

ACDA6020 Lab Session 3: Nitration Reactions

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General Introduction

The lab session covered in this report covers two nitration reactions, the first is to synthesise methyl-3-nitrobenzoate and second is produce nitroguanidine. The report is broken into 2 sections covering each nitration separately.

PART A: Preparation of Methyl-3-Nitrobenzoate

1. Aim

To safely synthesise methyl-3-nitrobenzoate via nitration [1]. The Procedure for this experiment can be found in Annex A.

2. Hypothesis

The nitro group formed from the nitric and sulfuric acid is expected to attach to the benzene ring [2]. This is because the benzene ring is electron attracting, which directs incoming reactants.

The reaction is predicted to be highly exothermic. If the temperature is not maintained below 15°C (via ice bath), the yield is expected to be affected.

3. Variables

Independent	Temperature of the nitrating mixture, rate of addition of acid
Dependent	Mass of product
Controlled	Mass of methyl benzoate used, volume of concentrated H ₂ SO ₄ and HNO ₃

4. Theory & Mechanism

Step 1: $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \rightarrow \text{NO}_2 + \text{H}_2\text{O} + 2\text{HSO}_4$

Step 2: The benzene ring attracts the NO₂.

Role of Reagents:

- **H₂SO₄:** Catalyst and dehydrating agent.
- **HNO₃:** The nitrating agent.
- **Ethanol:** Solvent for purification.

5. Observations & Data

Name	Mass (g)
Mass of bottle	8.639
Mass of methyl benzoate	2.694
Molar mass of methyl 3 nitrobenzoate	136.15
Molar mass of methyl benzoate	181.15
Mass of bottle + Product	10.153
Product mass	1.514
Theoretical mass	3.584415
Percentage yield	42.238413

Yield = mass of product / (mass of methyl benzoate * (Molar mass of Methyl 3 benzoate/ molar mass of methyl benzoate))

6. Results & Discussion

The yield in this experiment was significantly impacted by operator error, during the final phase of the experiment where the reactant is separated it was washed by distilled water which washed away product which is why we see such as poor yield. This was due to the operators being unfamiliar with the process. The yield achieved was 42.2% of the theoretical max. Each step during this process is not 100% efficient and product/reactant is lost throughout therefore getting 100% is unrealistic in the real world.

7. Importance in OME: From Lab to Munitions

This applies to the OME industry as this is the process of producing TNT however to produce this you begin with toluene instead of methyl benzoate and do this process 3 times to produce MNT, DNT and finally TNT [3]. Following through the stages the reaction is increasingly difficult since each time the ring gets decreasingly reactive. This is also why the reaction must be kept cool as in the process of TNT the reaction could run away and increasing the risk of ignition.

PART B: Preparation of Nitroguanidine

1. Aim

To safely synthesise nitroguanidine via the nitration of a guanidine nitrate.

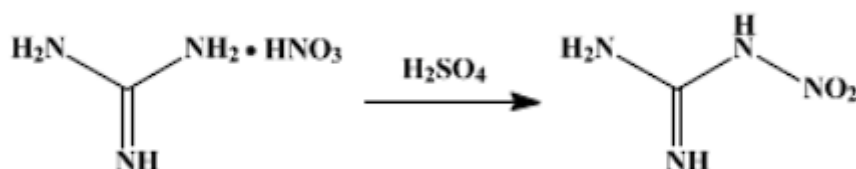
2. Hypothesis

In this experiment Guanidine nitrate is used as the foundation [4], the hydrogen atom is replaced by a NO₂ atom forming Nitroguanidine. This should form white crystalline solid. The procedure can be found in Annex B

3. Variables

Independent	Temperature of acid, Rate of addition reaction time
Dependent	Yield of Nitroguanidine
Controlled	Quantity of Sulfuric acid to the reaction

4. Theory & Mechanism



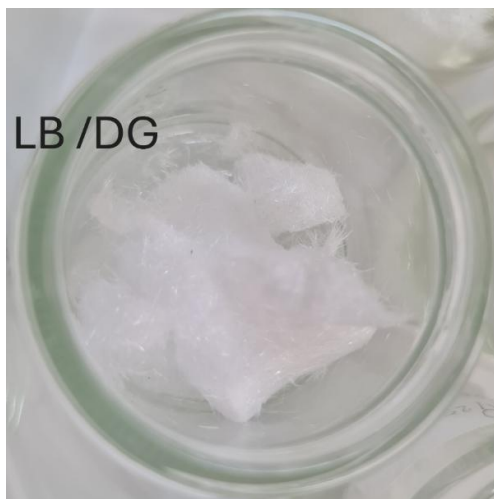
The experiment involved the nitration of Guanidine nitrate to produce nitroguanidine. Guanidine nitrate already contains the nitrate group needed so doesn't require nitric acid like the previous experiment. Sulfuric acid is used to enable the reaction and absorb the water produced to ensure the reaction kept occurring.

5. Observations & Data

Name	Mass (g)
Mass of bottle	83.73
Mass of Bottle + Dried sample	85.399
Mass of Guanidine nitrate	4
Mass of Nitroguanidine	1.669
Molar mass of Guanidine Nitrate	122.08
Molar mass of Nitroguanidine	104.07
Yield	48.945786%

$$\text{Yield} = (\text{mass of Nitroguanidine} / \text{Mass of Guanidine nitrate}) * (\text{Molar Mass of Nitroguanidine} / \text{Molar mass of Guanidine nitrate}) * 100$$

6. Results & Discussion



In industry this reaction would have yield of 85-90% [5] so this experiment was significantly below standard. However, this was to be expected as it was performed by students with little experience and time constricted environment. During the recrystallization process the crystals formed needle structure. Before the product can be used further it would be required to be ground down. The product was a clear white which suggests a pure product. If it was unpure, it would have a yellow/brown shade which would indicate contamination from the acid or guanidine nitrate.

7. Importance in OME: Propellants

Nitroguanidine is used to take propellant compounds from double base to triple [6] base, this propellant is primarily used in high calibre weapons. This is due to the reduce temperature of the deflagration improving barrel life and sustained firing rates. The product must be ground down from the needles to improve packing and consistency of burn rates [7].

Overall Conclusion

Overall, these experiments were successful in improving the understanding and practical knowledge of the students attending despite not the best yield being attained. A key improvement to the experiments would be greater temperature control and operator knowledge to increase the yield attained.

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Annex A – Methyl 3 Nitrobenzoate procedure

Reaction Procedure
ALL HANDLING OF ACIDS IS TO BE CARRIED OUT IN A FUME CUPBOARD (FC).
Label glassware appropriately throughout the practical.

- In a recrystallisation fume cupboard, weigh out 2.7g of methyl benzoate into a 250cm³ conical flask using a Pippet pipette.
- In the fume cupboard, measure out 5cm³ of concentrated sulfuric acid using a 10cm³ measuring cylinder, add to the methyl benzoate.
- Swirl the flask gently to mix and cool the mixture by placing the conical flask in ice.
- In a separate 50cm³ conical flask, prepare the nitrating mixture. Using a 10cm³ measuring cylinder, measure 2cm³ of conc. sulfuric acid and transfer to the conical flask labelled mixed acid.
- To this add 2cm³ of concentrated nitric acid, you can use the same measuring cylinder to measure both acids.
- Cool the mixed acids to 5°C by placing the conical flask in ice.

Turn the water bath on. During the nitration process make a note of any colour changes.

- When the methyl benzoate mixture reaches 5°C add the nitrating mixture drop by drop to the solution of methyl benzoate using a pipette, ensuring the nitrating mixture does not get into the rubber test.
- Stir the mixture with a glass rod keeping the temperature below 10°C. Allow the mixture to cool to 5°C between additions.
- When all the nitrating agent is added, leave the mixture to stand at room temperature for 15 minutes. This will be a very slow process for the first half of the mixed acid addition which will take ~1hr (due to the exothermic nature of the reaction) until equilibration when addition generates a lot less heat and addition is much faster.
- During the 15-minute waiting period weigh out ~25g of crushed ice and place in a 100cm³ beaker.
- Pour the reaction mixture from the conical flask onto the ice, stir until all the ice has melted and crystalline methyl-3 nitrobenzoate has formed.

Recrystallisation Procedure

- Move the filtration equipment from your bench into the ducted fume cupboard. Fit the Buchner funnel into a Buchner flask and clamp it to prevent it falling over. Place the filter paper in the Buchner funnel and damp with a little chilled, distilled water. Connect the flask to the vacuum line with the tubing supplied.
- Gently open the vacuum, pour the contents of the beaker into the filter funnel. Wash the crystals thoroughly with cold distilled water and remove excess water using the vacuum on high for 5 minutes.
- Transfer the crystals to a 50 cm³ beaker.
- Place 15 cm³ of ethanol into a small conical flask stand on the hot water bath to warm the ethanol to 50°C.

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- Place the beaker containing the sample on the water bath and pour small portions of the hot ethanol onto the crystals, stirring with a clean glass rod until the solid just dissolves.
- Remove the beaker from the water bath and place onto a white ceramic tile. Leave the solution to cool to room temperature then stir the beaker in ice water to allow the crystals of pure methyl nitrobenzoate to form.
- Place the used Buchner funnel & flask at the back of the fume cupboard. Set up a clean Buchner funnel and flask, with a clean filter paper in the funnel. Damp the filter paper with a small portion of ethanol before turning on the vacuum. Filter the product under vacuum, dry the product by leaving the vacuum on for a few minutes. Transfer the product into a labelled, weighed sample bottle.

Give the sample to a technician who will dry it in a vacuum desiccator overnight. After each weighing bottle and contents to calculate amount of product obtained. Carry out melting point investigation.

Disposal of materials

Spirit acid from the nitration step must be placed at the back of the ducted FC for a technician to dispose of.

Residual solvent from the purification step must be decanted into the waste solvent residue bottle supplied.

Methyl-3- nitrobenzoate to be handed to a technician, for drying in the vacuum desiccator

Questions

1. Had toluene been used as the starting material what are the three likely products?

MNT
DNT
TNT

2. Why keep the nitration mixture cool?

Stop run away
effects yield

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Annex B – Nitroguanidine Procedure

Reaction Procedure

1. In the fume cupboard, carefully measure out 5cm³ of concentrated sulphuric acid using the measuring cylinder. Pour into a 50cm³ beaker and place into the ice on the bench, taking care not to spill any acid. Using the thermometer wait for the temperature to fall below 5°C.
2. While the acid is cooling, weigh out 4 grams of guanidine nitrate into the weighing bottle.
3. When the acid has cooled, add small portions of guanidine nitrate with stirring to break up any solid lumps, ensuring that the temperature does not exceed 10°C.
4. When all the acid has been added, allow the mixture to stand for 2-3 minutes. Meanwhile place a filter paper into a Buchner funnel and damp it with a little distilled water. Clamp the Buchner flask, to prevent it falling over, and then fit the funnel to the flask using a rubber collar. Connect the flask to the vacuum line using the thick rubber hose.
5. After 2-3 minutes, pour out the mixture into a second 50cm³ beaker containing 30cm³ of water with a little ice and mix well with the glass rod. Ensure the product has fully precipitated by repeatedly pouring between the beakers.
6. Open the vacuum up and pour the contents of the beaker slowly into the funnel. Use a spatula to remove as much of your product from the beaker as possible.
7. Wash the crude product with a little cooled distilled water, then remove the water by vacuum filtration.

Recrystallisation Procedure

1. Transfer the crude product into a 150cm³ beaker. Add hot distilled water until the solid just dissolves, with stirring and heating on the boiling water bath.
2. When all the product has been dissolved remove the beaker from the heat, allow it to cool to room temperature, then place the beaker in the ice. Crystals of the product will begin to form as the solution cools.
3. Clean the Buchner flask and funnel and place a clean filter paper into the funnel.
4. When recrystallisation is complete filter the product under vacuum. Wash the material with a little cool distilled water and dry the product by maintaining the vacuum in the filter apparatus.
5. Transfer the partially dried product into a weighed labelled bottle.
6. Give your product to a member of staff, who will dry it under vacuum for the next practical class.
7. When the material is completely dried (next practical class) reweigh the bottle with its contents to calculate the amount of product obtained.

Disposal of materials

Diluted acid residues are to be washed down a fume cupboard sink.
Bottled nitroguanidine is to be handed to a technician for disposal.