OSA RISK ASSESSMENT FORM

for all entries in (✓) ☐ Models & Inventions and ☑ Scientific Inquiry

This must be included with your report, log book or entry. One form per entry.

STUDENT(S) NAME: Caleb Tang ID: 0526-009

SCHOOL: Prince Alfred College

Activity: Give a brief outline of what you are planning to do.

Investigate how conducting an SN1 reaction in solvent mixtures of differing polarity affects the rate of the reaction. This will be measured using phenolphthalein indicator.

Are there possible risks? Consider the following:

- Chemical risks: Are you using chemicals? If so, check with your teacher that any chemicals to be used are on the approved list for schools. Check the safety requirements for their use, such as eye protection and eyewash facilities, availability of running water, use of gloves, a well-ventilated area or fume cupboard.
- Thermal risks: Are you heating things? Could you be burnt?
- Biological risks: Are you working with micro-organisms such as mould and bacteria?
- Sharps risks: Are you cutting things, and is there a risk of injury from sharp objects?
- Electrical risks: Are you using mains (240 volt) electricity? How will you make sure that this is safe? Could you use a battery instead?
- Radiation risks: Does your entry use potentially harmful radiation such as UV or lasers?
- Other hazards.

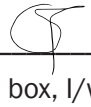
Also, if you are using other people as subjects in an investigation you must get them to sign a note consenting to be part of your experiment.

Risks	How I will control/manage the risk
Use of organic compounds. Organic compounds i.e. ethanol and halogenoalkanes are highly flammable, and 2-chloro-2-methylpropane may cause eye, skin and/or respiratory tract irritation if ingested.	Safety equipment worn when handling organic compounds, with first aid equipment nearby if needed. Furthermore, the experiment was performed in a fume hood in a well-ventilated lab to minimise fire hazards.
Use of glassware. Risk of laceration if equipment breaks	All apparatus was handled carefully and stored securely when not in use. Safety equipment such as gloves, glasses and a lab coat were worn.
Use of sodium hydroxide and production of hydrochloric acid.	Hands were washed immediately after each trial, safety equipment was worn at all times, and first aid equipment was nearby if needed.

(Attach another sheet if needed.)

Risk Assessment indicates that this activity can be safely carried out

RISK ASSESSMENT COMPLETED BY (student name(s)): Caleb Tang

SIGNATURE(S): 

☑ By ticking this box, I/we state that my/our project adheres to the listed criteria for this Category.

TEACHER'S NAME: Fidias Andari

SIGNATURE:  DATE: 30/6/24