

Lab 3

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LAB 3:

Preparation of Methyl-3-nitrobenzoate and Nitroguanidine

L6 -Advanced Chemistry of OME (ACDA6020)

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Appendix: Methodology

this is a detailed, well built ToC; all relevant sections are included (except Methodology in Appendix) and the report is structured properly

Table of Equations ???

Table of figures ???

Aim

This experiment aims to prepare two nitrated compounds, Methyl-3-nitrobenzoate and Nitroguanidine. This is done through the process of nitration and will show how energetic compounds from propellants to high explosives are manufactured at a lab scale for the OME industry and the importance of using the correct process to ensure a safe product.

Hypothesis

It is hypothesised that methyl benzoate will undergo nitration under the conditions of the experiment; the nitro group, forming methyl 3-nitrobenzoate. In the nitration of Guanidine, the nitric acid will react with the guanidine and attach to one of the nitrogen atoms in the molecule to become nitroguanidine.

Both nitration reactions will be slow reactions, as they must be kept under specific temperatures to avoid runaway reactions. At a lab scale, the predicted yield is around 60-80%.

Variables

Control – volume of reactants, reaction temperature, reaction time, stirring rate, cooling method, starting material

Independent – starting reactants, identity and purity, glassware and filtration technique
reaction temperature, addition rate of the nitrating mixture, reagent ratios,

Dependant – mass of nitrated compound, recrystallisation solvent volume
yield, purity

Theory

Methyl-3-nitrobenzoate

Methyl Benzoate undergoes an Electrophilic Aromatic Substitution to form methyl-3-nitrobenzoate. This happens with nitric acid and sulphuric acid are mixed, as the sulphuric acid is stronger, it donates a hydrogen to nitric acid, forming H_2NO_3^+ , then as this is an unstable molecule, it forms the **nitrenium** ion and water [1]. The overall reaction is shown below:

Equation 1 - Formation of the electrophile [2]



The products from this reaction are added slowly in small quantities to the methyl benzoate. The nitrenium ion is positively charged and is the electrophile in this reaction, as it wants to gain electrons from the methyl benzoate. The benzene ring contains a cloud of delocalised electrons, which is why the positive electrophile is attracted towards it. Two delocalised electrons form a bond to the electrophile, giving the benzene ring an overall positive charge.[3] In the second part of the reaction, the HSO_4^- from products shown in equation 1, this negatively charged ion is attracted to the positive benzene ring and takes the hydrogen from the benzene ring to reform sulphuric acid. The following shows the steps of the mechanisms, where the arrows represent the movement of electrons: [4]

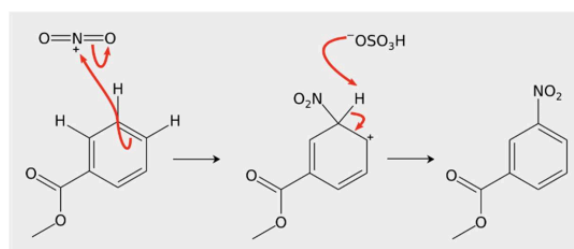


Figure 1 - Mechanism for nitration of Methyl Benzoate to Methyl-3-Nitrobenzoate [5]

This reaction is highly exothermic and produces large amounts of heat. This, however, can speed up the reaction and cause runaway reactions that are difficult to control, as the heat can cause it to react faster. To stop this, the reaction mixture and reactants are kept in an ice bath to keep it below 10 degrees, and reactants cannot be added until it cools back to 5 degrees

low temperature controls the product formed

Once the reaction is complete, the product is dissolved in ethanol at warm temperatures and left to cool. As it cools, crystals form; the ethanol helps promote this formation as well as dissolving some of the impurities in the solution. [6]

If the reaction was started using toluene instead of methyl benzoate, then di-nitrotoluene would be created when this is nitrated further, tri-nitrotoluene would be formed, which is also known as TNT.

Nitroguanidine

Nitroguanidine is an energetic ^{compound} ~~composition~~ that is used in triple base propellants, which are used most in artillery systems to give the product propulsion [7].

This reaction only uses a high concentration of sulphuric acid as well as guanidine nitrate. The sulphuric acid breaks down the nitrate ion in guanidine nitrate to form NO₃⁻, which is negatively charged. This is a negatively charged ion that will be used as a nucleophile for the reaction. The positive charge on the attracts the nucleophile charge at the end of the double bond. The nucleophile then offers electrons to the nitrogen ion in NH₂. This makes an overall positive charge with the 2 hydrogens. The sulphuric acid ion negative charge then takes the two positively charged hydrogen back and reforms as sulphuric acid and water. [8]

This reaction is exothermic, so to avoid over-nitration forming dangerous, highly sensitive chemicals, the reaction is kept below 10 degrees in an ice bath where the reactants are added slowly in small amounts and only when the temperature reduces to 5 degrees. [9]

Equation 2 - equation for the conversion of guanidine nitrate to nitroguanidine



The explanation of nitroguanidine formation contains significant mechanistic errors. The nitrate ion is not a nucleophile in this reaction. In concentrated sulphuric acid, nitrate is activated to a highly electrophilic nitrating species, which is attacked by the nucleophilic nitrogen in guanidine. Sulphuric acid acts as a strong acid and dehydrating agent, facilitating N-nitration and proton transfer. The reaction is nitrogen-centred nitration and should not be described using electrophilic aromatic substitution language.

Observations/Data

methyl-3-nitrobenzoate:

Before looking at the yield for the experiment, the theoretical yield can be calculated using the following equation. The results are shown below:

Equation 3 - Theoretical Yield

$$\text{theoretical yield} = \text{mass of methyl benzoate} \times \frac{M_r(\text{methyl 3-nitrobenzoate})}{M_r(\text{methyl benzoate})}$$

Mr of Methyl-3-nitrobenzoate = 181.15

Mr of Methyl benzoate = 136.15

$$\text{theoretical yield} = 2.699 \times \frac{181.15}{136.15}$$

$$\text{theoretical yield} = 2.699 \times 1.3305$$

$$\text{theoretical yield} = 3.5910$$

The masses collected are shown below in the table

Table 1 - methyl-3-nitrobenzoate results

Mass of methyl benzoate	2.699
Mass of the labelled glass bottle	8.639
Mass of labelled glass bottle + dried sample	10.153
Mass of methyl-3-nitrobenzoate	1.514 <i>units are missing</i>

Using these, a % yield can be calculated by comparing the actual vs the theoretical yield shown below

Equation 4 – yield question

$$\% \text{ yield} = \frac{\text{Actual yield}}{\text{Theoretical yield}} \times 100$$

$$\% \text{ yield} = \frac{1.514}{3.5910} \times 100$$

$$\% \text{ yield} = 42.2\%$$

Nitroguanidine:

The results from the experiment are shown in the table below

Table 2 - results for nitroguanidine

Mass of labelled bottle	83.730
Mass of labelled glass bottle + dried NQ	85.399
Mass of NQ	1.669

The percentage yield is then calculated using the equation below

Equation 5 - yield calculation for nitroguanidine

$$\% \text{ yield} = \frac{\text{Mass of NQ}}{4} \times \frac{122}{104} \times 100$$

$$\% \text{ yield} = \frac{1.669}{4} \times \frac{122}{104} \times 100$$

$$\% \text{ yield} = 0.417 \times 1.173 \times 100$$

$$\% \text{ yield} = 48.9\%$$

all calculations are correct

Results and Discussion

The synthesis of the Nitroguanidine and Methyl-3-Nitrobenzoate yields 48.9% and 42.2% respectively. These are very low yields for the materials. It was hypothesised that the experiment would have low yields; however, these are much lower than the expected amount, but the desired products were still produced.^[Ref] *this statement should be supported by literature*

The amount of the reactants used was lower in the initial reaction, which could have caused a higher likelihood of a low yield, as small amounts of product are lost while the solutions are transferred between vessels would have a greater impact on the results. The Buchner flask used could have drawn through some of the product; however, this is not expected to cause the yield to drop to 40%. Therefore, there is another factor involved.

For methyl-3-nitrobenzoate, the reaction requires strong acids to form the electrophile if these are not strong enough. The product is also slightly soluble in water, so when it is washed in the Buchner flask, some of the product can be lost. [3]

Another factor could be the temperature of the reaction, as they are exothermic. As there is a higher likelihood of forming unwanted products if the temperature gets too high, if the reactants are added too quickly, then the temperature gets too high, there is a higher likelihood of runaway reactions and over-nitrating, which can be dangerous. *good point*

The final factor to consider is the time it takes for all the products to form the solution is left to sit before the reaction takes place to form these crystals. If the reaction is not complete when it is extracted from the solution, then the yield will decrease, as not all the product has had a chance to form.

Nitroguanidine when synthesised, forms brittle needle-like strands; these become incredibly sensitive if they are snapped. When the product is pressed into a pellet, it can form voids and is more likely to snap. These two factors make the product less stable, making it more dangerous to handle and may not perform as expected, which poses a safety risk. Because of this, a very controlled process of breaking these crystals on purpose is done, so when they press, they are more compacted and less likely to get voids. This also makes the product more sensitive; however, if all are gridded, then it is much more

predictable, and performance is more consistent. Impurities in the product can also cause a more sensitive product; these can come from the original reactants or over-nitration during synthesis. The most likely impurity is unreacted guanidine nitrate. [7]

Error in this experiment can be due to measurement error and loss of product during transfer from one vessel to another, as well as allowing the temperature to get too high. - product losses during transfer, washing, and recrystallisation are noted but not chemically justified or quantified - temperature control and over-nitration are identified, but the explanation lacks mechanistic depth - discussion of nitroguanidine crystal morphology and grinding shows safety awareness but is weakly linked to purity and yield

Conclusions

The product's synthesis of the Nitroguanidine and Methyl-3-Nitrobenzoate, but with a much lower yield than expected this is most likely due to products lost in solvents and incomplete reaction times. If the product was manufactured with too many impurities, then the output could be a lot more susceptible than expected making it much more dangerous to handle and a change in performance of the overall system it is used in.

References (IEEE)

- [1] "Electrophilic substitution reactions can be used to introduce halogens or nitro (NO₂) groups onto a benzene ring,," *Senecalearning.com*, 2021. <https://senecalearning.com/en-GB/revision-notes/ib-diploma/chemistry/chemistry-ib-diploma-higher-level/6-5-1-electrophilic-substitution> (accessed Dec. 12, 2025).
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FINAL GRADE

61 / 100

GENERAL COMMENTS

Engagement with Literature 8/15

A reasonable range of sources is used to support background chemistry and applications; however, several claims are not adequately supported. In particular, statements describing the percentage yields as “very low” are not benchmarked against literature or expected laboratory values, and a supporting reference is missing. There are also inconsistencies and omissions in IEEE formatting, including incomplete reference details (access dates). Greater use of the literature to contextualise results, rather than only describe processes, would strengthen this section.

Knowledge and Understanding 9/20

The EAS mechanism for methyl-3-nitrobenzoate is shown, and the formation of the nitronium ion is described. However, key mechanistic terms (e.g. σ -complex) are not explained, and the roles of reagents and solvents are only partially justified. The explanation of NQ formation contains significant mechanistic errors: the nitrate ion is incorrectly described as a nucleophile, and the reaction is inappropriately discussed using EAS terminology. In reality, this is a nitrogen-centred nitration in which activated nitrating species attack nucleophilic nitrogen in guanidine, with sulphuric acid acting as a strong acid and dehydrating agent. These conceptual inaccuracies substantially limit the mark for this criterion.

Cognitive and Intellectual Skills 10/20

The report presents a clear aim and hypothesis, and there is awareness of safety considerations such as runaway reactions. However, variables are incomplete and not clearly distinguished. The discussion of yield losses identifies several relevant factors (scale, transfer losses, washing, temperature, reaction time), but the analysis is largely descriptive and repetitive. Factors are not prioritised, nor are they supported by chemical reasoning or literature comparison. The discussion of NQ crystal morphology and grinding shows good awareness of safety and performance, but it would benefit from clearer linkage to purity, yield, and experimental outcomes rather than extended narrative.

Practical Application Skills 22/30

All calculations are carried out correctly, and % yields are determined appropriately. Significant figures are generally handled well, though units are occasionally missing. Chemical equations are presented and balanced. Practical issues such as temperature control, recrystallisation losses, and grinding of nitroguanidine are recognised, indicating sound laboratory awareness, but the experimental implications could be explained more concisely and quantitatively.

Transferable Skills 12/15

The report is clearly structured with a detailed table of contents, and all required sections are present, except for a dedicated methodology section in the appendix. Presentation is clear, though minor spelling errors are present (e.g. toluene). Greater concision in the discussion section and more consistent technical language would improve overall clarity.

PAGE 1

PAGE 2

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Text Comment. Appendix: Methodology

Text Comment. ???

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PAGE 3

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PAGE 4

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PAGE 7

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