

ACDA6020 LAB #3

Preparation of Methyl-3-Nitrobenzoate and nitroguanidine

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Introduction

As part of the Advanced Chemistry module students had the opportunity to visit Cranfield University's teaching laboratory at the Defence Academy of the United Kingdom (Shrivenham). Two syntheses were conducted: the nitration of methyl benzoate to form methyl-3-nitrobenzoate, and the nitration of guanidine nitrate. This report will detail the results of these syntheses and describe the processes involved.

Background

Methyl-3-nitrobenzoate

The synthesis of methyl-3-nitrobenzoate (M3NB) is closely related to the nitration of toluene (making TNT) but is non-energetic allowing a safe introduction to lab nitration.

To synthesize M3NB, first the nitrating mixture is prepared, this is a combination of nitric acid and sulphuric acid. The sulphuric acid donates a hydrogen atom [1] protonating the nitric acid [2], which decomposes to form nitronium ions (NO_2^+) and water. Figure 1 shows this process in detail.

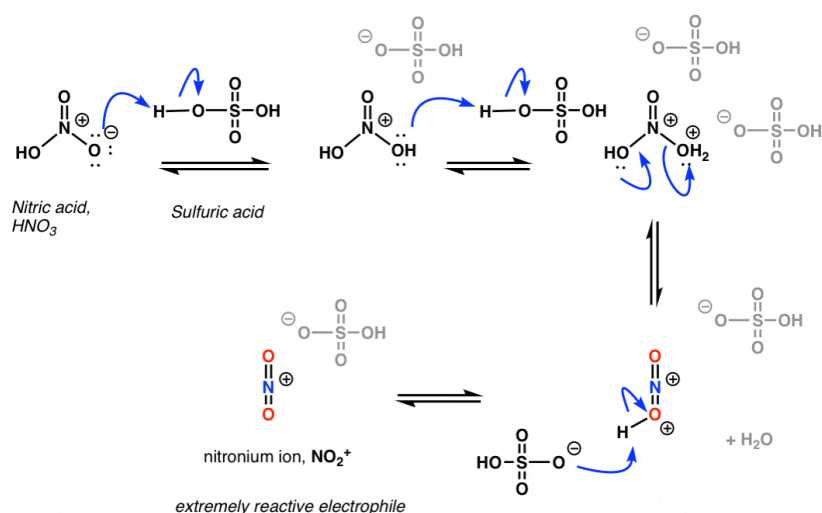


Figure 1 Full protonation of Nitric acid [2]

To this solution the methyl benzoate is added. This now undergoes Electrophilic Aromatic Substitution (EAS), forming Methyl 3 Nitrobenzoate. EAS involves:

- Electrophiles (Nitronium)
- Aromatic (Benzene ring)
- Substitution (exchanging hydrogen atom for the nitro group)

The full mechanism and EAS reactions can be seen below in Figure 2.

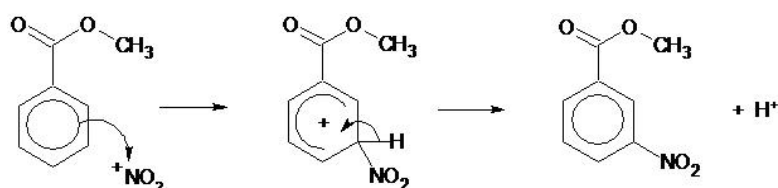


Figure 2 EAS nitration of Methyl Benzoate [3]

The remaining Hydrogen reacts with the Hydrogen sulphate reforming the sulphuric acid.

Ethanol is used as a solvent, allowing recrystallization of the M3NB– purifying the product.

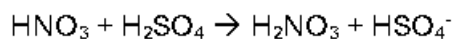
Variables:

Table 1 Variables for M3NB production

Control	Independent	Dependent
• Volume of acids • Rate of stirring • Volume of solvent • Cooling method • Rate of addition of reactants	• Temperature of solution • Rate of reaction	• Yield • Purity • Crystal morphology • Colour of crystals

Reactions:

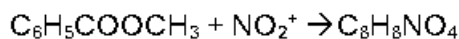
Protonation of Nitric Acid



Creation of nitronium



EAS



Restoration of Aromaticity

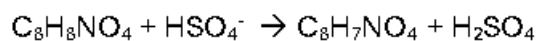


Figure 3 M3NB reactions

This is important to OME as the reaction is an analogue to the nitration of toluene (methyl Benzene), which creates the commonly used explosive TNT.

Nitroguanidine

Nitroguanidine (NQ) is an energetic material and is a key component in triple base propellant. It is relatively stable but can still present a hazard especially if mixed with an oxidiser.

NQ is also produced using sulphuric acid but does not require external nitric acid. The solvent used is distilled water, as Guanidine nitrate is water soluble. Figure 4 shows the structure of guanidine nitrate, with the nitrate anion $[\text{NO}_3]^-$ (nitric acid), which is held in an ionic bond with the guanidinium cation.

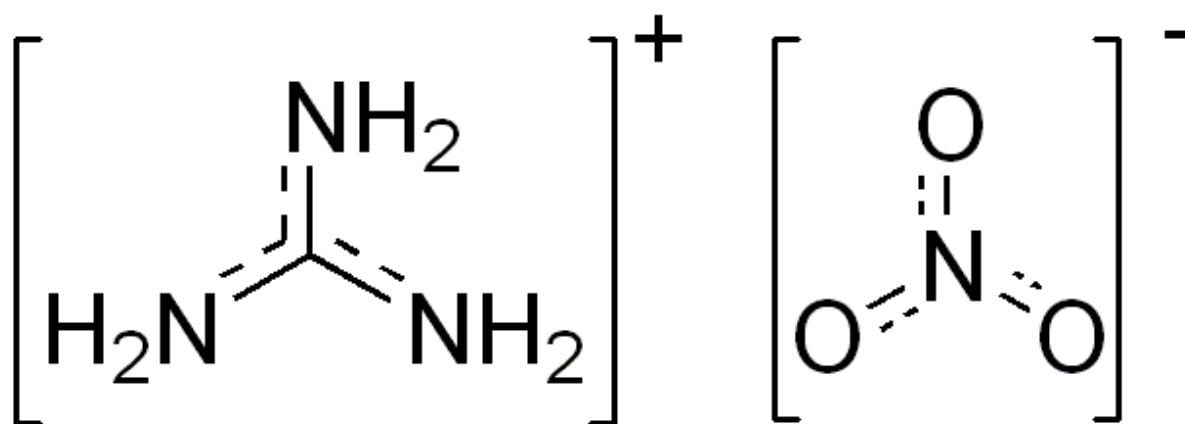


Figure 4 structure of guanidine nitrate

The guanidine nitrate is added in small quantities to sulphuric acid, where it is important to keep temperatures in the solution below 10°C for both yield and safety reasons. In this step the nitrate ion is protonated, forming nitronium, $[\text{NO}_2^+]$, hydrogen sulphate $[\text{HSO}_4^-]$ and water.

The nitronium then attacks one of the amino groups liberating one of the two hydrogen atoms of the amino group forming nitroguanidinium. In dilute solutions, these decompose forming nitroguanidine which then precipitates out. [4]

Variables:

Table 2 Variables for Nitroguanidine Production

Control	Independent	Dependent
• Volume of acid • Rate of stirring • Rate of addition of reactants • Cooling method	• Temperature of solution • Volume of solvent • Rate of reaction	• Yield • Purity • Crystal morphology

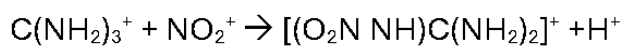
Reactions:

Intermediaries

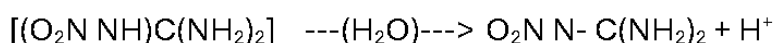
Production of Nitronium



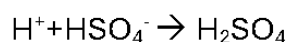
Production of Nitroguanidium salt



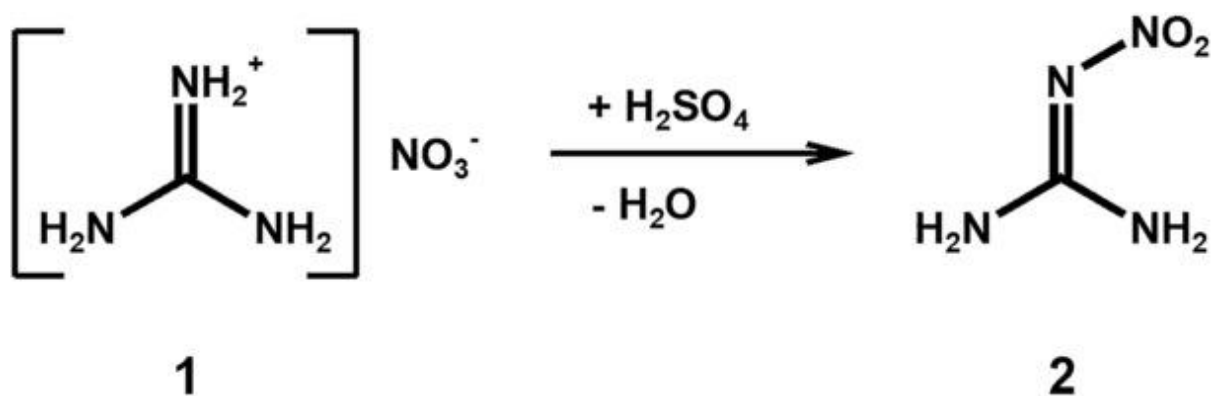
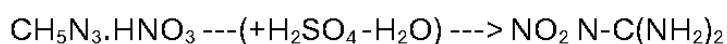
Production of Nitroguanidine



Restoration of Acid catalyst



Overall



Hypothesis

It is expected the yield for methyl-3-nitrobenzoate (M3NB) will be higher than the yield of nitroguanidine. This is because the M3NB is not soluble in water and during the initial crystallisation process, almost all products can be recovered. Whilst product is still lost in the recrystallisation of M3NB this will be limited as there is only one stage where the solvent (ethanol) this is involved, and limited quantities are used. This is unlike NQ, which is water soluble and has water introduced at two stages in the formation and recrystallisation processes.

In M3NB synthesis, if the reaction exceeds 10°C, the rate of reaction will increase, resulting in additional nitration occurring and the formation of Methyl Dinitrobenzoate or Trinitrobenzoate, both of which develop off white or yellow hues. This will result in poor yield and purity.

If the NQ synthesis is allowed to exceed 10°C, the rate of the reaction will greatly increase. As this is a strongly exothermic process, it is possible to reach the point of thermal runaway and ignition of the produced NQ may occur.

Results

Methyl-3-nitrobenzoate

The methyl 3-nitrobenzoate product was a white fluffy powder.

Table 3 M3NB masses

	Mass (g)
Mass of methyl benzoate	2.777
Mass of labelled glass bottle	8.630
Mass of labelled glass bottle and dried sample	11.187
Mass of methyl-3-nitrobenzoate	2.557

Yield:

Theoretical yield = mass of methyl benzoate x M_r [methyl 3 nitrobenzoate] / M_r [methyl benzoate]

$2.777 \times (181.15 [6]/136.15) [5] = 3.695\text{g}$.

Percentage yield = (Actual yield / theoretical yield) x 100

$2.557/3.695 \times 100 = 69.2\%$ yield

Table 4 M3NB Yield

Theoretical yield	3.695g
Actual yield	2.557g
Percentage yield	69.2%

Nitroguanidine

Nitroguanidine was produced as a white crystal matrix similar to that of glass fibre matting.

Table 5 NQ masses

	Mass (g)
Mass of guanidine nitrate	4.002
Mass of labelled glass bottle	83.307

Mass of labelled glass bottle and dried sample	85.190
Mass of nitroguanidine	1.883

Yield:

Theoretical yield = mass of guanidine nitrate x $\text{mr}(\text{nitroguanidine})/\text{mr}(\text{guanidine nitrate})$

$4.002 \times 104/122 [7] = 3.412\text{g}$

Percentage yield = $(\text{Mass of nitroguanidine}/\text{mass of guanidine nitrate}) \times (122/104) \times 100$

$1.883/4.002 \times 122/104 \times 100 = 55.2\%$

Discussion

Percentage yield was higher in the M3NB synthesis (69.2%) compared to nitroguanidine (55.2%). The actual yields may be slightly lower, as purity has not yet been confirmed, although the crystal appearance and colour suggest reasonable product quality. As expected, the additional solvent washes in the NQ procedure led to greater product loss, particularly during recrystallisation, and small crystals may also have remained on the filter paper or adhered to glassware in both syntheses. Some guanidine nitrate may not have fully reacted or may have formed side-products such as ammonium salts, which do not contribute to the final yield. Improved recovery from glassware, more efficient filtration, and reduced solvent volumes would likely increase overall yield.

Conclusion

In conclusion, the syntheses conducted are good introductions to lab preparation of energetic materials. As discussed, M3NB is a good analogue for toluene nitration (product of TNT) and NQ is itself a vital energetic product used in propellants. It demonstrates the importance of safety measures as well as controlling all stages of the processes to ensure maximum possible yields. It is also a reminder of how difficult it can be to achieve industrial scale production of these materials in a cost-effective, safe, and sustainable way.

References

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