Factors affecting the rate of reaction of benzyl alcohol oxidation with potassium permanganate in nonpolar solvent using crown ethers

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Naloga je bila prijavljena kot Extended Essay (EE) na programu International Baccalaureate Diploma Programme

Avtor je prijavil nalogo Prihodnost je zapisana v qubitih na razpis Krkine nagrade 2021/22

Izjava o samostojnem delu

Izjavljam, da je prijavljena naloga rezultat samostojnega raziskovalnega dela.

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Kaj vpliva na hitrost oksidacije benzil alkohola s kalijevim permanganatom v nepolarnem topilu z uporabo kronskih etrov

V raziskovalnem delu raziskujemo praktično uporabo spojine kronski etri v laboratoriju. Kronski etri so organske spojine ciklične oblike. Zaradi tega, imajo edinstveno sposobnost vezave s takšnimi ioni velikosti, ki se prilega v praznino. Zaradi nepolarne narave, kronski eter tvori nepolaren ščit okoli polarnega iona in spojine, ki so prej bile topljive zgolj v polarnih topilih, in postanejo topljive v nepolarnih topilih. Najti rešitev s topilom pri reakcijah nepolarnih in polarnih spojin je kompleksen problem v raziskovalnem laboratorijskem delu, alternative kot so DMSO pa so okolju nevarne. Zato smo v tej nalogi raziskovali kolikšna je idealna koncentracija kronskih etrov in pri kakšni temperaturi delujejo optimalno. Za eksperiment smo uporabili benzil alkohol, ki je topljiv v nepolarnih topilih in ga poskušali oksidirati s soljo kalijev permanganat, za katero smo dokazali, da je topljiva samo v polarnih topilih. Za topilo smo uporabili dietil eter (nepolarno). Brez kronskih etrov reakcija ne steče, saj KNO_4 ostane trd na dnu. S kronskimi etri pa reakcija steče in dobimo produkt benzaldehid (oksidiran bezil alkohol). V eksperimentih smo raziskovali različne koncentracije kronskih etrov pri temperaturi 30°C in v standardnih pogojih. Različne koncentracije benzaldehida v spojini smo v intervalih po 5 minut z ATR-FTIR spektrofotometrom merili po 1 uro za vsako varianto. Na enak način smo raziskovali vplive različnih temperatur pri isti koncentraciji kronskih etrov. Rezultate smo preučili na več različnih načinov, na primer absolutne razlike v koncentraciji, merjenje ploščine pod krivuljo …. Ključna ugotovitev je, da je koncentracija benzaldehida najvišja pri 35°C in 0.4g na raztopino kronskega etra. Navedeni številki, ki sta glavna rezultata raziskave, sta bili ugotovljeni kot vmesna testna vrednost, kar je zanimivo.

Factors affecting the rate of reaction of benzyl alcohol oxidation with potassium permanganate in nonpolar solvent using crown ethers

In our research work, we researched the practical use of crown ethers in laboratory practice. Crown ethers are organic compounds in cyclic form. Thus, they have a unique property of binding with ions of the fitting size (which can fit the middle vanity). Due to their non-polar nature, crown ethers form non-polar shield around polar ion, transforming previously exclusively polarly soluble compounds to be also soluble in non-polar solvents. Dealing with reactions with different solubility factors is a common and inconvenient problem in many laboratory research practices, while the alternatives to crown ethers (e.g. DMSO) can be dangerous to the environment. Therefore, we decided to explore the optimal concentration of crown ethers in solution and the optimal temperature of the reaction. We used the oxidation of benzyl alcohol (soluble in non-polar solvents) with salt potassium permanganate (soluble in polar solvents) for our reaction, where crown ether serves as a catalyst. We used non-polar solvent Diethyl ether. Without crown ethers, the reaction does not occur as KNO_4 remains solid and sinks on the bottom. With crown ethers, on the other hand, oxidation completes and benzylaldehyde results as the product. In our experiments, we tested different concentrations of crown ethers at the temperature of 30°C. We measured the concentration of benzaldehyde in the solution every 5 minutes for 1 hour using ATR-FTIR spectrophotometer. We did the same with different temperatures at constant crown ether concentration. After different data analyses (from comparing the absolute difference in concentration to measuring the area under the data curve), we have determined that the highest concentration of benzaldehyde in the solution occurred at 35°C and the crown ether concentration of 0.4g/solution. In both cases, the values are not at the extremes of all that we tested, which came as a great surprise to us.

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Introduction

Via the process of primary alcohol oxidation, we produce aldehydes and carboxylic acids. Besides aldehydes' uses in the perfume and flavouring industry, they are also significant in some lab procedures. For the oxidation of alcohols to occur oxidising agent is needed. Most commonly potassium permanganate is used as an agent. However, the problem arises when we attempt to perform the oxidation in a nonpolar solvent. In this case, the oxidation does not occur as the potassium permanganate ($KMnO_4$) is salt soluble only in polar solutions, such as water. However, sometimes the experiment setting does not allow us to use polar solvents, as in the case of benzyl alcohol oxidation, where benzyl alcohol is not soluble in polar solvents. There exist some solvents that can dissolve polar and nonpolar substances, but they are expensive and dangerous to the environment (e.g. DMSO ($(CH_3)_2SO$) (Capriotti, 2012)). The other way to perform the oxidation is to utilise phase transfer catalyst. This is a catalyst that enables reaction between reactants that are present in different phases by promoting one from one phase to another (Jose, 2009). We will use phase transfer catalyst crown ether. By adding it into the solution, a substance otherwise soluble in exclusively polar solvent is now also soluble in nonpolar solvents. In our case, after adding crown ether to the solution, potassium permanganate is soluble in a non-polar solvent like diethyl ether. In this way, we were able to successfully react the oxidising and reducing agents to perform the oxidation. But crown ethers are still a very unexplored topic. Their discovery in 1987 was awarded the Nobel Prize in chemistry (Pedersen, 1988). Because of their hard-to-produce and expensive nature, we want to minimise their use in the experiments. But usually, we also want the reaction to be completed as quickly as

possible since this reduces costs and allows researchers to perform more experiments. In our research, we will examine what factors might affect the rate of the oxidation reaction when using crown ether as a phase-shift catalyst. We will focus on different temperatures of the environment and different concentrations of catalyst in the solution. This means that we will explore whether adding more crown ether is worth it for speeding the reaction significantly. Or whether instead of speeding it up by adding more catalyst it is easier and cheaper to just increase the temperature? Maybe in contrast to other similar reactions in organic chemistry increasing the catalyst concentration or temperature do not increase the rate of reaction at all. We summarise our interest in the following research question:

How do the temperature of the environment and the concentration of phase-shift catalyst crown ether affect the rate of the oxidation of benzyl alcohol with potassium permanganate in a nonpolar solvent?

Independent variables: Temperature and catalyst concentration.

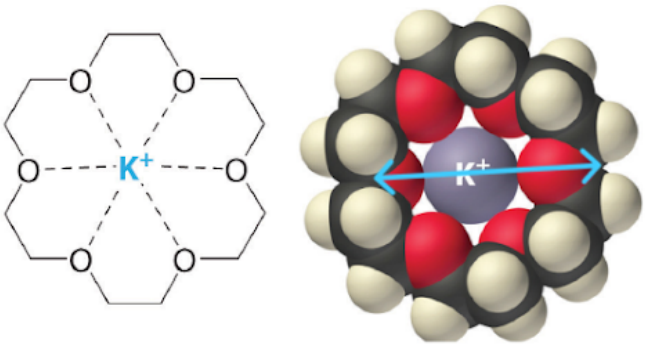
Dependent variable: Rate of the oxidation reaction.

Main body

Theoretical background

We will be using crown ethers as our catalysts for the reaction, thus first familiarize ourselves with them.

Crown ethers are ionophores, the structures which carry ions. Ionophores are most noticeably present in our cell membrane to transport substances in and out of the cell. Crown ethers are named after the number of carbon atoms in the ring (x) and the number of oxygen atoms (y): x-crown-y (Pedersen, 1988). Figure 1 shows a model of the crown ether’s structure.



(Figure 1: Structure of 18-crown-6, (Reusch, 2023))

There exist many varieties of crown ethers, they are mainly differentiated by the number of carbon and oxygen atoms in their structure. In the middle of the ring, a cavity is formed. The diameter of this cavity determines the type of ion that crown ether bonds to. Since we are using $KMnO_4$ as an agent in our reaction, we are looking for a crown ether that would fit the potassium cation. See Figure 1: we can determine the needed crown ether by measuring the diameter of the cavity and comparing it to the space needed for potassium ion to bond in the middle of two oxygen atoms. To determine the space needed we sum the radii of the potassium ion and the covalent radii of two oxygen atoms (presented with the blue arrow). The potassium cation radius is 1.33 Å and the covalent radius of oxygen is 0.74 Å. We sum the whole diameter to be $1.33\,\text{Å} + 2{\cdot}0.74\,\text{Å} = 2.8\,\text{Å}$, which is almost exactly the diameter of the cavity in the middle of 18-crown-6, which is between 2.8 Å and 3.2 Å. Thus the cation fits precisely. (McBride, 2011).

In our experiment, we will do the oxidation of benzyl alcohol ($C_6H_5CH_2OH$) with potassium permanganate ($KMnO_4$) in the nonpolar organic solvent diethyl ether ($(C_2H_5)_2O$) using catalyst 18-crown-6. $KMnO_4$ is broken into MnO_4^- ions and potassium K^+ cations. The oxidation follows the reaction:

$$C_6H_5CH_2OH + KMnO_4 Crown\ ether \rightarrow C_6H_5CHO + H_2MnO_4 + K^+ \text{(Jose, 2009)}$$

Potassium cation remains bonded to the crown ether molecule and becomes soluble due to the non-polar shield around it. “The MnO_4^- ion then attacks benzyl alcohol and a transition complex is formed which consequently gives benzaldehyde and manganic acid.” (Jose, 2009, p.154). Dissolved potassium permanganate in a nonpolar solvent (in our case we used diethyl ether) results in a colour change. (McBride, 2011).

Predictions before the experiment and preliminary experiments

As we know, by increasing the temperature of the reaction, the molecules move with higher velocity. This makes molecules collide more often and a greater proportion of collisions have energy greater or equal to the activation energy. As a consequence, the rate of reaction increases. Thus, it is reasonable to assume that the increase in temperature will increase the rate of the reaction. Also, we assume that the increase in the concentration of the catalyst should increase the rate of reaction until hitting the oversaturation of the catalyst, from which point there would be no further difference. The reason is that with a greater concentration of catalyst, the reactant is more likely to interact with the catalyst, meaning that the reaction will achieve the state of equilibrium faster.

First, we have experimented without crown ethers to illustrate the issue. Figure 2 shows the result when we tried to mix potassium permanganate and diethyl ether in the right beaker and in the left beaker we tried to dissolve benzyl alcohol and potassium permanganate in diethyl ether. Benzyl alcohol dissolved with dimethyl ether as expected, thus no layers were formed. On the other hand, potassium permanganate remained in a solid form and did not dissolve. We did not see the colour change and solid crystals remained on the bottom of the beaker. Note that the

slight colour change in the left beaker was probably a result of some water impurities present in the beaker. Almost all of the potassium permanganate remained at the bottom.

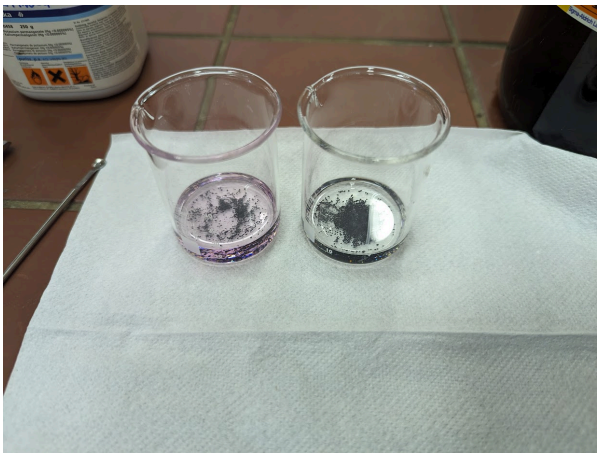


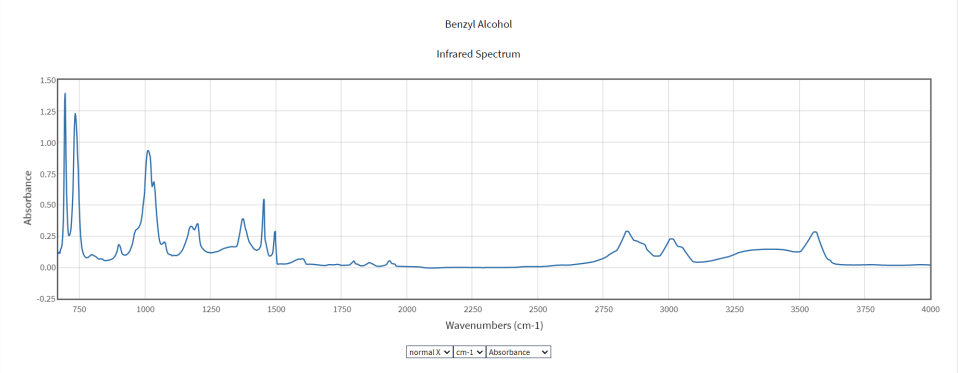
Figure 2: Preliminary experiment

We can add water to the nonpolar solvent. Water dissolves potassium permanganate but it does not mix with the nonpolar solvent, we see this in 2 phases: the purple one with potassium permanganate dissolved in water and the colourless one with the nonpolar solvent. Then we added crown ethers to the solution of all 3 substances and saw the colour of the solution change immediately after. The process is called phase transfer catalysis.

Method

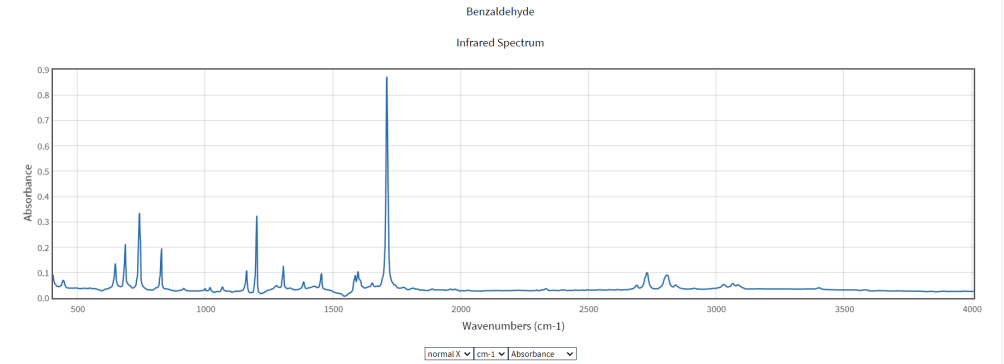
Measurements: For similar experiments to determine the concentration of aldehydes the technique of HPLC was used (Jose, 2009). Unfortunately, such measuring equipment is impossible to get at the high school level, thus we needed to come up with a more practical and feasible alternative. After some research, we found that benzaldehyde has a lot different absorbance spectrum than benzyl alcohol. We can compare the two in the figures below:

If we compare the absorbance spectrum of benzyl alcohol in Figure 4:



(Figure 4: absorbance spectrum of benzyl alcohol (NIST))

And the absorbance spectrum of benzaldehyde in Figure 5:



(Figure 5: absorbance spectrum of benzaldehyde (NIST))

We see the biggest difference in peak at the wavenumber of 1700 cm^{-1}, which is characteristic of aldehydes. Meaning, that if we measure this peak's magnitude, we should have a good idea of what share of the substance contains aldehydes and what share contains alcohol. In this way, we can measure the rate of the reaction.

For absorbance spectrum measurements we used an ATR-FTIR spectrophotometer.

Experiment outline

Equipment:

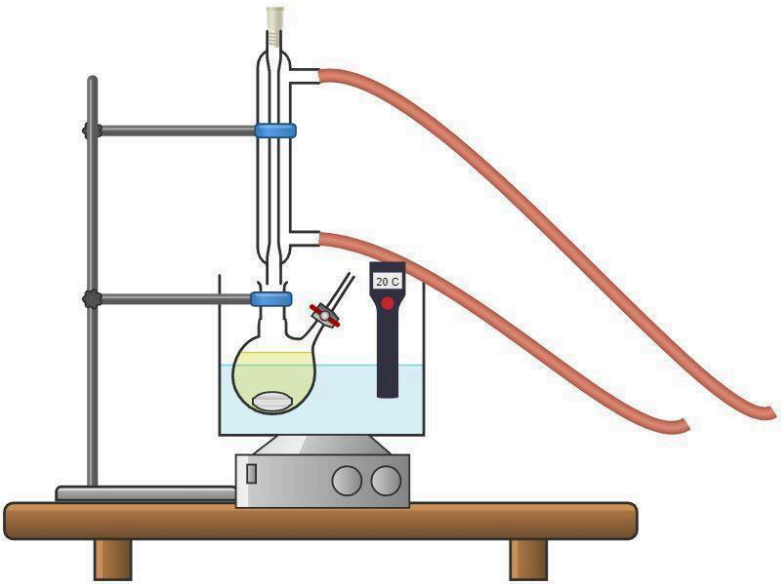
Glassware:

- Two-neck round bottom flask (about $250ml$)
- 25ml pipette ($\pm 0.03ml$)
- 50ml beakers
- 5ml pipette ($\pm 0.015ml$)
- Small spoons or wooden sticks

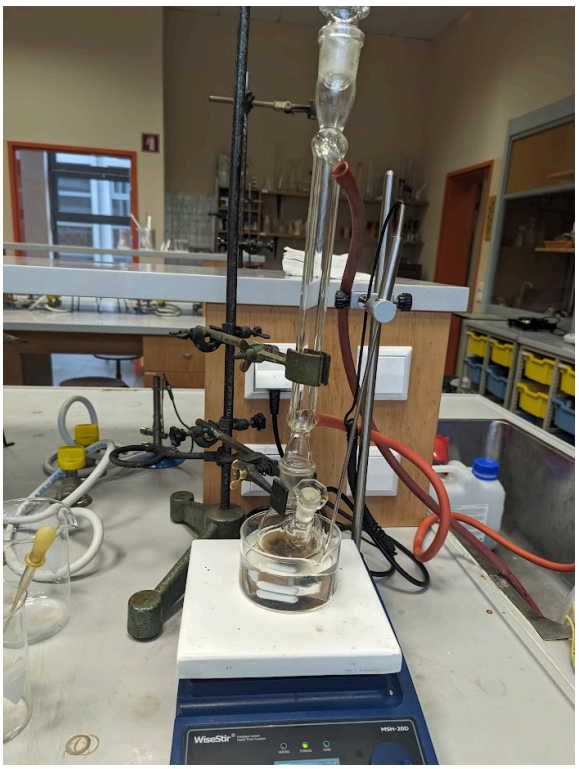
- Small dropper (about $1ml$)
- Seals for flask
- Leibig condenser with tubes
- Glass container for heat bath (about $0.5l$)

Other equipment:

- ATR-FTIR spectrophotometer
- Analytic scale ($\pm 0.0001g$)
- Heater and stirrer
- Retort stand
- korasilon paste
- Thermometer ($\pm 0.05°C$)
- Stirring bars
- Computer
- Weighing paper
- Safety goggles, gloves, and coat



(Figure 6: a sketch of the experimental setup (Created in https://chemix.org/))



(Figure 7: the final setup according to sketch)

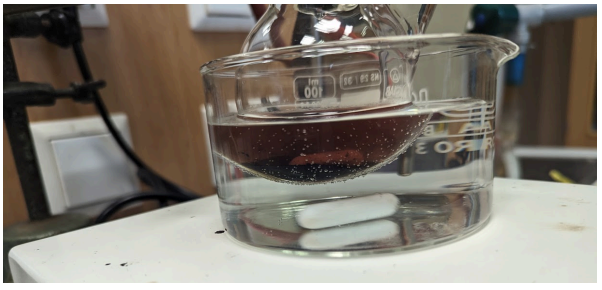
Figure 6 presents a sketch of our experiment setup and Figure 7 is the photograph of the actual setup. The basic setup is constructed from a two-neck round bottom flask which is inserted into a retort stand. On the top neck, a Liebig condenser is attached. This is done to reduce the escape of evaporated diethyl ether out of the system, considering that the boiling temperature of diethyl ether is just 34.6°C. In the joint between the flask and the condenser, we recommend using korasilon paste to further reduce vapour escaping the system. The other (the lower) neck is sealed with a glass seal and will be used to take out samples for ATR-FTIR spectroscopy measurements. Under the flask water bath is placed and under it an electric heater. In the water bath is placed a thermometer connected to the heater to keep the temperature constant. Ideally, it would be more precise to place the thermometer in the flask since we are interested in the temperature of the substance, but we can assume that the glass conducts heat very well thus the temperature in the flask is

very close to the temperature in the heat bath. In the flask and the heat bath are also stirring bars set at the constant agitation speed of 200 rpm.

For the experiment, we will use a constant amount of solvent, potassium permanganate, and benzyl alcohol. In one aspect we will vary the temperature and in the other the amount of catalyst. We will do a spectroscopy measurement every 3 minutes for the first 15 minutes and then every 5 minutes for the rest of the experiment (60 minutes in total).

We have decided to use 2.5 ml of benzyl alcohol per experiment. According to our main source paper (Jose, 2009), the solvent and solute ratio should be around 10:1, but since the abundance of solvent would not affect the reaction if it is constant, we opted to use 30 ml of diethyl ether assuming that some of the diethyl ether will inevitably escape the system anyways. We also decided to add a bit more oxidising agent than calculated since this should not affect the reaction as long as it is constant for all measurements. We settled add 3*g* of $KMnO_4$ per solution.

For our catalyst constant, we went with 0.4 g of 18-crown-6 per solution, as this is proportionally calculated as in our source paper (Jose, 2009). As for the temperature constant, we decided to keep it at 35°C as we found that the reaction was quick enough to make the results more visible. Qualitative observation of the change in colour of the solution from transparent to yellow to brown, when the reaction occurs, is shown in Figure 8.



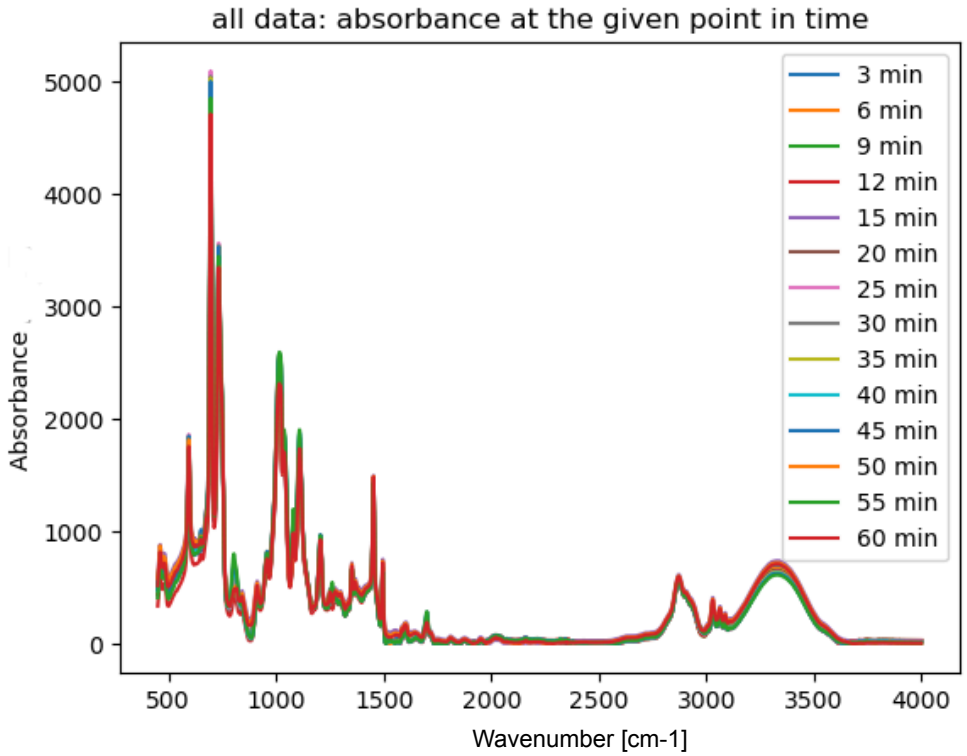
(Figure 8: change in colour of the solution)

Safety precautions

Besides applying standard safety precautions such are wearing gloves and lab coats it is worth pointing out that diethyl ether is a very evaporative substance and inhaling it too much for longer periods of time may cause some health issues. If the use in the fume hood is not possible, like in our case due to water supply, we recommend frequent airing of the lab and avoiding opening the sealings as much as possible. All substances are highly flammable. The waste is thrown into organic waste. Safety, time, and cost factors were also the reason why only 7 trials of the experiment were performed instead of 30.

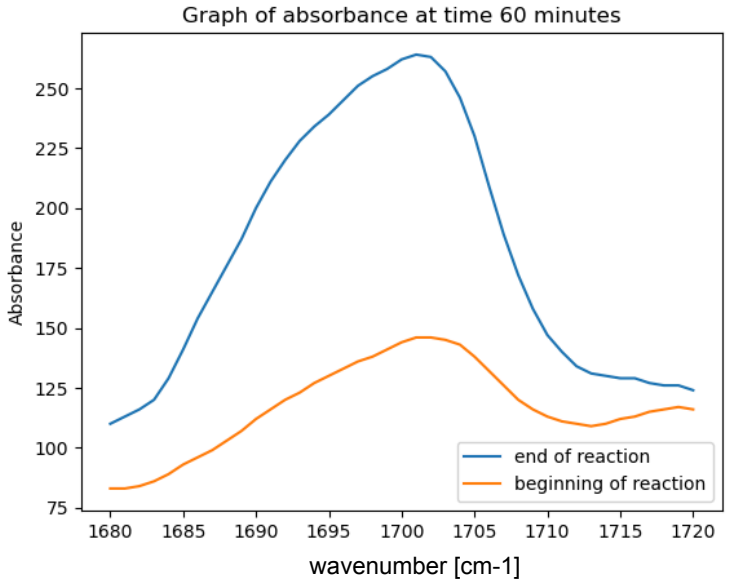
Results and analysis

In Figure 9 below we see the graph of absorbance at the given wavenumber for every point in time we have measured it:



(Figure 9: the graph of the absorbance at the given wavenumber for every point in time)

If we zoom into the peak between 1680 cm^{-1} and 1720 cm^{-1} at the beginning of the reaction and compare it with the peak at time 60 minutes after the reaction started, we see that there indeed is a big difference between the peaks. This is shown in Figure 10:



(Figure 10: Comparison between the peaks at the beginning and at the end)

Our goal is to measure the difference between the peaks at each point in time of the reaction to determine the concentration of reactants and products and calculate the rate of the reaction.

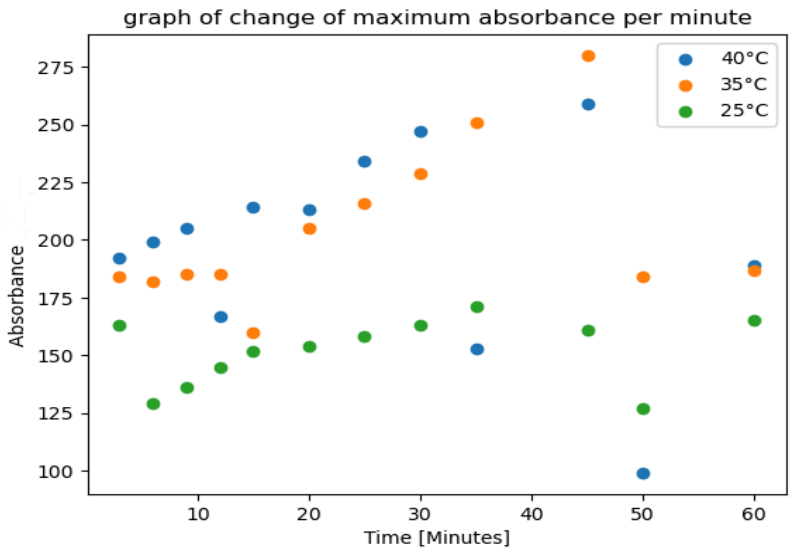
1. Temperature data analysis:

The first approach that may come to our mind is to find the maximum value of the peak at the wavenumber between 1680 and 1720 cm^{-1} and compare the values between them. In this case, we simply took the interval of wavenumber between 1680-1720 cm^{-1} and found the maximum value in the interval. We can present all the maximum values in Table 1:

Time after the start of the reaction [minutes]	Maximum value of the peak at Temperature 25°C	Maximum value of the peak at Temperature 35°C	Maximum value of the peak at Temperature 40°C
3	163	184	192
6	129	182	199
9	136	185	205
12	145	185	167
15	152	160	214
20	154	205	213
25	158	216	234
30	163	229	247
35	171	251	153
40	170	253	/
45	161	280	259
50	127	184	99
55	130	284	/
60	165	187	189

(Table 1: The maximum value of the peak at time t minutes after the beginning of the reaction)

To visualise the data we can plot a scatter plot of the maximum value of the peak versus time for each temperature in Figure 11:



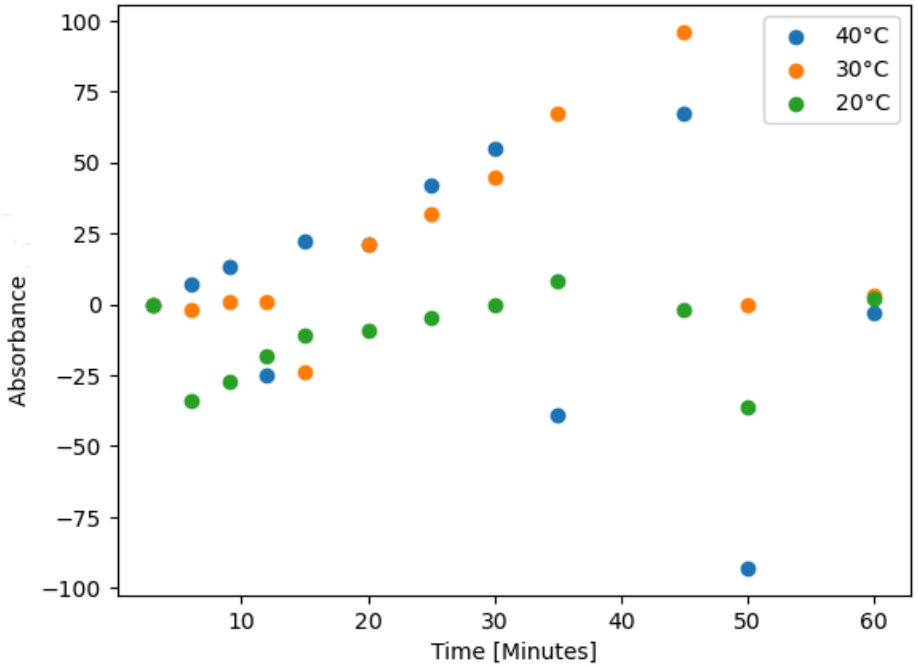
(Figure 11: scatter plot of the maximum value of the peak versus time for each temperature)

On this graph, we can see that the values are roughly linearly rising with the time of the reaction. However, there is an outlier at the point of 50 minutes. Strangely, this is an outlier for every different temperature, which is too unlikely to categorise it as a random error. There is also a caveat to these observations: we started measuring the absorbance at point 3, where the concentration of aldehydes should be almost 0. But as we see from our graph the values of absorbance at point 3 are unpropsionally different. This might be a result of a poorly calibrated spectrophotometer or an impure solution. We try to solve the problem by calculating the difference between the absorbance at 3 and the maximum absorbance. In this manner, we calculated the difference between the starting and final maximum values of the peak between 1680-1720 cm^{-1}. This is shown in Table 2:

Temperature	The difference in absorbance
25°C	8
35°C	96
40°C	67

(Table 2: the difference between the maximum value of the peak in the reaction and the initial value)

From the table, it seems that the reaction was the fastest/yielded the most product at the temperature of 35°C. We calculate the difference between the initial value and the measured value at the time for every measurement. We can plot these differences on the graph in Figure 12:



(Figure 12: the difference between the initial value of the peak and the maximum value at time *t* for every temperature)

With the results of comparing the maximum values of the peaks and the difference between the highest maximum and the absorbance at the beginning of the reaction, we could conclude that the reaction yields the most product at the temperature of 35°C.

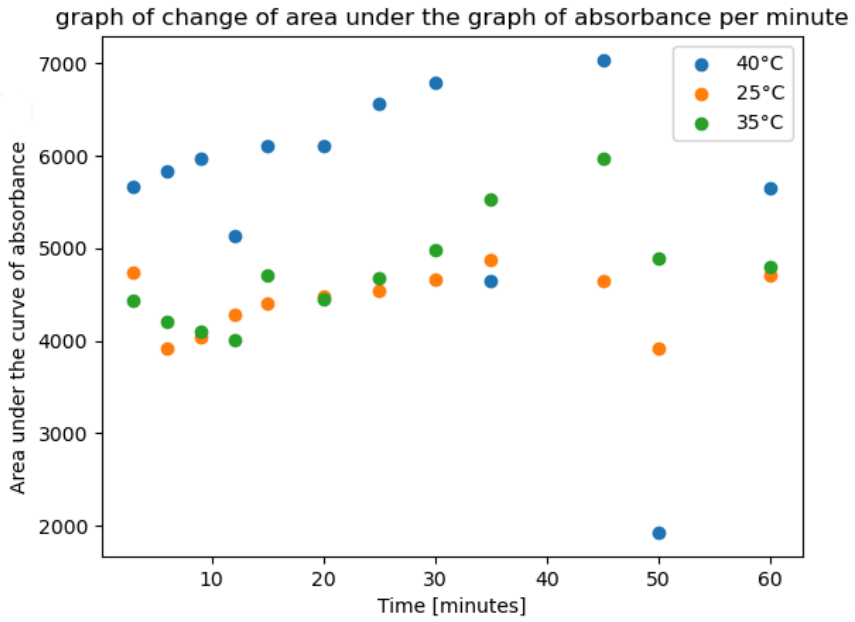
But the maximum value of the peak might not tell us the whole story. Another way to look at the peak is to calculate its area under the curve. Here we take a certain interval of the graph and calculate the total area under the curve. In our case is the interval between wavenumber 1680 cm^{-1} and 1720 cm^{-1}. By doing this we neglect

potential extremes of the peak and compare by how much the whole peak increased. We can do this on a computer easily. We used the trapezoid method where the computer inserts many small trapezoids under the curve and estimates the area under it. We present the results of the calculation in Table 3:

Time [minutes]	Area at 25°C	Area at 35°C	Area at 40°C
3	4739	4433	5664
6	3917	4208	5829.
9	4041	4094	5963
12	4278	4012	5131
15	4401	4705	6102
20	4480	4453	6102
25	4543	4671	6555
30	4659	4981	6788
35	4876	5526	4642
40	4869	5521	/
45	4645	5962	7032
50	3911	4887	1928
55	3944	6061	/
60	4710	4792	5651

(Table 3: The area under the curve of the peak)

The area under the peak at different times *t* at different temperatures is presented in the graph in Figure 13:



(Figure 13: Area under the curve of the peak versus time after the start of the reaction)

Here we see that the situation is quite different. The area under the peak is the greatest at 40°C while the area at 25°C and 35°C look very similar. But again, since we are measuring from the beginning of the reaction we can calculate the difference between the area at the starting value and the maximum value of the peak.

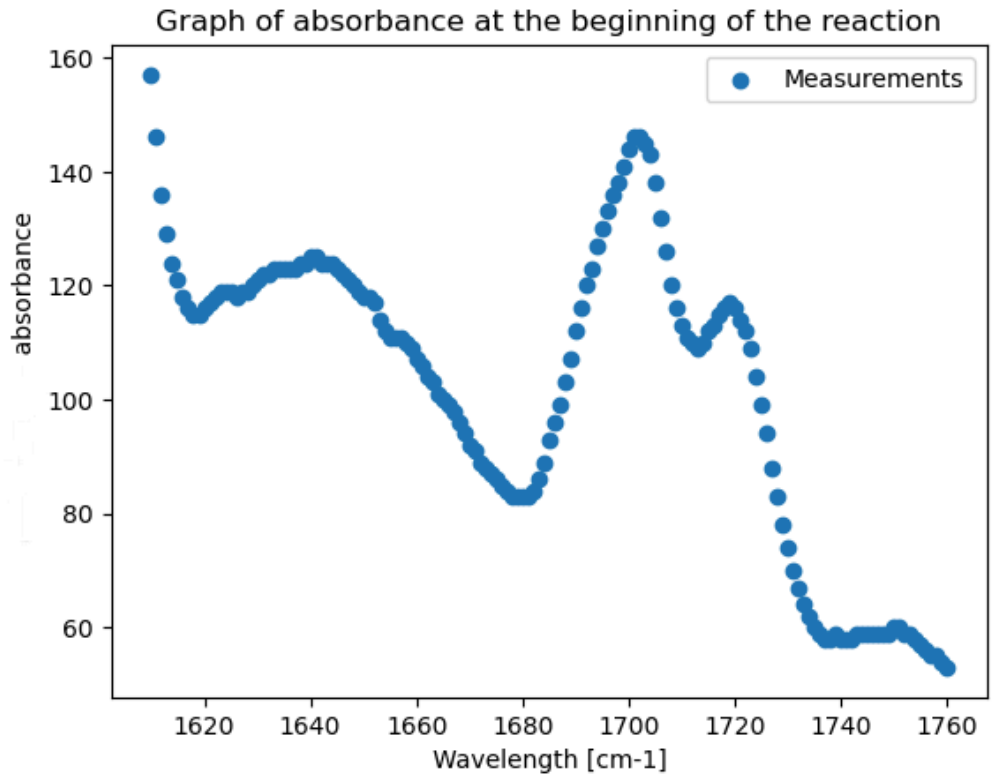
Table 4 shows the difference between the maximum value of the peak and the initial value of the peak:

Temperature	The difference in absorbance
25°C	137
35°C	1529
40°C	1368

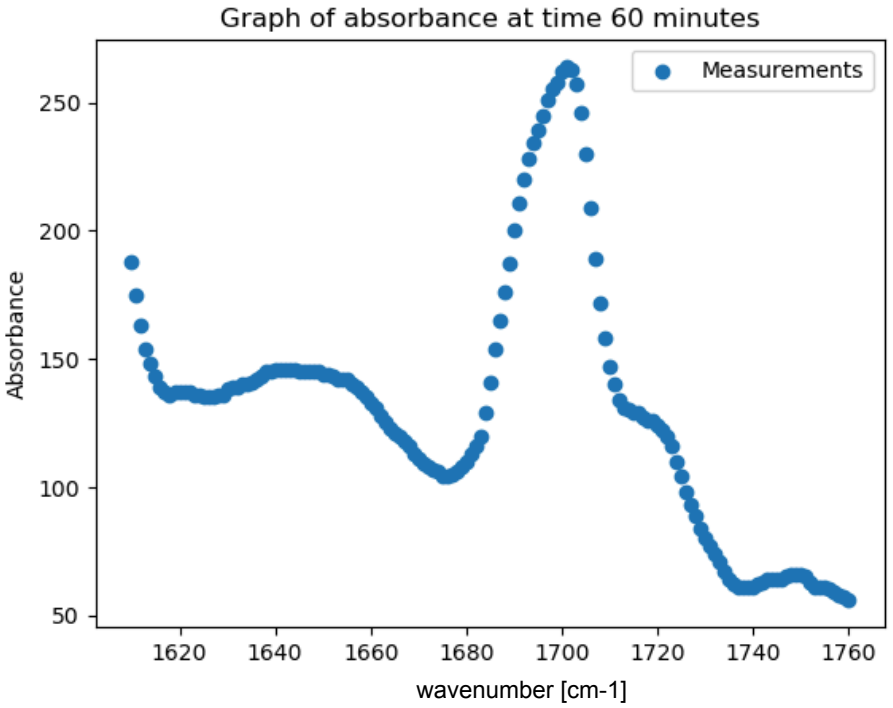
(Table 4: The difference between the area under the curve and the initial area under the curve)

In this case, we see that the greatest difference between the starting area under the peak and the maximum area under the peak was at a temperature of 35°C, which correlates with our results from comparing the maximum value of the peak.

Soon we realised that it may not be so straightforward. We must measure the magnitude of the peak compared to the rest of the spectrum since the rest should not shift with the peak (see Figures 4 and 5). But if we plot a greater area of the curve beside the peak, we see that the rest of the measurements also shift a bit. We see that if we compare Figures 14 and 15:



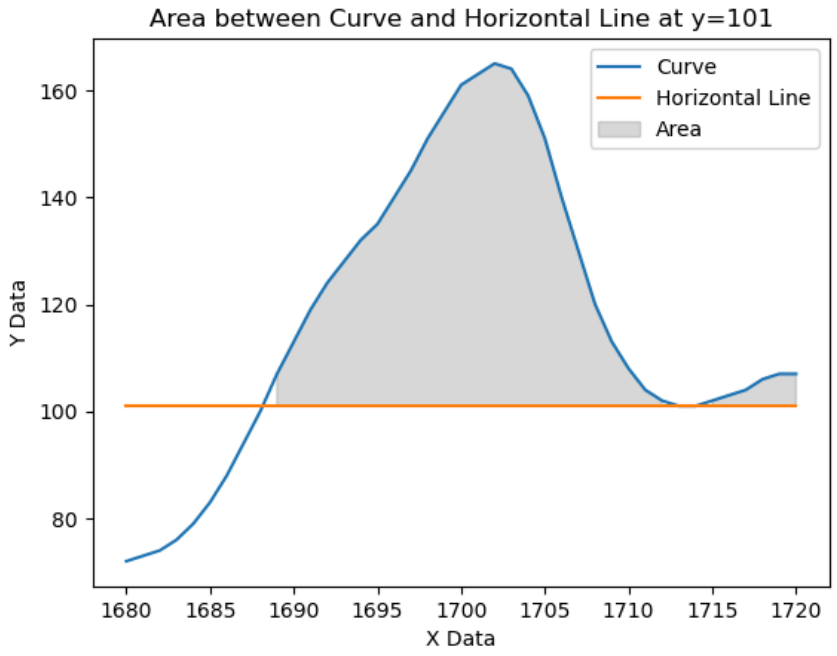
(Figure 14: at the beginning of the reaction)



(Figure 15: at the end of the reaction)

We see that the values at 1680 cm^{-1} also shift up, this should be ignored by our peak area measurements since we should focus on the peak only.

So we need to find a way to isolate the area of the peak from the rest of the graph. This can be done by drawing a new line at the minimum value of the peak as presented in Figure 16:



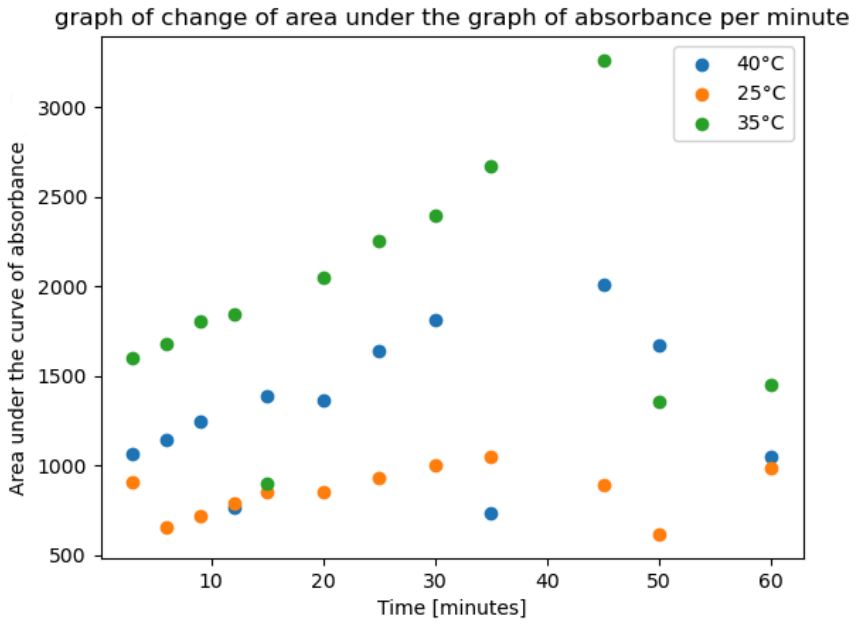
(Figure 16: Focus on the dark area only)

In this manner, we calculate the area of the peak only and exclude the differences in absorbance of the rest of the graph. This data is again presented in table 5:

Time [minutes]	Area at 25°C	Area at 35°C	Area at 40°C
3	907	1597	1061
6	653	1677	1139
9	714	1802	1246
12	785	1841	764
15	850	894	1383
20	854	2049	1361
25	933	2248	1638
30	999	2390	1811
35	1046	2666	736
40	1018	2775	2008
45	891	3260	/
50	615	1354	1669
55	638	3314	/
60	981	1447	1045

(Table 5: area between the curve and the minimum value of the peak)

We also present a plot of such areas in dependence on time in Figure 17:



(Figure 17: Area of the peak limited by its minimum value in dependence of time)

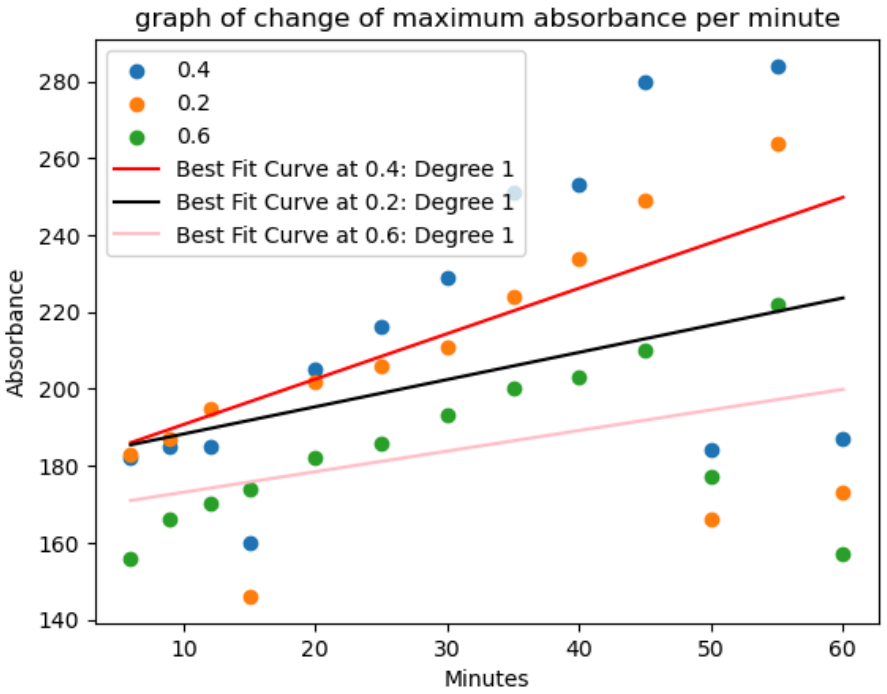
Again we see that the most product was yielded in case of the temperature being 35°C. As before we can calculate the difference between the starting value and the largest value of the area of the peak (table 6).

Temperature	The difference in absorbance
25°C	139
35°C	1663
40°C	947

Table 6: the difference between the initial area between the peak and the minimum value and the maximum area between the peak and the value.

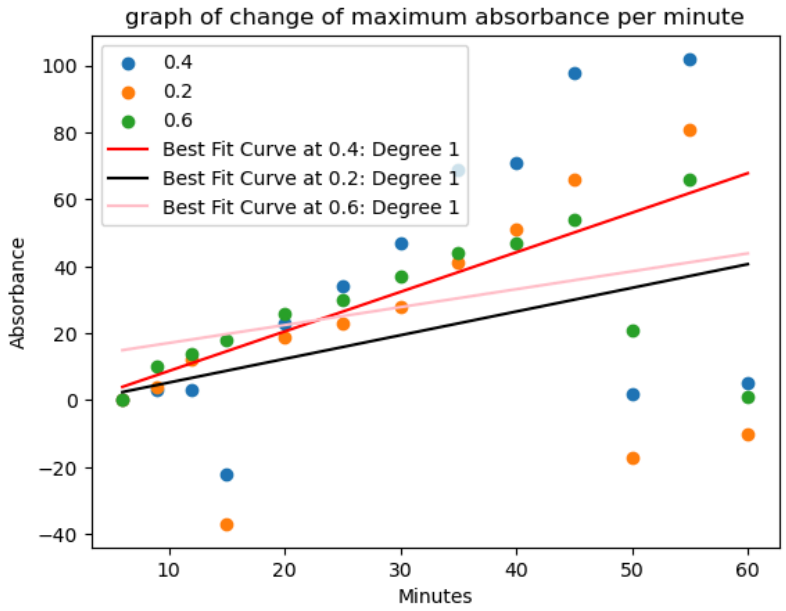
2. Catalyst data analysis

We will analyse the catalyst data in the same way as we did with the temperature data. First, we plot the maximum value of the peak between 1680-1720 cm^{-1}. We plot them on the following graph in Figure 18 and add best-fit lines to compare the gradient between them:



(Figure 18: the maximum value of the peak vs time at each catalyst concentration value)

Trends are clearly present and it looks like the most product is yielded at the concentration of 0.4 g of crown ether per solution, which is also somewhat surprising. However, we still got clear outliers at points 50 and 60 minutes, although these measurements are completely independent of measurements of the temperature. Similarly, let's again plot the difference between the initial maximum absorbance and the maximum at the given time in Figure 19:



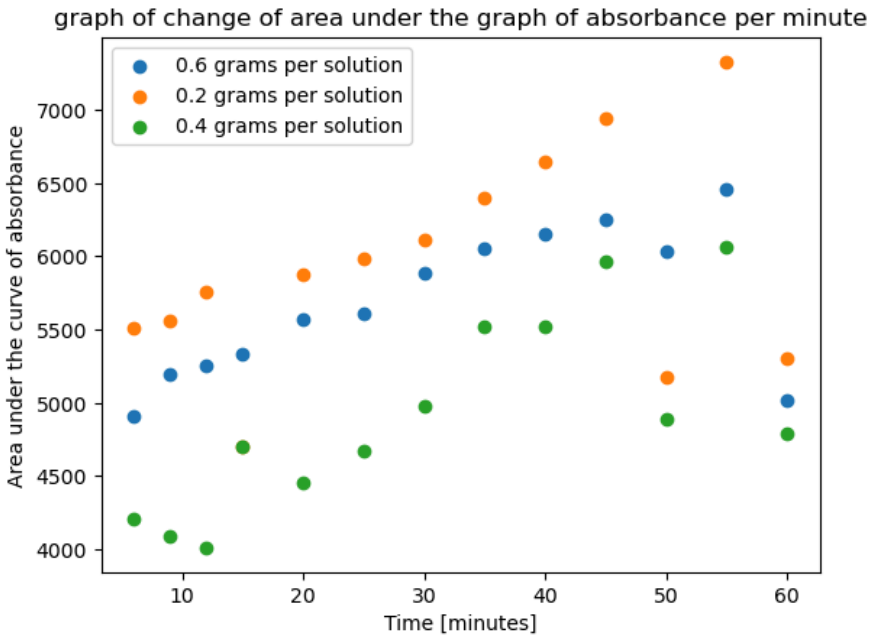
(Figure 19: The difference between the maximum peak and initial peak value versus time)

This time the trend is a lot less clear and points are very close for the first half an hour. Only if we look at the best-fit lines do we see that again at the catalyst concentration of 0.4g/solution the final product concentration is the greatest. If we present the differences in the table we get the following:

Mass of catalyst per solution [g]	The difference in absorbance between the initial and maximum peak value
0.2	81
0.4	102
0.6	66

(Table 7: The difference in absorbance between the initial and maximum peak value and concentration)

In the previous example, we saw that we got more reliable results if we considered the area under the peak. First, we calculate the total area under the curve at the peak between $1680cm^{-1}$ and $1720cm^{-1}$. We plot the area of the peaks in Figure 20:



(Figure 20: area under the curve of peaks versus time for every concentration)

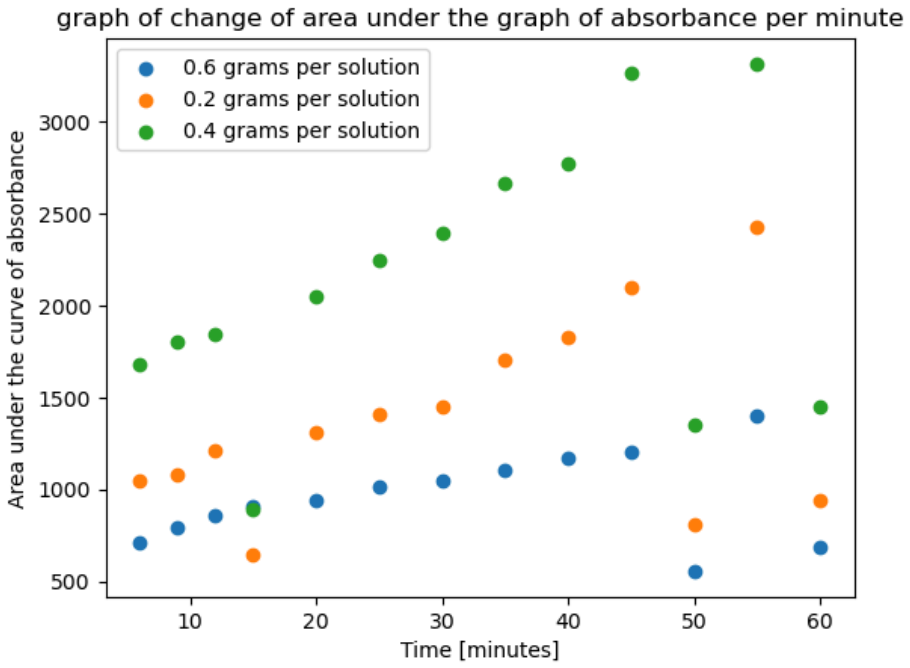
Here surprisingly the concentration of 0.2g/solution is on top, which does not make much sense. As we also see the big difference between starting areas we will not consider these results as very relevant. If we again consider the area under the peak where the lower limit is the minimum value of the peak as shown in Figure 16 we can calculate Table 7:

Time [minutes]	Area at a concentration of 0.2g/solution	Area at a concentration of 0.4g/solution	Area at a concentration of 0.6g/solution
6	5506.5	4208.5	4906.5
9	5562.5	4094.0	5191.0
12	5756.0	4012.0	5255.5
15	4697.5	4705.5	5337.5
20	5878.5	4453.0	5567.0
25	5984.5	4671.0	5606.5
30	6111.0	4981.0	5885.5
35	6395.0	5526.0	6055.5

40	6643.0	5521.5	6154.0
45	6946.5	5962.5	6248.0
50	5177.5	4887.0	6034.0
55	7328.0	6061.5	6458.0
60	5308.5	4792.0	5020.0

(Table 7: area under the peak limited with its minimum value)

We plot everything in figure 21:



(Figure 21: Area under the peak limited with its minimum value versus time)

In the final plot, we see that the data is correlated very linearly as we predicted. In this case, again the concentration of 0.4 g/solution yielded the most product.

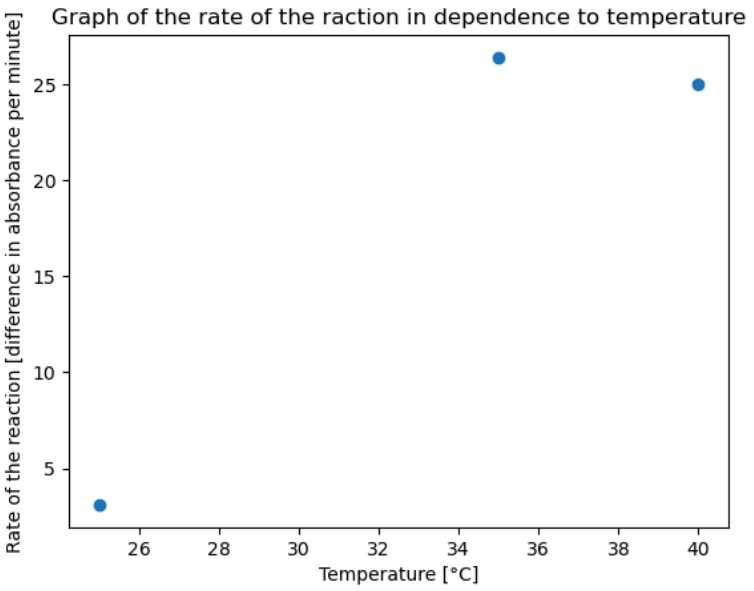
Finally, we get to answer our question and compare rates of the reaction under different conditions. As noticeable from the graph, measurements at the end of the experiment follow the linear trend less clearly, thus we decided to use only the measurements from the first 30 minutes of the reaction to calculate each rate of reaction. For the average rate of reaction calculation, we used the measurements of the area between the curve and line at the minimum value of the peak. According to

Beer's Law, we know that the absorbance and concentration of the solution are linearly correlated. To calculate the average rate of reaction we take the initial value of the area of the peak and the final one and divide it by the time of the reaction, in our case 30 minutes. The results are the following:

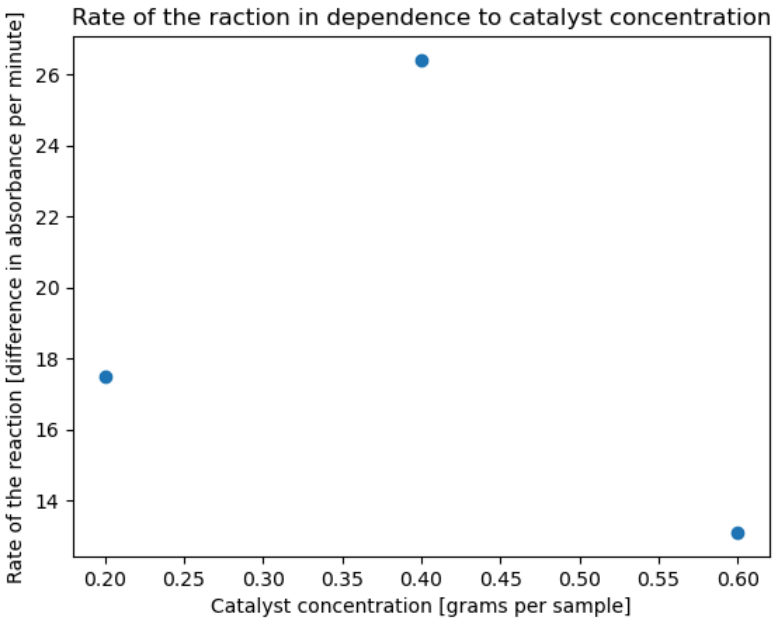
	25°C	35°C	40°C	0.2 g/solution	0.4 g/solution	0.6 g/solution
Rate (difference in absorbance per minute)	3.1	26.4	25.0	17.5	26.4	13.1

(Table 8: rates of the reaction, the difference between the initial and final area between the peak and the minimum value divided by 30 minutes.)

We can present both in scatter plots:



(Figure 22: Rate of the reaction in dependence of temperature)



(Figure 23: Rate of the reaction in dependence of catalyst concentration)

Conclusions

At first, we predicted that increasing the temperature and the concentration of the catalyst would both increase the rate of the reaction. Based on our results, we refute our hypothesis. From the analysis, we saw that in both cases the middle value (temperature of 35°C and catalyst concentration of 0.4g per solution) yielded the most product (see Table 8). To answer our initial research question: Temperature and catalyst concentration do affect the rate of the reaction: the rate increases as the temperature increases until hitting the optimal temperature. Then, the rate slowly starts decreasing. Similar holds for the catalyst: At first, as the catalyst concentration increases the rate also increases until hitting optimal concentration after which the rate decreases rapidly. The difference in rate at low temperatures (25°C) and the optimal one (35°C) is a lot more significant than the difference in rate between different concentrations of the catalyst (0.2 and 0.4): 23.3 at temperature and 8.9 at

catalyst. The reason why this is so for temperature may be the fact that too high temperature affects the catalyst destructively. Maybe high temperature causes crown ether to decompose. One reason might also be that although we used a condenser some solvent escaped the system and the lack of solvent in the solution slowed the reaction down (the boiling point of diethyl ether is 34.6°C). We could verify this by measuring the final volume of the solution. Now consider the fact the highest concentration of catalyst did not produce the most product. The reason that came to our mind is that the catalyst might saturate. This happens if two catalyst molecules react with each other since the catalyst is too abounded. As an effect of this we run out of catalyst molecules to react with molecules and the reaction slows down. By more complex calculations we could find the optimal concentration of catalyst in the solution, while for the optimal temperature, it is not as straightforward. The easiest way would probably be to find it experimentally. Finally, we have to discuss the outliers of the experiments. At the points 50 minutes and 60 minutes we measured outliers in every of the measurements that we performed. This is still a mystery for us since it is impossible that the concentration of aldehyde would rapidly fall out of nowhere. There might have been an issue with computer readings or the spectrophotometer, but the probability of both happening at the same time is extremely low. To further examine these outliers we recommend performing even more experiments. Otherwise, we cannot propose any reasonable explanation.

Final Evaluation

Finally, we can discuss the uncertainties present in our experiment. These are mostly the same for both independent variables. We have calculated the total relative uncertainty based on the uncertainties of measuring equipment to be around

2%. But by far the greatest uncertainty is a result of time measurements during the performance. Although we tried our best to minimize the differences in time when taking measurements between all experiments, the difference was $\pm\ 5s$ at best. This is significant when the differences in measurements are very subtle. To minimise other factors that may affect the final result included: preventing evaporated substances from escaping the system, keeping constant temperature and substances in the system, etc. Ideally, we would perform the experiment more times and measure the mass of the solution to approximate the amount of substance escaping the system. We could not perform this experiment more times because of time, cost, and safety constraints.

Bibliography

- Our main source: N. Jose, S. Sengupta, J.K. Basu, Selective production of benzaldehyde by permanganate oxidation of benzyl alcohol using 18-crown-6 as phase transfer catalyst, Journal of Molecular Catalysis A: Chemical, 18 August 2009, https://doi.org/10.1016/j.molcata.2009.05.009. https://www.sciencedirect.com/science/article/pii/S1381116909002581 Accesed: 23 Jan 2024
- Capriotti K, Capriotti JA. Dimethyl sulfoxide: history, chemistry, and clinical utility in dermatology. J Clin Aesthet Dermatol. 2012 Sep:24-6. PMID: 23050031; PMCID: PMC3460663. Accessed 22 Feb. 2024.
- Clark, Jim. “The Oxidation of Alcohols.” *Chemistry LibreTexts*, Libretexts, 23 Jan. 2023, chem.libretexts.org/Bookshelves/Organic_Chemistry/Supplemental_Modules_(Organic_Chemistry)/Alcohols/Reactivity_of_Alcohols/The_Oxidation_of_Alcohols. Accessed 17 Jan 2024

- McBride, J Michael. “CHEM 125b: Freshman Organic Chemistry II.” Yale University, spring 2011, https://oyc.yale.edu/chemistry/chem-125b/lecture-5. Accessed 10th Nov 2023
- NIST Office of Data and Informatics. *Benzyl Alcohol*, National Institute of Standards and Technology, webbook.nist.gov/cgi/cbook.cgi?ID=C100516&Type=IR-SPEC&Index=1 . Accessed 22 Feb. 2024.
- Pedersen, Charles J. “The Discovery of Crown Ethers | Science.” *Science*, Science, 29 July 1988, www.science.org/doi/10.1126/science.241.4865.536 . Accessed 22 Feb 2024
- Reusch, William, and Stephen Contakes. “18.7: Crown Ethers.” *Chemistry LibreTexts*, Libretexts, 8 Oct. 2023, chem.libretexts.org/Bookshelves/Organic_Chemistry/Organic_Chemistry_%28Morsch_et_al.%29/18%3A_Ethers_and_Epoxides_Thiols_and_Sulfides/18.07%3A_Crown_Ethers .Accessed 22 Feb 2024
- The experiment setup sketch was created on the website https://chemix.org/ on 8 Dec. 2023