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Examination session (May or November)	MAY	Year	2013

Diploma Programme subject in which this extended essay is registered: CHEMISTRY

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Title of the extended essay: An investigation into the synthesis of vanillyl alcohol through the reaction of vanillin and sodium borohydride based on Green Chemistry Principles

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The extended essay I am submitting is my own work (apart from guidance allowed by the International Baccalaureate).

I have acknowledged each use of the words, graphics or ideas of another person, whether written, oral or visual.

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Please comment, as appropriate, on the candidate's performance, the context in which the candidate undertook the research for the extended essay, any difficulties encountered and how these were overcome (see page 13 of the extended essay guide). The concluding interview (viva voce) may provide useful information. These comments can help the examiner award a level for criterion K (holistic judgment). Do not comment on any adverse personal circumstances that may have affected the candidate. If the amount of time spent with the candidate was zero, you must explain this, in particular how it was then possible to authenticate the essay as the candidate's own work. You may attach an additional sheet if there is insufficient space here.

The candidate worked extremely hard in coming up with the title of the essay, carrying out detailled experiments and judging the results of her investigation. During the extended essay period she undertook independent work and research into the surrounding literature and designed suitable methodology to successfully answer her research question. During the concluding viva voce she showed excellent holistic judgement + reasoning in deciding the viability of her results + the true scientific meaning of her findings. I feel that the candidate went beyond "normal" efforts to successful complete this essay to the highest of Standards.

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Assessment form (for examiner use only)

Criteria	Achievement level				
	Examiner 1	maximum	Examiner 2	maximum	Examiner 3
A research question	2	2		2	
B introduction	2	2		2	
C investigation	4	4		4	
D knowledge and understanding	4	4		4	
E reasoned argument	4	4		4	
F analysis and evaluation	4	4		4	
G use of subject language	4	4		4	
H conclusion	2	2		2	
I formal presentation	4	4		4	
J abstract	2	2		2	
K holistic judgment	4	4		4	
Total out of 36	36				

An investigation into the synthesis of vanillyl alcohol through the reaction of vanillin and sodium borohydride based on Green Chemistry Principles

Name:

Subject: Chemistry

Candidate number:

Supervisor:

Word Count: 3990

Abstract

Paul Anastas, director of Yale University's centre for Green Chemistry and Green engineering, first proposed the concept of Green Chemistry. Anastas and Warner (1998) proposed 12 Green Chemistry Principles (Appendix 1) which encouraged the design of chemical processes that minimize the use and generation of hazardous substances.[1]

In the synthesis of vanillin alcohol from vanillin the aldehyde motif is prone to the nucleophilic attack by hydride ions present in reducing agents to form alcohols. The reaction between vanillin and sodium borohydride uses excess of the reducing agent. However, sodium borohydride is hazardous and has a serious potential health effect (Appendix 2 - MSDS sheet). Hence, the use of sodium borohydride, according to Green Chemistry principles[1], should be minimised. The focus of my experiment is to determine the compromising amount of sodium borohydride used in this reaction based on the two factors: the conversion and efficiency of the reaction, and how the reaction follows the principles of Green Chemistry.

The extended essay investigates the research question "What is the compromising reaction stoichiometry in a green synthesis of vanillyl alcohol from the reduction of vanillin using sodium borohydride?"

Reactions with 5 different amounts of sodium borohydride were conducted. In each reaction, samples of the reacting mixture were taken out at regular time periods and analysed by thin layer chromatography. It was found that all reactions achieved full conversion of vanillin. It was proposed that the compromised amount of sodium borohydride used in the production of vanillyl alcohol lies towards 0% to 50% excess, i.e. the compromising stoichiometry in terms of vanillin to sodium borohydride is 4:1 to 4:1.5.

Word count: 267

Contents

Glossary and Abbreviations

1. **Green Chemistry**[1]

   The American Chemistry Society stated that Green chemistry is the design, development, and implementation of chemical products and processes to reduce or eliminate the use and generation of substances hazardous to human health and the environment.

2. **Green Chemistry Principle 2 – Atom Economy**[1]

   Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.

3. **Green Chemistry Principle 3 – Less Hazardous Chemical Syntheses**[1]

   Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. **Green Chemistry Principle 6 – Design for Energy Efficiency**[1]

   Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

5. **Green Chemistry Principle 12 – Inherently Safer Chemistry for Accident Prevention**[1]

   Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

6. Full Reaction Conversion

The reaction has reached full conversion when the all reacting reagents, or the limiting reagents, have reacted and been used up. Vanillin is the limiting reagent in the reactions conducted in this investigation, full conversion of the reaction is therefore reached when all vanillin has reacted.

7. Reaction stoichiometry

This describes the quantitative relationships among substances as they participate in chemical reactions.[2] The reaction stoichiometry of the reactants in the reaction investigated is 4:1(Stoichiometric ratio of vanillin to sodium borohydride). This means that every four moles of vanillin react with one mole of sodium borohydride.

8. Reaction time

In this investigation, the reaction time of each reaction is defined as the time required for a reaction to reach full conversion. The reaction time of reactions in this investigation is the point when all vanillin in the reaction has reacted.

Below is the list of abbreviations used to represent the full name of chemicals and technology in this essay:

Full name (in order of appearance)	Abbreviation
Sodium Borohydride	$NaBH_4$
Borohydride ion	BH_4^- ion
Hydride ion	H^- ion
Hydrochloric acid	$HCl_{(aq)}$
Thin layer chromatography	TLC
Retardation factor	R_f
Liquid Chromatography – Mass Spectrometry	LCMS

Introduction

Vanillin is an aromatic compound with the smell of vanilla, as the primary component of the extract of vanilla beans. It has the chemical formula $C_8H_8O_3$ with carbonyl, phenol and ether groups. The reduction of vanillin by sodium borohydride produces vanillyl alcohol. Vanillyl alcohol has many commercial and pharmaceutical applications, including flavouring and as a treatment of Parkinson's disease (Hsu, Wen & Lee, 2009)[3]. This investigation aims to design a greener pathway to synthesise vanillyl alcohol, with respect to the Green Chemistry Principles proposed by Paul Anastas in 1998[1].

Sodium borohydride ($NaBH_4$), the reducing agent in the reaction, is hazardous. As stated in the MSDS report (Appendix 2), $NaBH_4$ is harmful upon inhalation, irritant upon skin and eye contact, potentially resulting in skin burns. Green Chemistry principles 3, "Less Hazardous Chemical Syntheses" and 12 "Inherently Safer Chemistry for Accident Prevention" concern the toxicity and safety of chemicals used (Anastas and Warner, 1998)[1]. Furthermore, Green Chemistry principle 2, "Atom Economy" states that synthesis should be designed to maximise the incorporation of materials used into the final product. With respect to the two principles, a more green synthesis is achieved by using less $NaBH_4$.

On the other hand, principle 6 of Green Chemistry (Design for Energy Efficiency) states that it is best to minimise the amount of external energy wasted and applied to the reaction. The reaction between vanillin and $NaBH_4$ takes place at room temperature and pressure. The main concern for this principle would therefore reaction time required. In general, the shorter the reaction, the less external energy, for example, the energy supplied to the magnetic stirrer, is used.

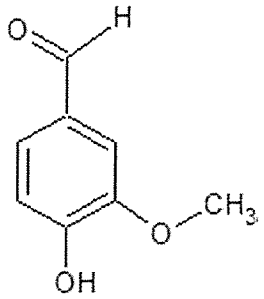
In a past research paper on this reaction, Lecher (2007) stated that "In practice, it is best to use 50 -100% excess $NaBH_4$ to compensate for any $NaBH_4$ that reacts with the solvent or decomposes from other causes".[4] This means that using over 50% excess $NaBH_4$ should improve the conversion rate of the reaction, which shall then enhance the yield of the reaction. This is also beneficial in achieving a green reaction in terms of principle 6, since using a larger amount of reactant ($NaBH_4$) improves reaction rate and reduces reaction time. However, it is doubtful and ambiguous in Lecher's report whether full conversion can be attained when $NaBH_4$ used less than 50% excess. This is therefore one aspect of my investigation.

Although using higher amounts of excess $NaBH_4$ would potentially lead to benefits in the yield and rate of reaction, it is unfavourable to use large amounts of excess $NaBH_4$ based on principles 2, 3 and 12. The conflict between the two aspects leaves an unanswered question as to what the optimum green conditions could be, in terms of amount of $NaBH_4$ used. The focus of my investigation is therefore to achieve a balance between the two conflicts, which seeks to answer the question:

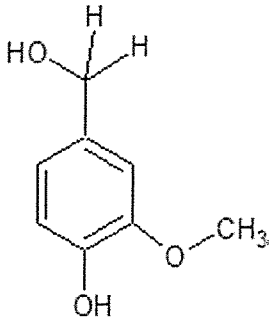
"What is the compromising reaction stoichiometry in a green synthesis of vanillyl alcohol from the reduction of vanillin using sodium borohydride?"

Background Information

Reaction Mechanism



Structure 1 – Vanillin molecule

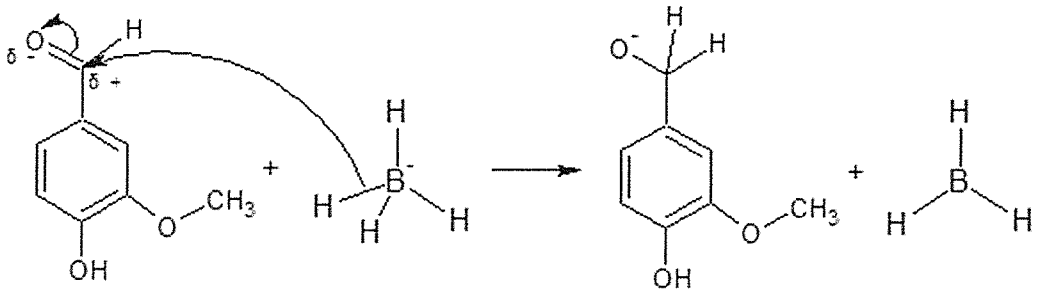


Structure 2 – Vanillyl alcohol molecule

Vanillin is a phenolic aldehyde with a carbonyl group outside the benzene ring. The oxygen in the carbon-oxygen double bond is highly electronegative and draws electron density in the double bond towards itself. This results in a delta negative charge on the oxygen and a delta positive charge on the carbon. The carbon, with a delta positive charge, attracts negatively charged nucleophiles, which are BH_4^- ions in this case.

Nucleophilic attack by 'hydride' on vanillin as an aldehyde

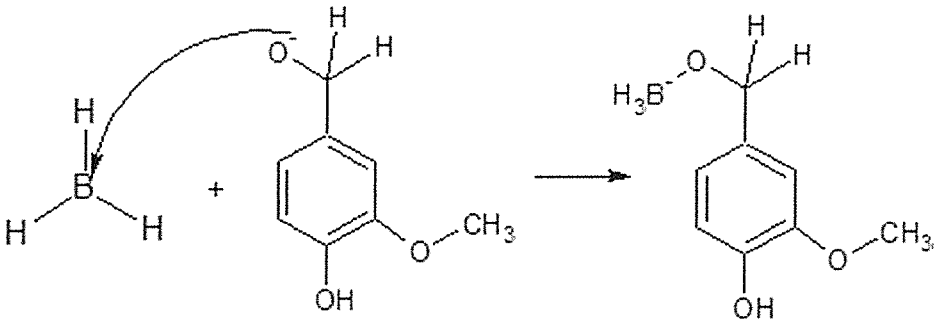
In organic chemistry, a reduction reaction occurs when there is a gain in hydrogen or electrons. Sodium borohydride, as a reducing agent, has 4 hydrogen atoms and is commonly believed that hydride ions (H^-) in $NaBH_4$ serve as nucleophiles. However, since H^- has a full 1s orbital, it is too small to interact with carbon's relatively diffused 2p orbital in the pi component of the carbon-oxygen double bond (Clayden, Greeves and Warren, 2012).[5]



Structure 3 Structure 4 - Borane

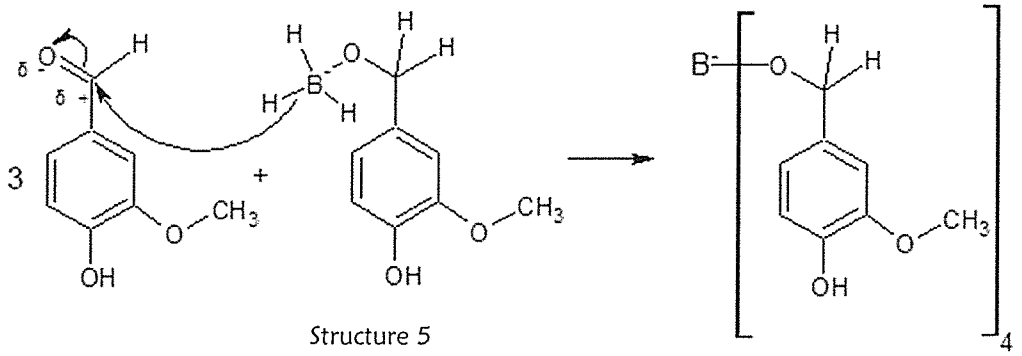
In the reaction, the BH_4^- ion acts as a nucleophile which is attracted to the delta positive carbon. A pair of electrons from the B-H bond, together with the hydrogen in the bond, is transferred to this carbon. This can be regarded as a 'hydride transfer'.

The formation of the new carbon bond forces the pi component in C=O bond to break. The bonded pair of electrons is transferred to oxygen. Oxygen now carries a negative charge.



Structure 4 - Borane Structure 3 Structure 5

Since boron does not have a noble gas structure on its outer shell, borane is electron-deficient. The negative oxygen in structure 3 stabilises borane by forming a new B-O bond. A negatively charged boron centre is regenerated, serving as another nucleophile.



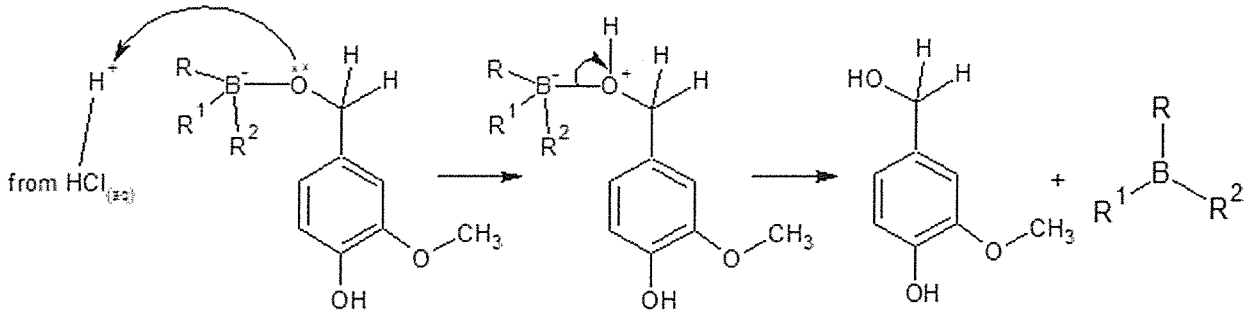
Structure 5 Structure 6 - tetraalkylborate

The negative boron centre in Structure 5 donates a "hydride ion" to another vanillin molecule. This process can continue until all 4 hydrogen atoms in a BH_4^- ion are transferred, giving structure 6 (Brown et. al., 2009) as the intermediate.[6]

Addition of Hydrochloric acid to stop the reaction

Hydrochloric acid is added to stop the reaction in the end to achieve three functions (Towson, n.d.):[7]

1. $HCl_{(aq)}$ hydrolyses the B-O bond in the intermediate and protonates the oxygen atom in structure 6, illustrated as follow:



Structure 2 - Vanillyl alcohol

2. $HCl_{(aq)}$ destroys any excess $NaBH_4$ that is left in the reaction mixture. It reacts with $NaBH_4$ as follow(Mayo, Pike, Forbes,2010)[8]:

$$4NaBH_4 + 2HCl + 7H_2O \rightarrow Na_2B_4O_7 + 2NaCl + 16H_2$$

Borax, $Na_2B_4O_7$, is hydrolysed to $Na_2B_4O_7{\cdot}10H_2O$, which further reacts with $HCl_{(aq)}$:

$$Na_2B_4O_7{\cdot}10H_2O + 2\ HCl \rightarrow H_3BO_3 + 2NaCl + 5H_2O$$

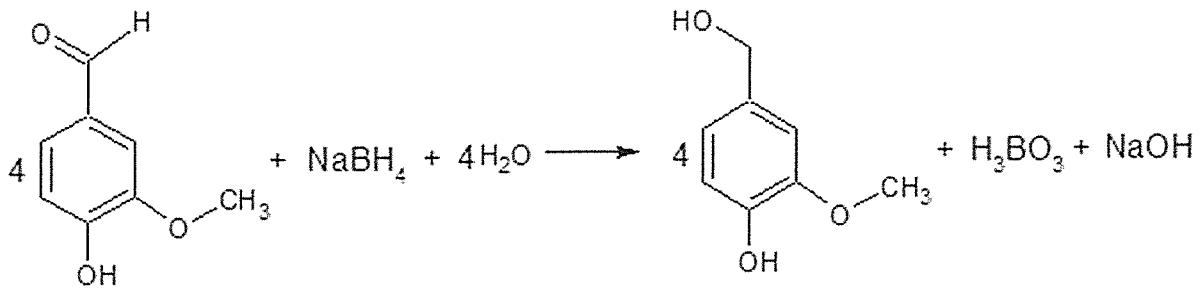
Boric acid is formed as a final product of the reaction and hydrogen is produced.

3. $HCl_{(aq)}$ neutralizes excess sodium hydroxide used as a solvent of $NaBH_4$. The equation is:

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(g)}$$

Overall Chemical Equation

In principle, if all 4 hydride ions of BH_4^- are 'transferred', each BH_4^- ion could reduce four vanillin molecules. The mole ratio of $NaBH_4$ to vanillin in the stoichiometric equation is therefore 1:4. The overall stoichiometry of reaction is given by the following equation:



Overall Equation of the reaction between vanillin and sodium borohydride

However, in reality, the reduction by $NaBH_4$ may not be so effective. Each BH_4^- ion cannot necessarily transfer all of its "hydride" ions to reduce four vanillin molecules. In addition, $NaBH_4$ sometimes decomposes or reacts with other solvents It is a common practice for chemists to use excess $NaBH_4$ to compensate (Lecher, 2007).[4]

Atom Economy of a reaction

Green Chemistry Principle 2 introduces the concept of Atom Economy.[9] This describes the conversion efficiency of a chemical process in terms of all atoms involved and desired products produced. Ideally, the amount of reactants equals the amount of desired products generated, so that no atom is wasted. It is calculated by the equation:

$$Percentage\ atom\ economy = \frac{molecular\ weight\ of\ desired\ product}{sum\ of\ molecular\ weight\ of\ all\ reactants} \times 100\%$$

Amount of $NaBH_4$ in excess	Stoichiometric ratio (vanillin: $NaBH_4$)	Sum of molecular weights of reactants	Molecular weight of desired product (vanillyl alcohol)	Atom Economy
0%	4:1	4 x 152 + 1 x 38 = 646	154	23.8%
25%	4:1.25	4 x 152 + 1.25 x 38 = 655.5	154	23.5%
50%	4:1.5	4 x 152 + 1.5 x 38 = 665	154	23.1%
75%	4:1.75	4 x 152 + 1.75 x 38 = 674.5	154	22.8%
100%	4:2	4 x 152 + 2 x 38 = 684	154	22.5%

Table 1 Atomic economy of reactions with different stoichiometric ratios

The table above illustrates the range of independent variables, including 0%, 25%, 50%, 75% and 100% excess $NaBH_4$. The stoichiometric ratio in terms of vanillin to $NaBH_4$ is varied with respect to the amount of $NaBH_4$ used in each reaction. The reaction with 100% excess $NaBH_4$ has the lowest atom economy since it uses the highest amount of reactant ($NaBH_4$). The higher the atom economy, the more green the reaction. This explains why the reaction with 0% excess $NaBH_4$ is the greenest in terms of Principle 2.

Hypothesis

Conversion and Yield:

It is hypothesised that optimum conversion of vanillin would occur in reactions with 50% to 100% excess $NaBH_4$ and reactions may not reach full conversion when $NaBH_4$ is in 0% to 50% excess. Since the yield should be proportional to the degree of conversion of the reaction, it is also hypothesised that optimum yield would be achieved at the highest conversion.

Reaction time:

It is expected that the reaction with 100% excess $NaBH_4$ would take the shortest time to reach full conversion. According to the collision theory, the concentration of when more amount of $NaBH_4$ reacts, the chance of collisions between BH_4^- ions and vanillin molecules is higher.

Results and Discussion

Development of methodology

Design of methodology

The method of the experiment was mostly based on that of the Lecher's (2007) experiment conducted on the same reaction.[4] Some amendments were made to cater the focus of my investigation as well as the scope of chemicals and apparatus in my school laboratory. Below is a table comparing my methodology to Lecher's methodology.[4]

Lecher's Methodology	My methodology (Appendix 3)
The amount of $NaBH_4$ used was constant throughout the experiment.	Since the independent variable of my investigation is the stoichiometric ratio of the vanillin to $NaBH_4$, the amount of of $NaBH_4$ used in each reaction from 0% excess, 25% excess, 50% excess, 75% excess and 100% excess. Each amount of $NaBH_4$ used corresponds to the stoichiometric ratios of vanillin to $NaBH_4$: 4:1, 4:1.25, 4:1.5, 4:1.75 and 4:2, where the 4:1 ratio is the original reaction stoichiometry.
Infrared and NMR spectroscopies were used to identify the product	My school laboratory did not have these instruments. Ultraviolet-visible spectrometer and Thin layer chromatography analysis were used instead.

In addition, since the reaction time of each reaction is the dependent variable of my investigation, thin layer chromatography on samples taken at regular time periods was conducted. This obtained information regarding the progress of conversion of vanillin over time.

Procedure as it was carried out

The reaction with 100% excess $NaBH_4$ was first carried out. The time given for the reaction to occur was 10 minutes with samples of the reacting mixture collected at 2-minute intervals. The results of the TLC indicated vanillin was still present in the final product. Not all vanillin had been converted to vanillyl alcohol given the time of reaction (Appendix 5).

In the investigation, the reaction with 100% excess $NaBH_4$ has the most reactant of $NaBH_4$. The reaction should attain the highest conversion rate and the fastest reaction rate compared to the other reactions. The failure of this reaction to reach full conversion was attributed to the insufficient time for vanillin and $NaBH_4$ to react. I lengthened the reaction time of each reaction from 10 minutes to 18 minutes so that reactions could attain a higher reaction conversion rate. Samples were still taken at 2 minute intervals as indicated in step 14 of the methodology.

Furthermore, the reaction time for the reaction with 0% excess $NaBH_4$ was extended to 90 minutes. This was done to testify whether the reaction with 0% excess $NaBH_4$ would reach full conversion. Whether all the vanillin would be reacted given the $NaBH_4$ used, according to the original reaction stoichiometry, would be an indicator of whether $NaBH_4$ decomposes in the reaction.

Synthetic results

1. Results of Thin Layer Chromatography

Thin layer chromatography provides an analysis on chemicals in a sample. Wall (2005, P.1) states the principle of TLC that when the solvent front migrates through the sorbent, the components of the sample also migrate, but at different rates, resulting in separation.[10] The positions of the migrated components and solvent front could on be seen and marked when placed beneath the UV lamp.

Wall (2005, P. 70 -71) mentions that the retardation factor (R_f) of each component spot is:[10]

$$\frac{\text{Migration distance of component spot}}{\text{Migration distance of solvent front from origin}}$$

By comparing R_f of spots present, components of each sample can be differentiated. The chemical compositions of samples at different time intervals of the reactions are identified and compared. This gives information to the degree of conversion of the reaction.

The conditions of different TLC tests might vary since the TLC of samples from different reactions was carried separately. The same chemical may give a dissimilar retardation factor in two TLC tests given different test conditions. Thus, only results of samples on TLC plates in the same TLC test are compared. The results of the TLC analysis are represented by graphs with the sample tested on the x-axis and the retardation factor(s) of the spot(s) present on the y-axis. The spots in each TLC analysis are grouped and interpreted as the following:

Spots identified as vanillin

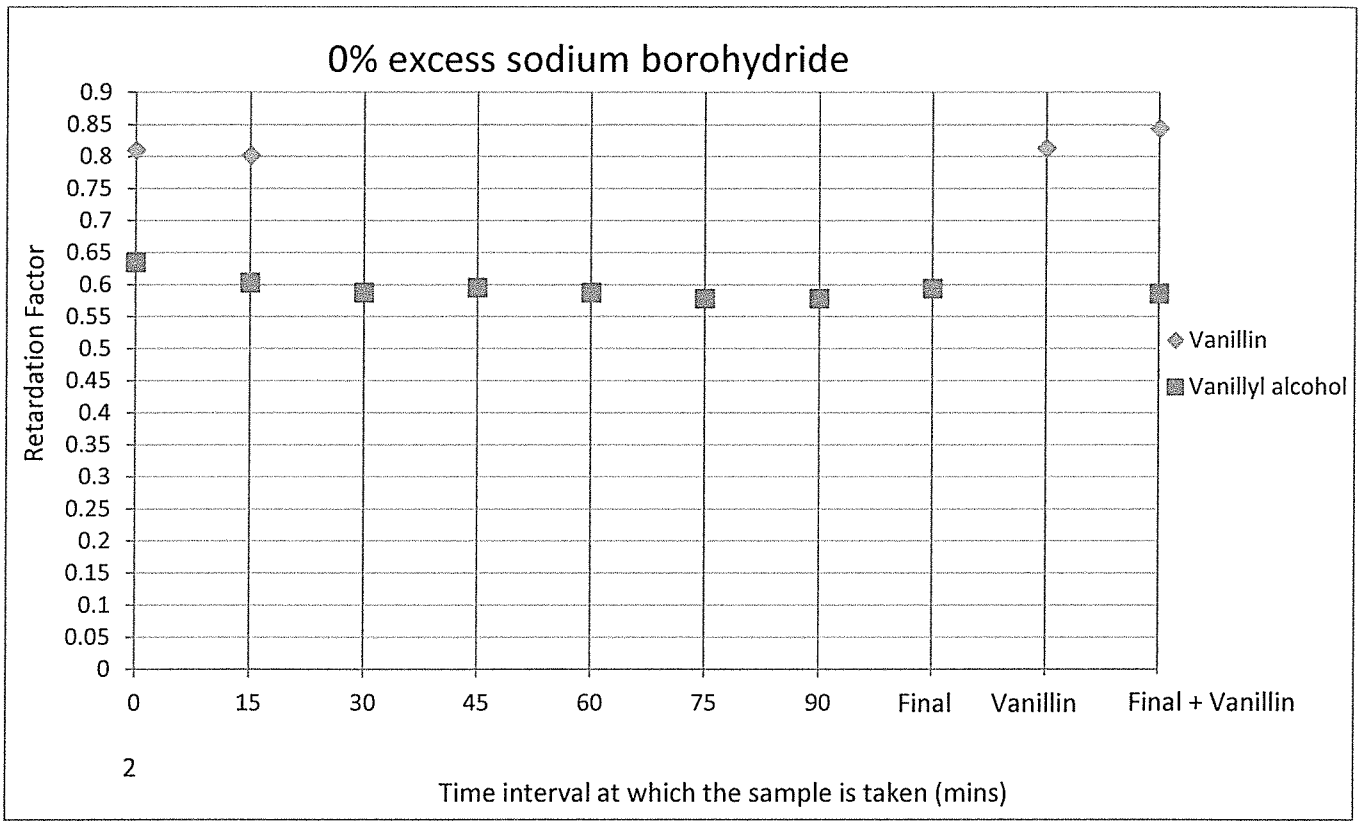
In the each of the TLC analysis, the retardation factor of the spot in the pure vanillin sample was first identified. Samples with spots that had retardation factors ±0.05 that of the spot in the vanillin sample are considered to contain vanillin.

Spots identified as vanillyl alcohol

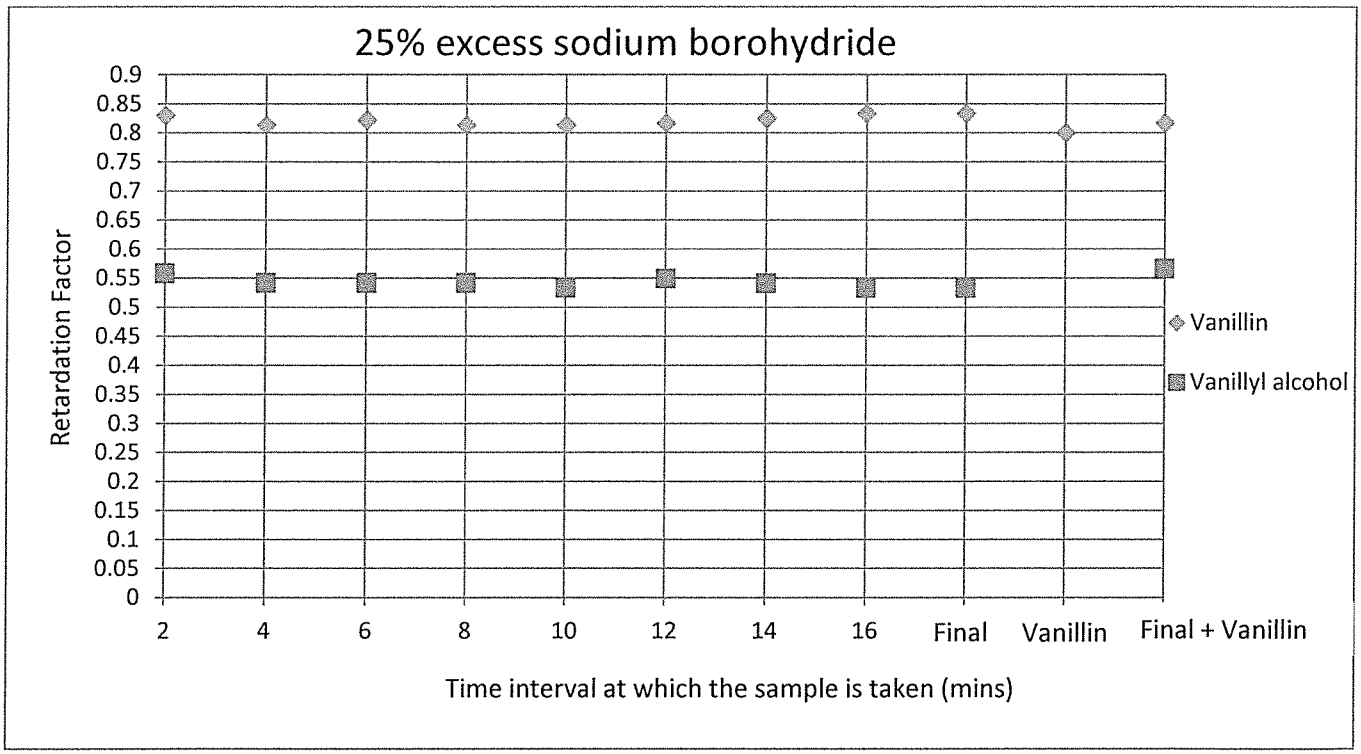
Other than the vanillin spots, another group of spots in each TLC analysis with retardation factors within the range of ±0.05 were identified. These spots were present in all samples except the sample with pure vanillin. Since these spots were present once the reaction started till the reaction ended, they were interpreted as the product of the reaction, vanillyl alcohol.

Spots identified as intermediate product

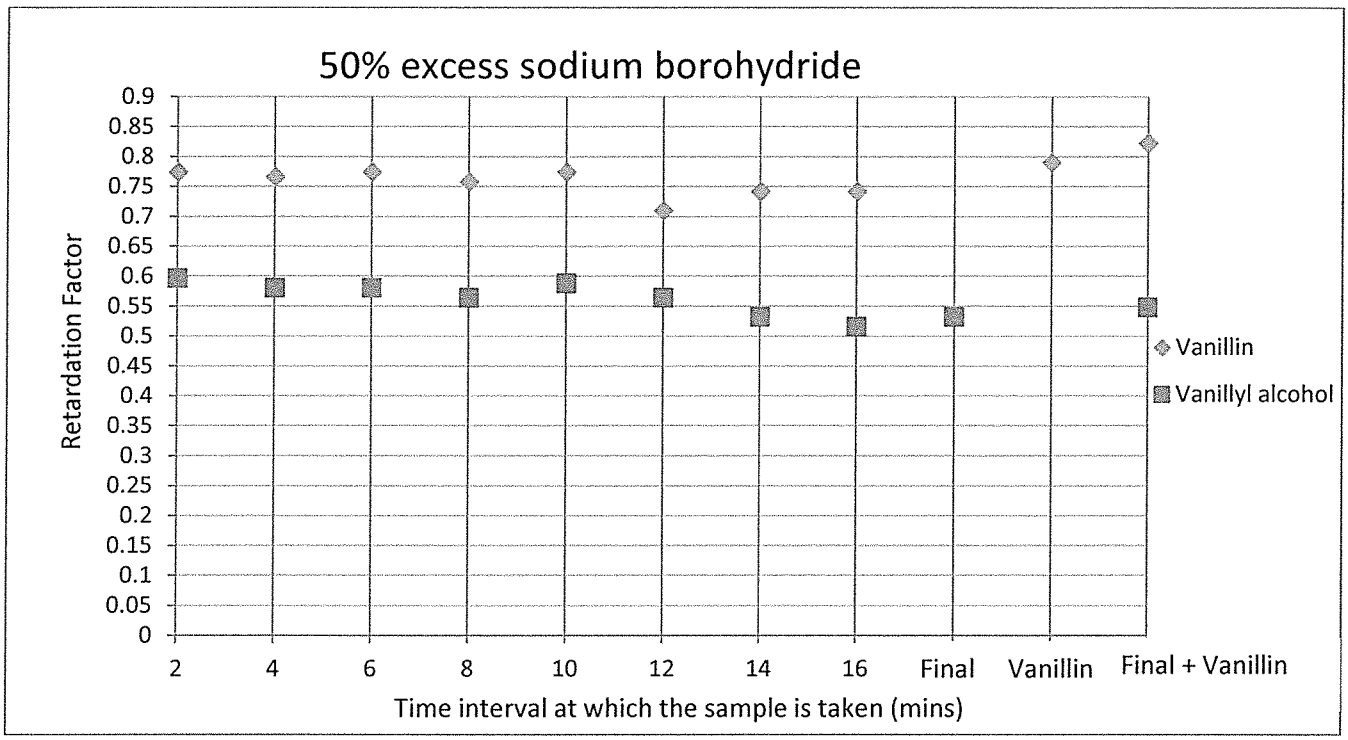
In 10-minute and 12-minute from the reaction with 100% excess $NaBH_4$, spots that neither belonged to vanillin nor vanillyl alcohol were identified. These were interpreted as an intermediate product formed during the reaction (Appendix 5).



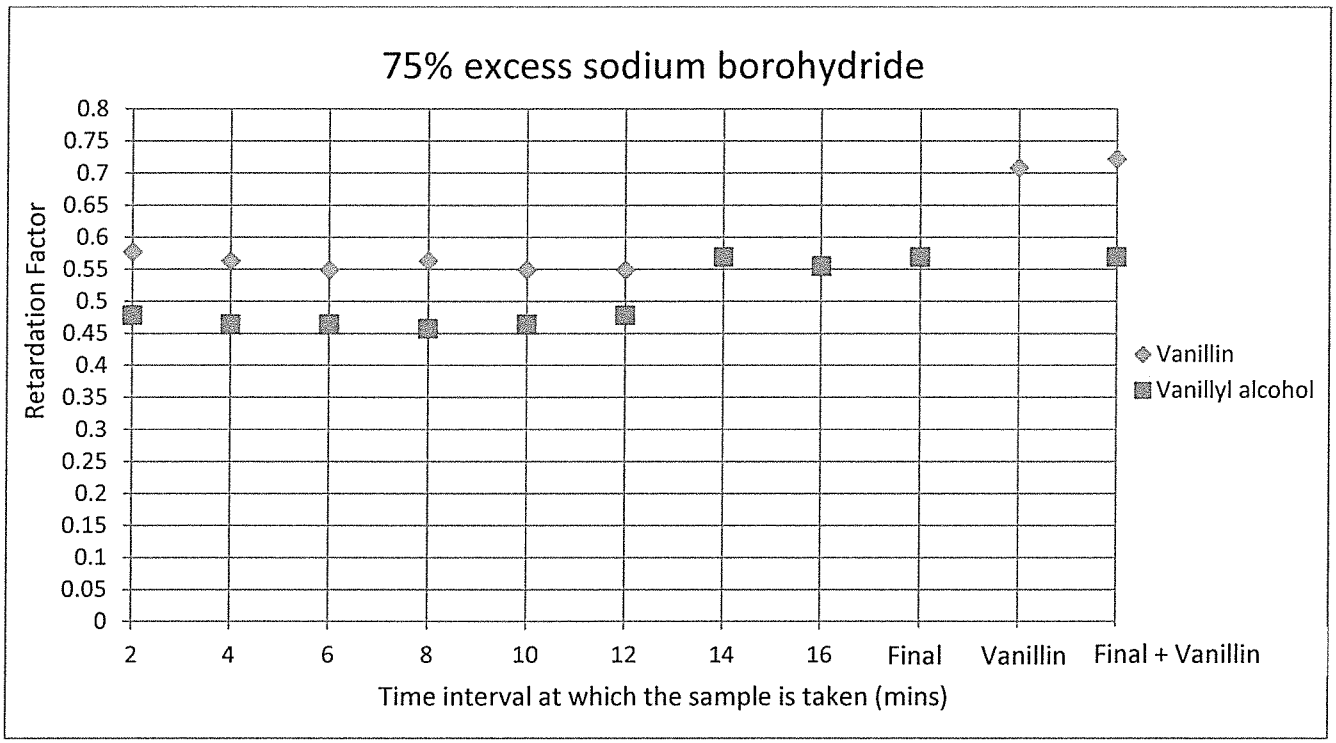
R_f of samples from the reaction with 0% of $NaBH_4$ in excess



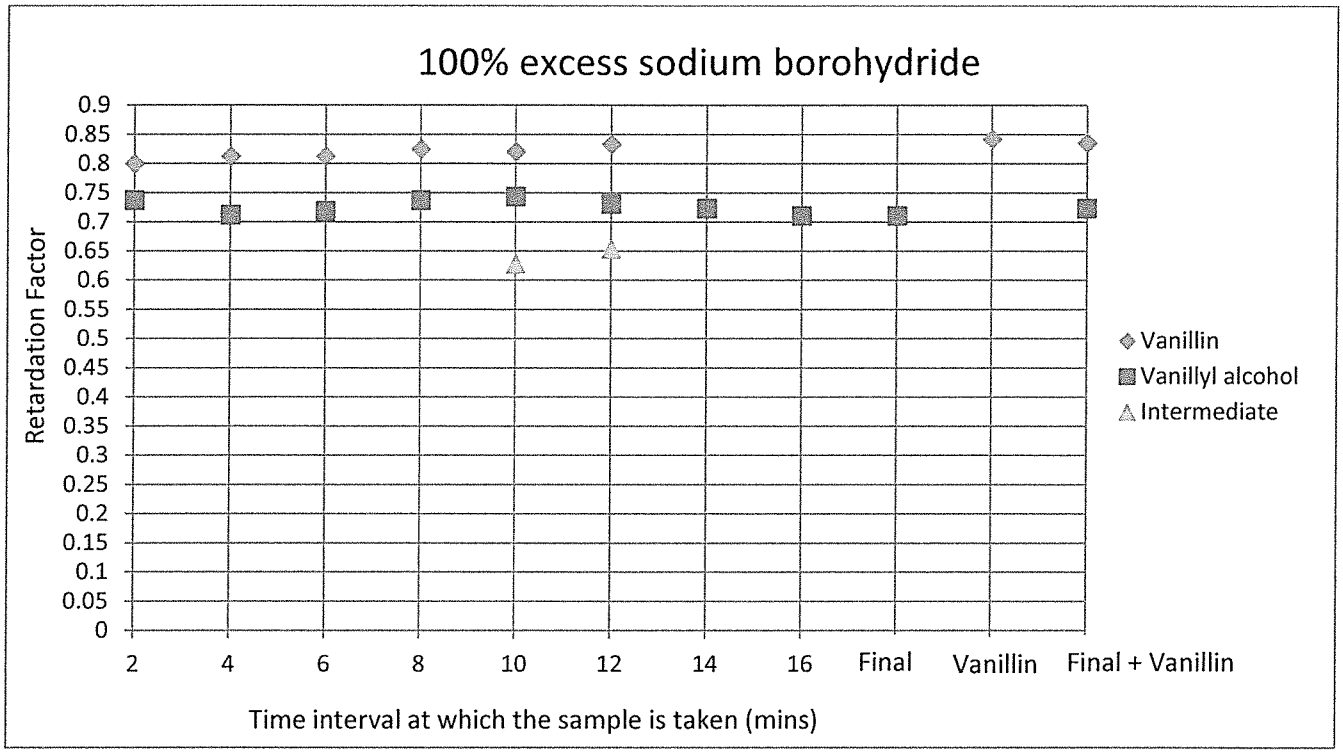
R_f of samples from the reaction with 25% of $NaBH_4$ in excess



R_f of samples from the reaction with 50% of $NaBH_4$ in excess



R_f of samples from the reaction with 75% of $NaBH_4$ in excess



R_f of samples from the reaction with 100% of $NaBH_4$ in excess

The results of the TLC analysis of each reaction are summarised in the table below. In the reaction with 100% excess $NaBH_4$, vanillin was last identified in the 12-minute sample. No vanillin appeared in samples taken after 14 minutes. This indicates that the vanillin was used up between 12 to 14 minutes. Hence, reaction had reached full conversion, with reaction time between 12 to 14 minutes.

Amount of $NaBH_4$ in excess	Sample which vanillin last appeared	Sample which vanillin disappeared	Did reaction reach full conversion? If yes, what was the reaction time?
0%	15-minute	30-minute	Yes, between 15 to 30 minutes
25%	Final product	N/A	No
50%	16-minute	Final product (18-minute)	Yes, between 16 to 18 minutes
75%	12-minute	14-minute	Yes, between 12 to 14 minutes
100%	12-minute	14-minute	Yes, between 12 to 14 minutes

Table 2 – Results of TLC analysis showing whether reaction reached full conversion and when full conversion occurred

Discussion of TLC results

Reaction Conversion with respect to the amount of $NaBH_4$ used

All reactions, except the reaction with 25% excess $NaBH_4$, reached full conversion. This did not agree with my hypothesis that optimum conversion can only be reached by reactions with 50% excess $NaBH_4$ or above.

The TLC analysis showed that the reaction with 0% excess $NaBH_4$ reached full conversion. Vanillin was used up in between 15 to 30 minutes given no excess amount of $NaBH_4$ was used. Full conversion was achieved and that disagreed with what Lecher (2007)[4] mentioned, $NaBH_4$ might decompose or react with other substances during the reaction. 0% excess $NaBH_4$ would be the minimum amount of NaBH4 required to achieve full conversion of vanillin.

Reaction Time

Reactions with 75% and 100% excess $NaBH_4$ both reached full conversion within 12 to 14 minutes, the least amount of time of all reactions. This partially agreed with the hypothesis, but samples should be taken out more frequently to differentiate the time difference between the two reactions. It is predicted that the reaction with 100% excess would reach full conversion earlier than that of 75%. The reaction with 100% excess $NaBH_4$ is the greenest in terms of Green Chemistry Principle 12[1].

In general, reactions reached complete conversion within the range of 12 to 30 minutes regardless the amount of $NaBH_4$ used. Reaction time did not quicken by a vast amount when more $NaBH_4$ was used. Since the reaction time was relatively short and the reaction conditions were moderate which did not require specifically high temperature or pressure, Green Chemistry Principle 12[1] may be a less important factor in the decision of a compromising amount of $NaBH_4$.

2. Percentage yield of vanillyl alcohol

According to the results, the reaction with 50% excess $NaBH_4$ attained the highest percentage yield, followed by the reactions of 0%, 100%, 75%, 25%.

The mass of the product is measured and considered as the actual yield. The percentage yield of each reaction is calculated by the equation:

$$percentage\ yield = \frac{Actual\ yield}{Theoretical\ yield}$$

Amount of $NaBH_4$ in excess	Mass of $NaBH_4$ used (g) ±0.01g	Mass of product (g) ±0.02g (Mass of product with filter paper – mass of filter paper)	Percentage yield $(\frac{Actual\ yield}{Theoretical\ yield})$
0%	0.10	0.93	60.4%
25%	0.12g	0.65	42.2%
50%	0.14g	0.98	63.6%
75%	0.17g	0.81	52.6%
100%	0.19g	0.91	59.1%

Table 3 - Results of the actual and percentage yields of vanillyl alcohol

My hypothesis suggested that the yield of a reaction should be proportional to the reaction conversion. The TLC analysis showed that most reactions reached full conversion; they should therefore give the same yield since the conversion was the same. Theoretically, equal amounts of vanillyl alcohol should be produced in the end of the reaction. The difference in yields signified a potential problem in the isolation of vanillyl alcohol, regardless of the amount of $NaBH_4$ used.

Further investigation to confirm the identity of the product

It was believed that the product from the reaction with 0% excess $NaBH_4$ was the purest out of products from all reactions since the reaction occurred for the longest time. The product from the reaction with 0% excess $NaBH_4$ was therefore chosen to undergo the identification tests.

Melting point Test

The melting point of vanillyl alcohol ranges from 110°C to 117°C according to various online sources, including ChemSpider[11], Sigma-Aldrich[12] and PubChem[13].

The melting point of the product from the 0% excess $NaBH_4$ reaction was obtained using the melting apparatus. The sample began to melt at 115°C. This lies within the range of melting point of vanillyl alcohol, indicating the sample of 0% in excess is quite pure.

The Ultraviolet-visible spectra of my product

The UV-vis spectrum of my product was compared with the UV-vis spectra of vanillin, the starting material of the reaction, and vanillyl alcohol, the designated product my reaction should yield. Two UV-vis spectra were referenced, including one from a research (Manners, 1965)[14] and one from a science journal (Carreira et. al. 2012).[15]

Both references identified peak absorbance of light at around 315nm for the vanillin spectra (Appendix 6). On the other hand, the spectra of vanillyl alcohol identified peak absorbance at 280 nm (Manners, 1965)[14] and at around 278 (Carreira et. al. 2012)[15] respectively. Both vanillyl alcohol spectra have nearly zero absorbance for light at wavelength of 300nm onwards.

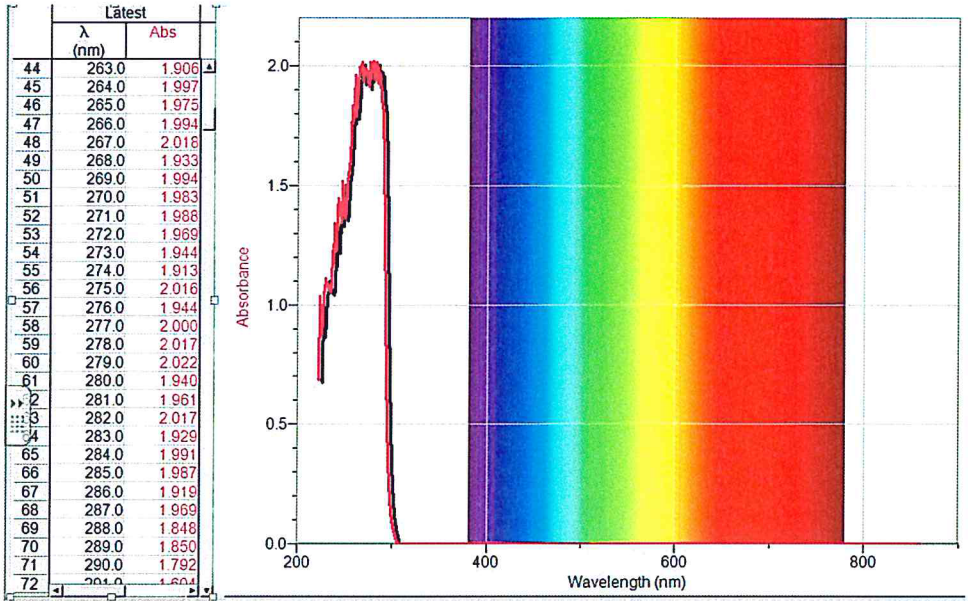


Figure 1 The UV-visible spectra of my sample product from the reaction with 0% excess $NaBH_4$

The UV-vis spectrum of my product had peaks at around 277nm to 279nm. The light absorbance also dropped to nearly zero straight after the wavelength of 300nm. Both characteristics correspond to the spectra of vanillyl alcohol from the two references. There spectra was nearly flat after 300nm. Since there was no peak at 315nm, there should be no vanillin in my product collected. The product I collected was quite pure of vanillyl alcohol.

Conclusion

"What is the compromising reaction stoichiometry in a green synthesis of vanillyl alcohol from the reduction of vanillin using sodium borohydride?"

The reaction with 0% excess $NaBH_4$ was the greenest reaction in terms of Green Chemistry principles 2, 3 and 12[1] since the least amount of hazardous reactant was used. My investigation proves that the reaction with 0% excess $NaBH_4$ could reach full conversion, just like the reaction with 100% excess $NaBH_4$. There is therefore no conflict between using a less amount of $NaBH_4$ and obtaining a high reaction conversion.

The results suggested that the reaction using 100% excess $NaBH_4$ took the least amount of time to reach full conversion. This reaction was hence the greenest in terms of Green Chemistry Principle 12[1] since the least amount of external energy would have to be supplied to this reaction given the shortest reaction time. However, since the reaction time for all reactions were relatively short (within 12 to 30 minutes) and the reaction conditions were moderate, Green Chemistry Principle 12 may be a less important factor in the decision of a compromising amount of $NaBH_4$.

Based on the results that the reaction could reach full conversion with no excess $NaBH_4$ used, and the difference in time of reaction of reaction between the reaction with 0% excess and 100% was not too significant, it is proposed that the compromising amount of sodium borohydride used in the synthesis of vanillyl alcohol should lie in the range of 0% to 50% excess. Since the stoichiometric ratio of vanillin to sodium borohydride is 4:1 according to the reaction equation, the compromising stoichiometry of vanillin to sodium borohydride would be 4:1 (0% excess) to 4:1.5 (50% excess).

Evaluation and Improvements

In evaluating and analyzing the results, a number of problems have been identified with the reliability of the concluding remarks. This section evaluates the random errors, systematic errors, as well as the reliability of sources involved in the investigation.

Random Errors

1. Mass measurements

Amount of $NaBH_4$ in excess	Percentage error in mass of vanillin	Percentage error in mass of $NaBH_4$	Percentage error in mass of product	Total Percentage error
0%	0.658%	10%	2.15%	12.8%
25%	0.658%	8.33%	3.08%	12.0%
50%	0.658%	7.14%	2.04%	9.83%
75%	0.658%	5.88%	2.47%	9.01%
100%	0.658%	5.26%	2.20%	8.12%

Table 4 - Percentage errors in mass measurements

The smallest unit of the electronic balance used for the mass measurements was ±0.01g. The total percentage errors were relatively large, ranging from 8.12% to 12.8%. The errors in mass measurements of $NaBH_4$ especially large since only small amounts were required.

Improvement: The electronic balance can be replaced by a milligram balance that measures up to 0.001g, or an analytical balance that measures up to 0.0001g. Using a more accurate balance reduces the huge uncertainties in small mass measurements. Another way to reduce this error is to enlarge the scale of the experiment. If the amounts of reactants used are increased in corresponding ratio, the same uncertainty would result in smaller percentage errors relative to larger measurements.

2. Imprecision in collection of samples at regular periods

   Samples of the reacting mixture were taken every 2 minutes in most reactions, and every 15 minutes in the reaction with 0% excess $NaBH_4$. The reaction time was measured based on the time period with vanillin last appeared in the sample and the next time period. Since most reactions that reached full conversion in 20 minutes, the random errors in reaction time were over 10% with 2-minute time intervals. In the reaction with 0% excess $NaBH_4$, the random error was over 50% in reaction time if the upper boundary of the reaction time (30 minutes) was taken.

   Improvement: If the samples of the reacting mixture were taken out every 30 seconds or even more frequently, more accurate measurements of time required to reach full conversion can be obtained. This will better differentiate the reaction time and hence the rates of different reactions.

3. **General Improvement on reliability of results:** The reaction for each amount of $NaBH_4$ used was only carried out once. Through repeating the experiment and obtaining more results, the reliability of the results obtained can great increase.

Systematic Errors:

1. From the TLC results, most reactions reached completion except for that with 25% excess $NaBH_4$. It has been proved that a reaction can reach full conversion regardless the amount of $NaBH_4$ in excess. A failure to reach full conversion would result in a smaller yield, as identified from the percentage yield of the reaction, 42.2%, which is significantly lower than those of all other reactions. This affected the fairness in deciding a compromising amount of $NaBH_4$ used is that not all reactions above reached full conversion in the given reaction time.

Improvement: The TLC analysis identified that all vanillin in the reaction with 0% excess $NaBH_4$ had reacted by 30 minutes. Since the reaction with 0% excess $NaBH_4$ was deemed to be the slowest, all other reactions should also reach full conversion given 30 minutes of reaction time. A proposed reaction time is 30 minutes to ensure all reaction reaches full conversion.

2. **General Improvement:** Liquid Chromatography–Mass Spectrometry can be used instead of TLC and the product identification tests. The chromatography of LCMS has high separation capability, allowing "pure" compounds to be introduced into the mass spectrometer with the identification capability of the mass spectrometer (Ardrey, P. 3, 2003).[16] By replacing TLC and the melting point test with LCMS, a more definitive identification and quantitative determination of the product can be obtained.

Reliability of sources

The references quoted in this essay are from sources including books, past research, journals and the internet. Some of the past research or experimental write up from the internet sources are self-published materials which have not been academically proven or gained authenticity yet. For instance, statements from Lecher's (2007) report[4], which one of my hypotheses was based on was proved untrue in my investigation. The reliability of self-published sources from the Internet is questionable.

Most of the sources in my investigation are reliable since they are known academic publications written by qualified experts and databases from widely adapted Chemistry websites such as PubChem and ChemSpider.

Unresolved questions

Reaction Yield

Why did the reactions that reached full conversion have different yields?

Theoretically, with vanillin being the limiting reagent, reactions above that reached full conversion should give the same yield of vanillyl alcohol. Yet, reactions in the above experiment had various yield and no obvious trend in the yields could be identified. It is suggested that the cause of greatly varying yields was in the isolation and purification of the product. This could confirm whether the highest yield obtained by the reaction with 50% of $NaBH_4$ in the experiment above was a coincident. The results of my investigation would be useful in the further investigation on the isolation of product since it proves that the yield of this reaction is not associated with the amount of $NaBH_4$ used.

Conversion Rate of the Reaction

What is the ratio of the vanillin to vanillyl alcohol as the reaction proceeds?

The TLC analysis only identified the presence of vanillin and vanillyl alcohol in the samples throughout the reaction. It did not show the amount of vanillin and vanillyl alcohol present. The LCMS mentioned in the evaluation could help answer this question.

Identification of the product

How can I be sure that the product obtained from the reaction was vanillyl alcohol?

There were only two tests that identified the product, the melting point and the UV-vis spectroscopy. A more reliable method of analysing the structure of the product would be conducting the NMR spectroscopy.

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Appendices

Appendix 1

12 principles of Green Chemistry from the ACS (American Chemistry Society), adapted from Green Chemistry: Theory and Practice (written by Paul Anastas and John Warner)

The Twelve Principles of Green Chemistry*

1. **Prevention**
   It is better to prevent waste than to treat or clean up waste after it has been created.
2. **Atom Economy**
   Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. **Less Hazardous Chemical Syntheses**
   Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. **Designing Safer Chemicals**
   Chemical products should be designed to effect their desired function while minimizing their toxicity.
5. **Safer Solvents and Auxiliaries**
   The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.
6. **Design for Energy Efficiency**
   Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure.
7. **Use of Renewable Feedstocks**
   A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.
8. **Reduce Derivatives**
   Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of

physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

9. **Catalysis**

   Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. **Design for Degradation**

    Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11. **Real-time analysis for Pollution Prevention**

    Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

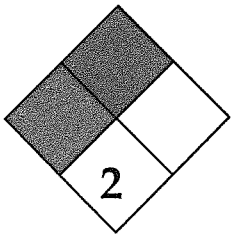
12. **Inherently Safer Chemistry for Accident Prevention**

    Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Appendix 2 – Material Safety Data Sheet of $NaBH_4$

http://www.sciencelab.com/msds.php?msdsId=9924969

ScienceLab.com
Chemicals & Laboratory Equipment



Health	3
Fire	4
Reactivity	2
Personal Protection	J

Material Safety Data Sheet Sodium borohydride MSDS

Section 1: Chemical Product and Company Identification

Product Name: Sodium borohydride

Catalog Codes: SLS4615

CAS#: 16940-66-2

RTECS: ED3325000

TSCA: TSCA 8(b) inventory: Sodium borohydride

CI#: Not available.

Synonym: Sodium tetrahydroborate

Chemical Name: Not available.

Chemical Formula: NaBH4

Contact Information:

Sciencelab.com, Inc.
14025 Smith Rd. Houston,
Texas 77396

US Sales: **1-800-901-7247**
International Sales: **1-281-441-4400**

Order Online: ScienceLab.com

CHEMTREC (24HR Emergency Telephone), call:
1-800-424-9300

International CHEMTREC, call: 1-703-527-3887

For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

Name	CAS #	% by Weight
Sodium borohydride	16940-66-2	100

Toxicological Data on Ingredients: Sodium borohydride: ORAL (LD50): Acute: 160 mg/kg [Rat].

Section 3: Hazards Identification

Potential Acute Health Effects:
Extremely hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Very hazardous in case of skin contact (corrosive). The amount of tissue damage depends on length of contact. Eye contact can result in corneal damage or blindness. Skin contact can produce inflammation and blistering. Inhalation of dust will produce irritation to gastro- intestinal or respiratory tract, characterized by burning, sneezing and coughing. Severe over-exposure can produce lung damage, choking, unconsciousness or death. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering.

Potential Chronic Health Effects:
Extremely hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. Very hazardous in case of skin contact (corrosive). CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Not available. TERATOGENIC EFFECTS: Not available. Developmental Toxicity: Not available. Repeated exposure of the eyes to a low level of dust can produce eye irritation. Repeated skin exposure can produce local skin destruction, or dermatitis. Repeated inhalation of dust can produce varying degree of respiratory irritation or lung damage. Repeated exposure to an highly toxic material may produce general deterioration of health by an accumulation in one or many human organs. Repeated or prolonged inhalation of dust may lead to chronic respiratory irritation.

Section 4: First Aid Measures

Eye Contact:
Check for and remove any contact lenses. Immediately flush eyes with running water for at least 15 minutes, keeping eyelids open. Cold water may be used. Do not use an eye ointment. Seek medical attention.

Skin Contact:
If the chemical got onto the clothed portion of the body, remove the contaminated clothes as quickly as possible, protecting your own hands and body. Place the victim under a deluge shower. If the chemical got on the victim's exposed skin, such as the hands : Gently and thoroughly wash the contaminated skin with running water and non-abrasive soap. Be particularly careful to clean folds, crevices, creases and groin. Cold water may be used. If irritation persists, seek medical attention. Wash contaminated clothing before reusing.

Serious Skin Contact:
Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek immediate medical attention.

Inhalation: Allow the victim to rest in a well ventilated area. Seek immediate medical attention.

Serious Inhalation:
Evacuate the victim to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. WARNING: It may be hazardous to the person providing aid to give mouth-to-mouth resuscitation when the inhaled material is toxic, infectious or corrosive. Seek immediate medical attention.

Ingestion:
Do not induce vomiting. Examine the lips and mouth to ascertain whether the tissues are damaged, a possible indication that the toxic material was ingested; the absence of such signs, however, is not conclusive. Loosen tight clothing such as a collar, tie, belt or waistband. If the victim is not breathing, perform mouth-to-mouth resuscitation. Seek immediate medical attention.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: Flammable.

Auto-Ignition Temperature: Not available.

Flash Points: Not available.

Flammable Limits: Not available.

Products of Combustion: Some metallic oxides.

Fire Hazards in Presence of Various Substances: Not available.

Explosion Hazards in Presence of Various Substances:
Risks of explosion of the product in presence of mechanical impact: Not available. Risks of explosion of the product in presence of static discharge: Not available.

Fire Fighting Media and Instructions:
Flammable solid. SMALL FIRE: Use DRY chemical powder. LARGE FIRE: Use water spray or fog. Cool containing vessels with water jet in order to prevent pressure build-up, autoignition or explosion.

Special Remarks on Fire Hazards: Not available.

Special Remarks on Explosion Hazards: Not available.

Section 6: Accidental Release Measures

Small Spill: Use appropriate tools to put the spilled solid in a convenient waste disposal container.

Large Spill:
Corrosive solid. Flammable solid that, in contact with water, emits flammable gases. Stop leak if without risk. Do not get water inside container. Do not touch spilled material. Cover with dry earth, sand or other non-combustible material. Use water spray to reduce vapors. Prevent entry into sewers, basements or confined areas; dike if needed. Eliminate all ignition sources. Call for assistance on disposal.

Section 7: Handling and Storage

Precautions:
Keep locked up Keep container dry. Keep away from heat. Keep away from sources of ignition. Ground all equipment containing material. Do not ingest. Do not breathe dust. Never add water to this product In case of insufficient ventilation, wear suitable respiratory equipment If ingested, seek medical advice immediately and show the container or the label. Avoid contact with skin and eyes Keep away from incompatibles such as oxidizing agents, acids, alkalis, moisture.

Storage:
Flammable materials should be stored in a separate safety storage cabinet or room. Keep away from heat. Keep away from sources of ignition. Keep container tightly closed. Keep in a cool, well-ventilated place. Ground all equipment containing material. Keep container dry. Keep in a cool place.

Section 8: Exposure Controls/Personal Protection

Engineering Controls:
Use process enclosures, local exhaust ventilation, or other engineering controls to keep airborne levels below recommended exposure limits. If user operations generate dust, fume or mist, use ventilation to keep exposure to airborne contaminants below the exposure limit.

Personal Protection:
Splash goggles. Lab coat. Vapor and dust respirator. Be sure to use an approved/certified respirator or equivalent. Gloves.

Personal Protection in Case of a Large Spill:
Splash goggles. Full suit. Vapor and dust respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits: Not available.

Section 9: Physical and Chemical Properties

Physical state and appearance: Solid.

Odor: Not available.

Taste: Not available.

Molecular Weight: 37.84 g/mole

Color: White. Grayish white.

pH (1% soln/water): Not

available. **Boiling Point:** Not

available. **Melting Point:**

Decomposes.

Critical Temperature: Not available.

Specific Gravity: 1.074 (Water = 1)

Vapor Pressure: Not applicable.

Vapor Density: 1.3 (Air = 1)

Volatility: Not available.

Odor Threshold: Not available.

Water/Oil Dist. Coeff.: Not

available. **Ionicity (in Water):** Not

available.

Dispersion Properties: See solubility in water.

Solubility: Easily soluble in cold water.

Section 10: Stability and Reactivity Data

Stability: The product is stable. **Instability**

Temperature: Not available. **Conditions of**

Instability: Not available. **Incompatibility**

with various substances:
Extremely reactive or incompatible with oxidizing agents, acids, alkalis, moisture. The product reacts violently with water to emit flammable but non toxic gases.

Corrosivity: Non-corrosive in presence of glass.

Special Remarks on Reactivity: Not available.

Special Remarks on Corrosivity: Not available.

Polymerization: No.

Section 11: Toxicological Information

Routes of Entry: Eye contact. Inhalation. Ingestion.

Toxicity to Animals: Acute oral toxicity (LD50): 160 mg/kg [Rat].

Chronic Effects on Humans: Not available.

Other Toxic Effects on Humans:
Extremely hazardous in case of skin contact (irritant), of ingestion, of inhalation. Very hazardous in case of skin contact (corrosive).

Special Remarks on Toxicity to Animals: Not available.

Special Remarks on Chronic Effects on Humans: Not available.

Special Remarks on other Toxic Effects on Humans: Not available.

Section 12: Ecological Information

Ecotoxicity: Not available.

BOD5 and COD: Not

available. **Products of**

Biodegradation:
Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.

Toxicity of the Products of Biodegradation: The products of degradation are as toxic as the original product.

Special Remarks on the Products of Biodegradation: Not available. **Section 13: Disposal Considerations**

Waste Disposal:

Section 14: Transport Information

DOT Classification: CLASS 4.3: Material that emits flammable gases on contact with water.

Identification: : Sodium borohydride : UN1426 PG: I

Special Provisions for Transport: Not available.

Section 15: Other Regulatory Information

Federal and State Regulations: TSCA 8(b) inventory: Sodium borohydride

Other Regulations: OSHA: Hazardous by definition of Hazard Communication Standard (29 CFR 1910.1200).

Other

Classifications:

WHMIS (Canada):
CLASS D-1B: Material causing immediate and serious toxic effects (TOXIC). CLASS D-2B: Material causing other toxic effects (TOXIC).

DSCL (EEC):
R14- Reacts violently with water. R25- Toxic if swallowed. R34- Causes burns.

HMIS (U.S.A.):

Health

Hazard: 3

Fire
Hazard: 4

Reactivity: 2

Personal Protection: j

National Fire Protection Association (U.S.A.):

Health: 3

Flammability: 4

Reactivity: 2

Specific hazard:

Protective

Equipment:
Gloves. Lab coat. Vapor and dust respirator. Be sure to use an approved/certified respirator or equivalent. Wear appropriate respirator when ventilation is inadequate. Splash goggles.

Section 16: Other Information

References: Not available.

Other Special Considerations: Not available.

Created: 10/09/2005 06:30 PM

Last Updated: 06/09/2012 12:00 PM

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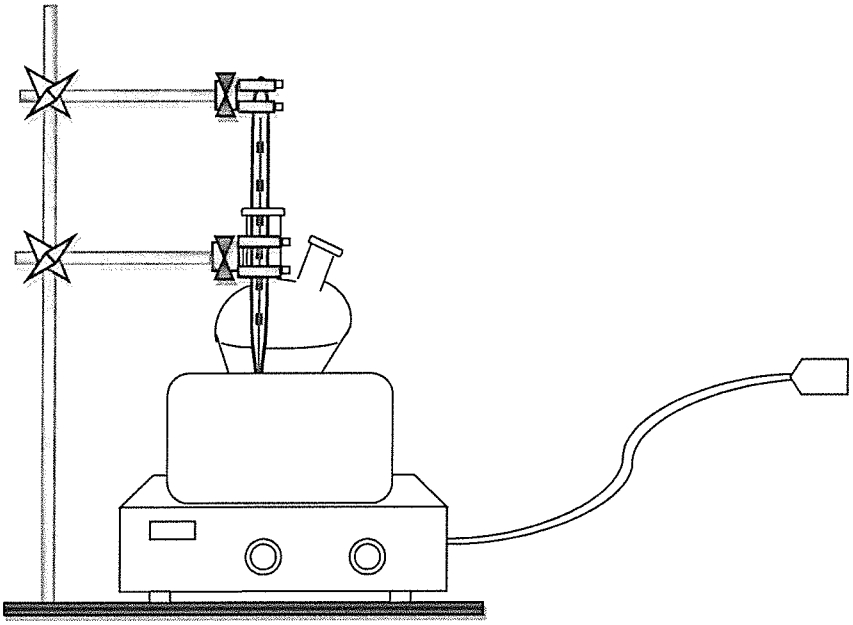
Appendix 3

Method

The literature suggested that using 50-100% excess sodium borohydride would increase the reaction rate and potentially the yield. The amount of sodium borohydride in excess is the independent variable of the experiment, and the amount of sodium borohydride used ranges from 0%, the original stoichiometric ratio, 25%, 50%, 75%, and 100%. At the same time, sample of the reacting mixtures are taken out for thin layer chromatography (TLC). The TLC test was conducted in order to show the approximate reaction time required for the reaction to happen.



Preparation and addition of reactants

1. Vanillin (1.52g, 0.999mol) is weighed and dissolved in $3cm^3$ of ethanol to give a concentration of $500gdm^{-3}$.
2. Sodium borohydride is dissolved in sodium hydroxide; the amount of $NaBH_4$ dissolved varies in each reaction while the amount of sodium hydroxide used is kept constant ($2.5cm^3$). By such, the amount of $NaBH_4$ in excess is different in each run.
3. Put an ice bath on top of the magnetic stirrer. The vanillin dissolved is transferred to a pear shaped flask which is secured in an ice bath with a stand and clamp. A thermometer is inserted to the vanillin solution through one of the mouths of the flask and is held by a clamp. The set-up is let to cool down to give room for rise in temperature when the reaction occurs.
4. The stirrer bar from the magnetic stirrer is added to the solution. Switch on the magnetic stirrer to ensure smooth and even stirring.
5. Add $2.5cm^3$ $NaBH_4$ solution dropwise to the vanillin solution across a time period of 2 minutes which $0.5cm^3$ of $NaBH_4$ is added using a dropper every 30 seconds (adding at

0 sec, 30 sec, 60 sec, 90 sec, 120 sec).

6. Since $NaBH_4$ decomposes upon higher temperatures and the reaction is highly exothermic, the temperature of the reacting solution has to be closely monitored to ensure that the temperature does not rise above 25°C. Ice should be added to the ice bath if the temperature comes close to 25°C

End point of the reaction and collection of product

7. At about 12 minutes after the addition of $NaBH_4$, remove the solution from the ice bath. Stir the reaction at room temperature for 5 minutes to ensure that the reaction has gone to completion.
8. Return the solution to the ice bath. Add 3M hydrochloric acid drop wise until hydrogen gas is no gas is evolved upon further adding.[2] The function of the hydrochloric acid is to kill $NaBH_4$ to stop the reaction from carrying on. Check with the universal indicator that the solution is now acidic. Reaction has now stopped.
9. Cool down the product with stirring in the ice bath for 10 minutes. A precipitate will form.
10. Collect the precipitate by vacuum filtration. Before the filtration, measure the weight of the filter paper placed on the filter.
11. With small portions of ice-cold deionised water transfer the precipitate into the filter funnel by rinsing the glass flask and washing the product. Wash the precipitate with the water. After the vacuum is applied, allow the solid to dry on the vacuum for about 2 minutes.
12. Air dry the product in the fume hood for at least 24 hours.
13. Weigh the dried product. Make sure to account for the weight of the filter paper.

Separation of reaction mixture as reaction proceeds for TLC to show degree of completion

14. At the same time, as the reaction proceeds, dip a glass rod into the reacting solution every two minutes[3] and place the glass rod with sample into a boiling tube. Add hydrochloric acid to the sample in the boiling tube immediately to stop the reaction.
15. The samples collected at 2-minute time intervals together with the final product and vanillin have to be dissolved for thin layer chromatography. Vanillin is soluble and dissolved in ethanol as stated above. The product, vanillyl alcohol, can also be dissolved in ethanol. The samples collected at 2-minute time intervals can also be dissolved in ethanol since they potentially contain both vanillin and vanillyl alcohol which are both soluble in ethanol.
16. Conduct thin layer chromatography. Dip all samples onto the silicon slits and put the silicon slits into a beaker with solvent of ethyl acetate and hexane mixed in a 2:3 ratio.

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[2] The gas is hydrogen evolved when

[3] At 2, 4, 6, 8, 10, 12, 14, 16 minutes after the start of addition of $NaBH_4$.

Cover the beaker with a watch glass and allow the solvent to ascend. Monitor the silicon slit and take out the silicon slit when the solvent front nearly reaches the end of the slit.

17. Dry the silicon slit. Under the UV lamp, mark the position, size and shape of the chemicals moved up.

Appendix 4 - Raw Data Table showing the masses of product and reactant used in different reactions

	Mass of vanillin used (g) ±0.01g	Mass of $NaBH_4$ used (g) ±0.01g	Mass of filter paper carrying vanillyl alcohol (g) ±0.01g	Final mass of product with filter paper ±0.01g
Run 1 – 0% excess	1.52	0.10	0.35	1.28
Run 2 – 25% excess	1.52	0.12	0.35	1.00
Run 3 – 50% excess	1.52	0.14	0.35	1.33
Run 4 – 75% excess	1.52	0.17	0.33	1.14
Run 5 – 100% excess	1.52	0.19	0.33	1.24

Appendix 5 – Raw results of the TLC tests

The reaction with 0% excess $NaBH_4$

Time	Distance of solvent front travelled (±0.5mm)	Distance of spot 1 travelled (±0.5mm)	Distance of spot 2 travelled (±0.5mm)	Retardation factor of spot 1	Retardation factor of spot 2
2	63.0	51.0	40.0	0.809524	0.634921
15	63.0	50.5	38.0	0.801587	0.603175
30	63.0		37.0		0.587302
45	63.0		37.5		0.595238
60	63.0		37.0		0.587302
75	64.0		37.0		0.578125
90	64.0		37.0		0.578125
Final Product	64.0		38.0		0.59375
Vanillin	64.0	52.0		0.8125	
Final Product + Vanillin	64.0	54.0	37.5	0.84375	0.585938

The reaction with 25% excess $NaBH_4$

Time	Distance of solvent front travelled (±0.5mm)	Distance of spot 1 travelled (±0.5mm)	Distance of spot 2 travelled (±0.5mm)	Retardation factor of spot 1	Retardation factor of spot 2
2	59.0	49.0	33.0	0.830508	0.559322
4	59.0	48.0	32.0	0.813559	0.542373
6	59.0	48.5	32.0	0.822034	0.542373
8	59.0	48.0	32.0	0.813559	0.542373
10	59.0	48.0	31.5	0.813559	0.533898
12	60.0	49.0	33.0	0.816667	0.55
14	60.0	49.5	32.5	0.825	0.541667
16	60.0	50.0	32.0	0.833333	0.533333
Final Product	60.0	50.0	32.0	0.833333	0.533333
Vanillin	60.0	48.0		0.8	
Final product + Vanillin	60.0	49.0	34.0	0.816667	0.566667

The reaction with 50% excess $NaBH_4$

Time	Distance of solvent front travelled (±0.5mm)	Distance of spot 1 travelled (±0.5mm)	Distance of spot 2 travelled (±0.5mm)	Retardation factor of spot 1	Retardation factor of spot 2
2	62	48.0	37.0	0.774194	0.596774
4	62	47.5	36.0	0.766129	0.580645
6	62	48.0	36.0	0.774194	0.580645
8	62	47.0	35.0	0.758065	0.564516
10	62	48.0	36.5	0.774194	0.58871
12	62	44.0	35.0	0.709677	0.564516
14	62	46.0	33.0	0.741935	0.532258
16	62	46.0	32.0	0.741935	0.516129
Final Product	62		33.0		0.532258
Vanillin	62	49.0		0.790323	
Final product + Vanillin	62	51.0	34.0	0.822581	0.548387

The reaction with 75% excess $NaBH_4$

Time	Distance of solvent travelled (±0.5mm)	Distance of spot 1 travelled (±0.5mm)	Distance of spot 2 travelled (±0.5mm)	Distance of spot 3 travelled (±0.5mm)	Retardation factor of spot 1	Retardation factor of spot 2	Retardation factor of spot 3
2	71		41.0	34.0	0.577465	0.577465	0.478873
4	71		40.0	33.0	0.56338	0.56338	0.464789
6	71		39.0	33.0	0.549296	0.549296	0.464789
8	71		40.0	32.5	0.56338	0.56338	0.457746
10	71		39.0	33.0	0.549296	0.549296	0.464789
12	71		39.0	34.0	0.549296	0.549296	0.478873
14	72		41.0			0.569444	0.569444
16	72		40.0			0.555556	0.555556
Final Product	72		41.0			0.569444	0.569444
Vanillin	72	51.0			0.708333		
Final product + Vanillin	72	52.0	41.0		0.722222	0.569444	0.569444

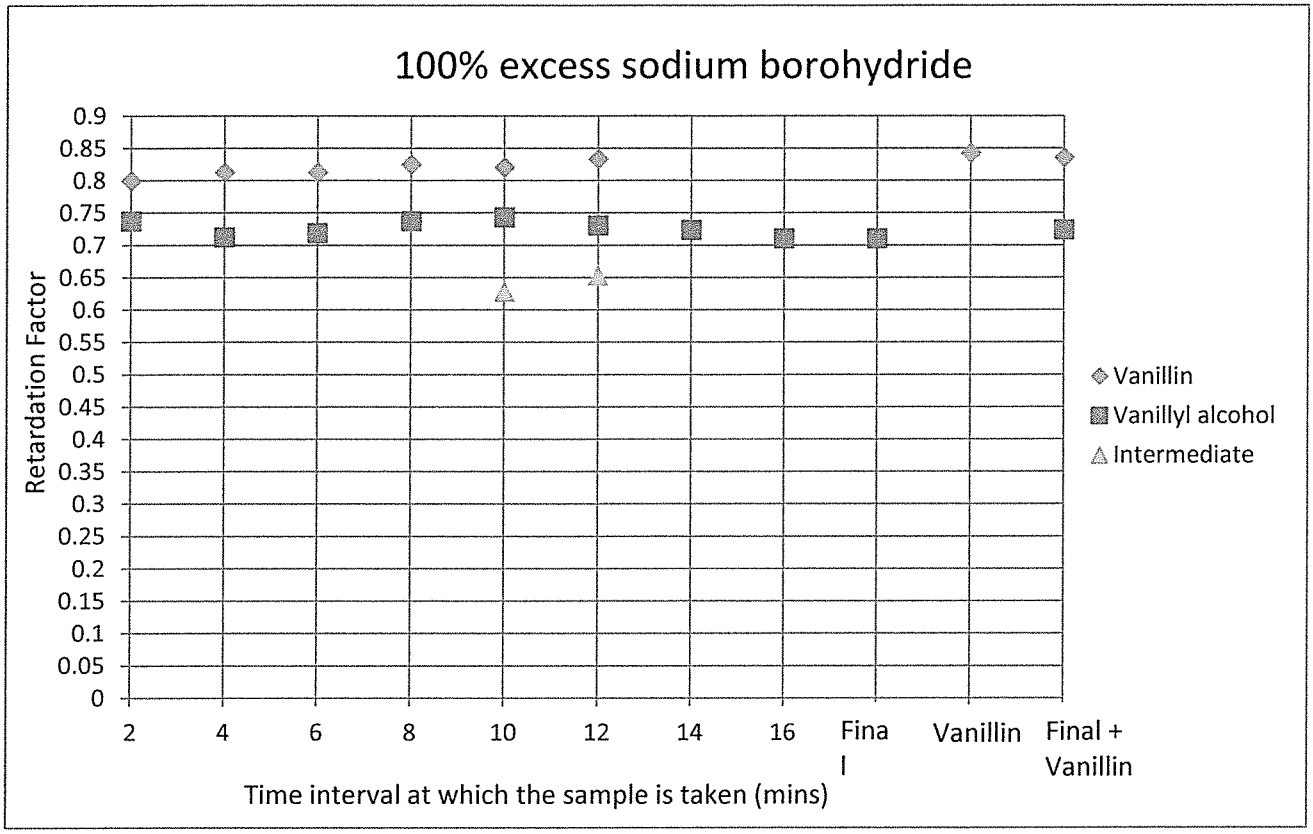
Reaction with 100% of $NaBH_4$ in excess (1st trial)

Time	Distance of solvent front travelled (±0.5mm)	Distance of spot 1 travelled (±0.5mm)	Distance of spot 2 travelled (±0.5mm)	Retardation factor of spot 1	Retardation factor of spot 2
2	57	44	34	0.77193	0.596491
4	57	42	33	0.736842	0.578947
6	57	42	34	0.736842	0.596491
8	57	44	34	0.77193	0.596491
Final Product	57	44	35	0.754386	0.614035
Vanillin	57	43		0.77193	
Final product + Vanillin	57	44	35	0.77193	0.614035

For the reaction with 100% of $NaBH_4$ in excess (2nd trial),

Time	Distance of solvent travelled (±0.5mm)	Distance of spot 1 travelled (±0.5mm)	Distance of spot 2 travelled (±0.5mm)	Distance of spot 3 travelled (±0.5mm)	Retardation factor of spot 1	Retardation factor of spot 2	Retardation factor of spot 3
2	80	64	59		0.8	0.7375	
4	80	65	57		0.8125	0.7125	
6	80	65	57.5		0.8125	0.71875	
8	80	66	59		0.825	0.7375	
10	78	64	58	49	0.820513	0.74359	0.628205
12	78	65	57	51	0.833333	0.730769	0.653846
14	76		55			0.723684	
16	76		54			0.710526	
Final Product	76		54			0.710526	
Vanillin	76	64			0.842105		
Final product + Vanillin	76	63.5	55		0.835526	0.723684	

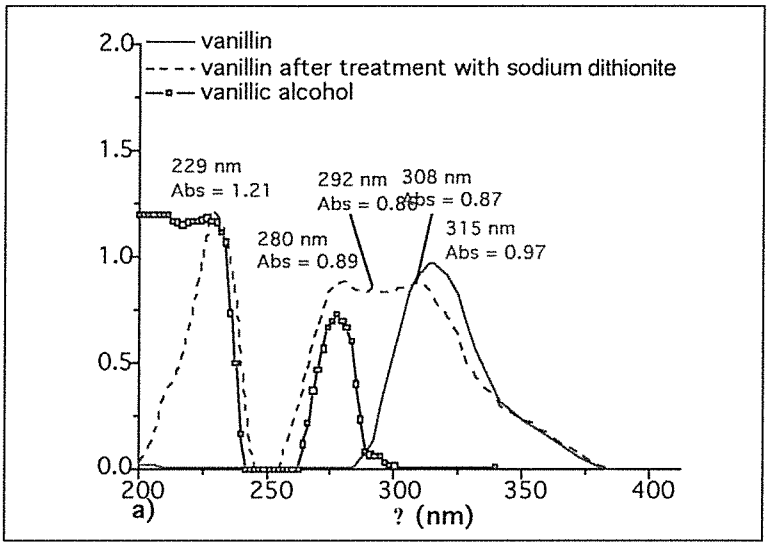
Appendix 5 – Identification of the intermediate product



A substance that is neither vanillin nor the product was present in the 10-minute and 12-minute samples. This is believed to be an intermediate product formed in the reaction. Since vanillyl alcohol is more polar than vanillin and vanillyl alcohol had smaller retardation factors than those of vanillin which identify that more polar sorbents tend to have smaller retardation factors in this TLC analysis. Since the intermediate product identified in this reaction has a retardation factor smaller than that of vanillyl alcohol, this could possibly be a molecule with a more electronegative group.

Appendix 6 - UV-Vis Spectra of Vanillin

1) UV-Vis spectrum of vanillin and vanillic alcohol (vanillyl alcohol) from Reductive degradation of residual chromophores in kraft pulp with sodium dithionite (Carreira, H.J.M. et. al.,2012)[15]



5. UV-vis spectra of vanillin (model 5), before and after treatment with sodium dithionite, and of vanillic alcohol.

2) UV-Vis spectrum of vanillin and vanillyl alcohol from *The Chemical Composition Of The Bark Extractuves Of Four Species Of The Genus Pseudotsuga* (Manners, 1965)[14]

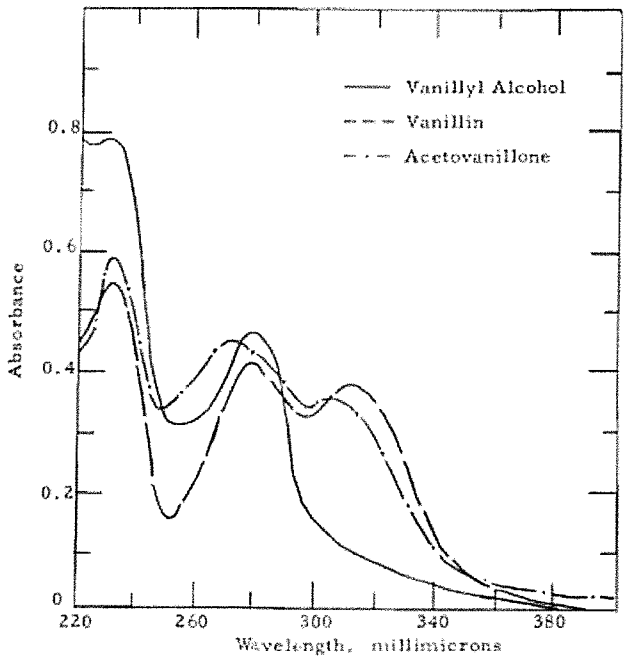


Figure 6 - The ultraviolet absorption spectra of vanillyl alcohol, vanillin and acetovanillone isolated from the ethyl alcohol and water extracts of all species and determined in 95 percent ethyl alcohol.