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The Importance of Nitration

- Compounds containing nitro- or nitrate ester groups are very versatile chemicals with diverse applications in:



Pharmaceuticals



Agrochemicals



Energetic Materials



Dyes and Resins

- Typically produced through nitration using strong acids such as nitric acid and sulfuric acid
- Range of applications results in a high demand for nitric acid – global annual production ~ 60 million tonnes^{1,2}

The Drawbacks

- While effective, the production and use of nitric acid for nitration presents issues:

- ⚠ Produces the greenhouse gas N₂O as a by-product²
- ⚠ Difficulty sourcing due to geopolitical issues¹
- ⚠ Poor chemical selectivity, low reaction yields³

- ⚠ Large quantities of waste acid³
- ⚠ Thermal runaway – toxic NO₂ fumes, fires, explosions⁴
- ⚠ Compatibility issues with some compounds

- For these reasons, an alternative and milder method is desirable

Clean and Controlled Nitration by N₂O₅

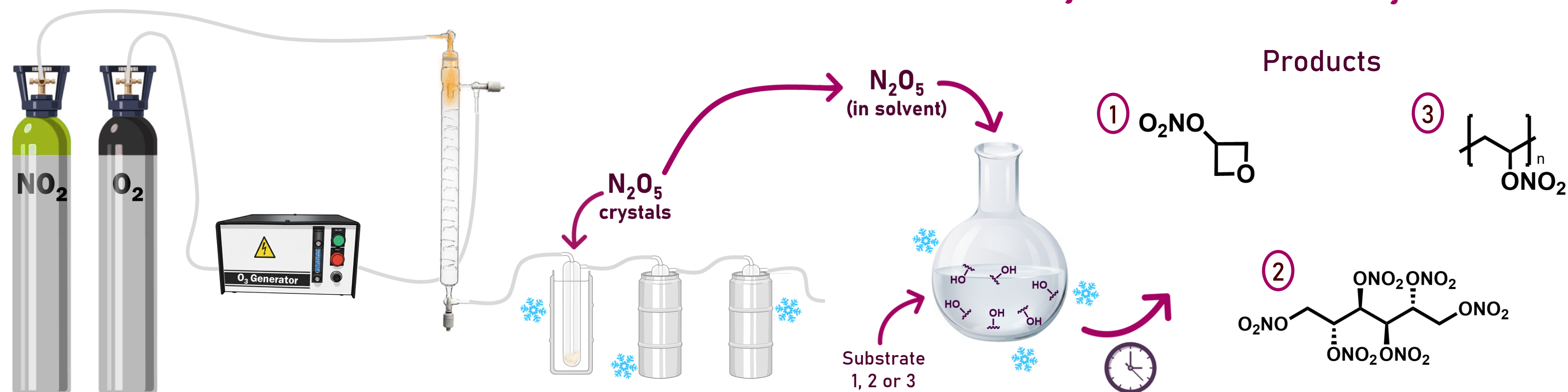
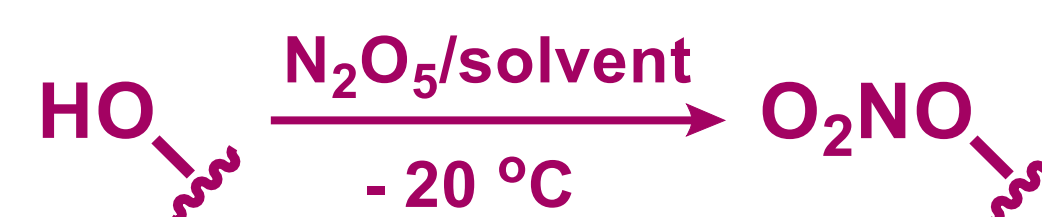
- N₂O₅ shows high selectivity without the use of strong acids,⁵ leading to:

- ✔ Single product formation
- ✔ Increased yields
- ✔ Improved safety
- ✔ Reduction in waste

- Synthesis of N₂O₅ follows the gas phase reaction



- Nitration reactions using N₂O₅ convert alcohol to nitrate ester in non-reactive solvents (DCM, MeCN) at -20 °C



① Ring-strained heterocycles

- Classical methods lead to acid-catalysed ring-opening
- N₂O₅ avoids the use of acid – ring remains intact and full -ONO₂ functionalisation is obtained

② Polyfunctional molecules

- Complete functionalisation obtained with N₂O₅
- No partial nitration or oxidation products observed leading to simpler purification

③ Polymers

- Classical methods lead to hydrolysis of -ONO₂⁶
- Rapid nitration of cellulose and polyvinyl alcohol using close to stoichiometric amounts

Conclusions and Future Work

- Demonstrated an efficient and quick method to nitrate 3 classes of compounds – milder conditions, reduced waste, improved safety
- Work to extend the range of suitable solvents for reaction
- Develop a route for scale up – flow chemistry
- Conduct life cycle analysis – sustainable and economic viability

References

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