

Evaluation of a 'Stabiliser Cocktail' for a plasticised Nitrocellulose Polymer Bonded Explosive

Harry Hope



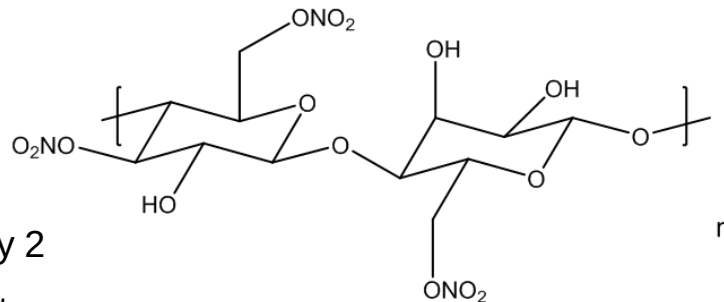
Aims of Project

- Isolate known degradation reactions and assess each stabilisers effectiveness in increasing NC lifetime
- Assess the effectiveness of using a 'stabiliser cocktail' as an alternative to a single stabiliser binder make up
- Compare and contrast the rates of degradation
- Monitor NC molecular mass by GPC and stabiliser content within the binders by HPLC

Binder Composition

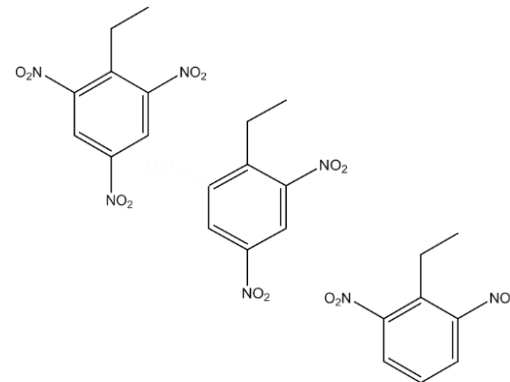
Polymer: Nitrocellulose (NC)

- Degree of Nitro-group substitution of approximately 2
- Lacquer grade NC with an approximate 12 wt% Nitrogen content

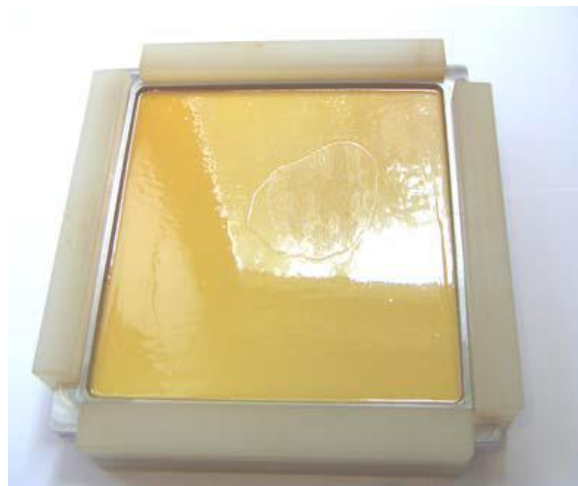


Plasticiser: Mixture of di-/tri- nitro ethylbenzene

- Nitro-energetic Plasticiser
- Modifies the physical properties of the polymer by sitting between the polymer chains, reducing the van der Waals interactions and hydrogen bonds between them
- Reduces the glass transition temperature, T_g , of the polymer

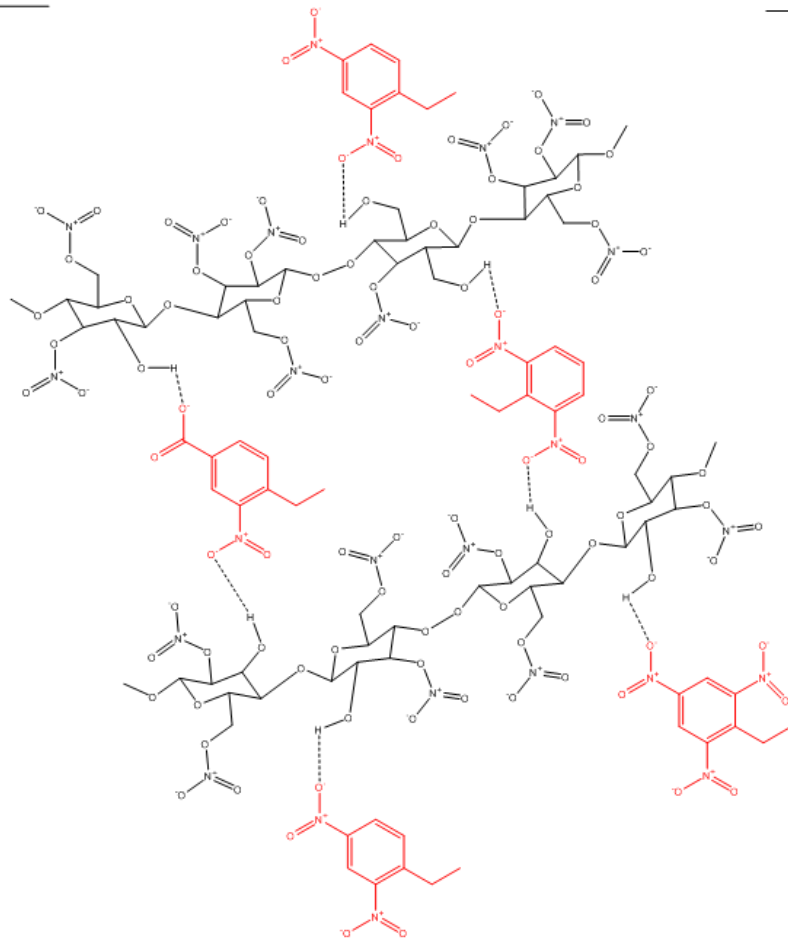


Binder Composition



Plasticised NC Binder sheet in mould

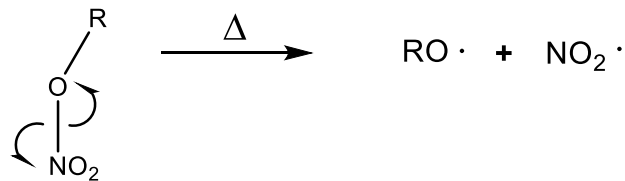
Structure of Plasticised NC



Degradation Reactions

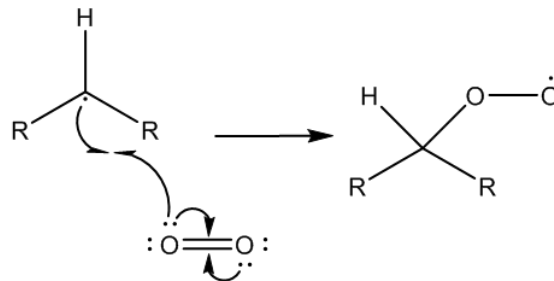
Thermolysis

- Bonding energy of CO-NO₂ bond = 160 kJ mol⁻¹



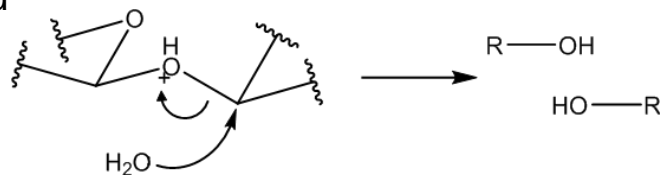
Oxidation

- NO_x radicals can abstract hydrogen generating alkyl radicals which will then react with oxygen in an autoxidation chain reaction forming peroxides



Hydrolysis

- The bridging oxygen atom can become protonated and chain scission of the polymer backbone can occur from attack at the neighbouring carbon

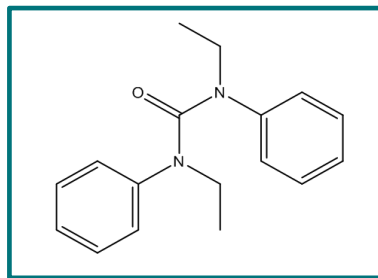


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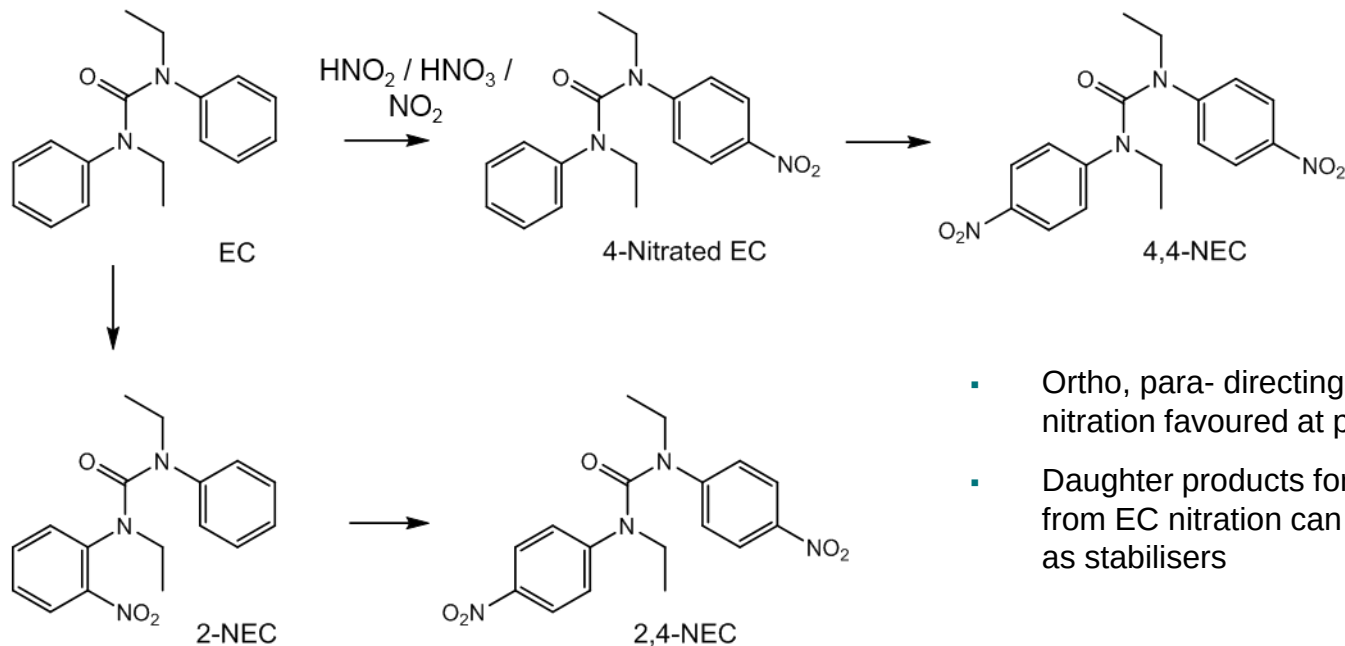
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Stabilisers of Interest

Ethyl Centralite (EC)



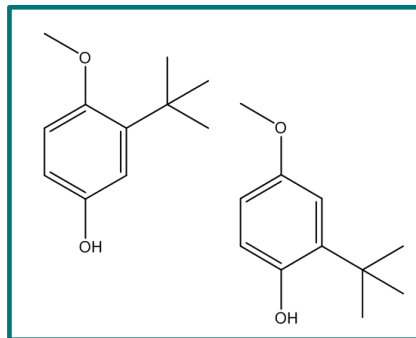
- NO_x scavenger
- Prevent auto-catalytic degradation from thermolysis



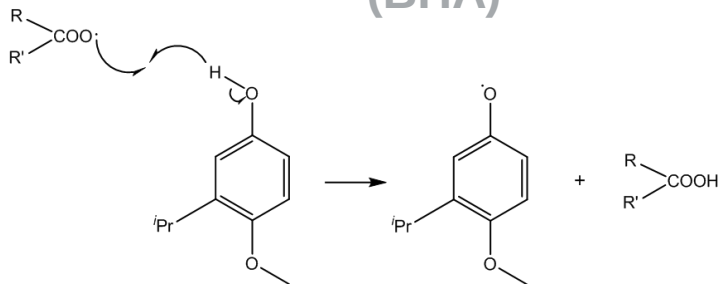
- Ortho, para- directing with nitration favoured at position 4
- Daughter products formed from EC nitration can also act as stabilisers

Stabilisers of Interest

Butylated hydroxyanisole (BHA)

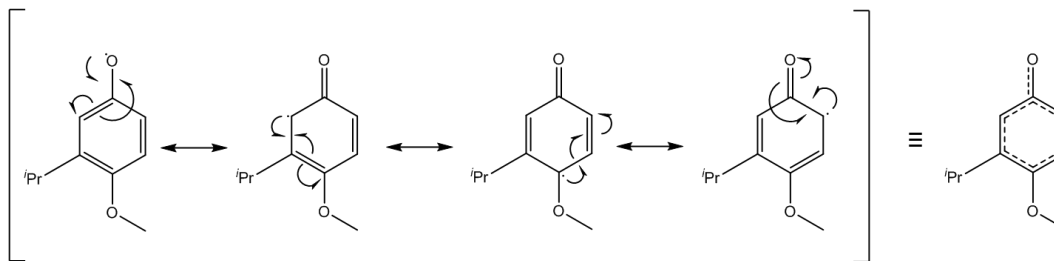


- Radical scavenger
- Anti-oxidant
- Two isomeric organic compounds



- Phenoxy radical much less reactive than initial peroxide radical
- Stabilisation of radical through mesomeric effects (π -conjugated system) and induction effects

- Abstraction of phenolic hydrogen
- Generates hydroperoxide and phenoxy radical

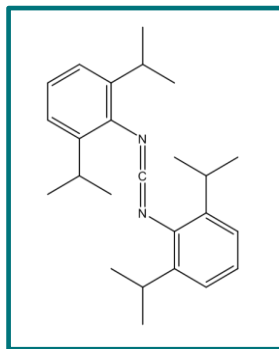
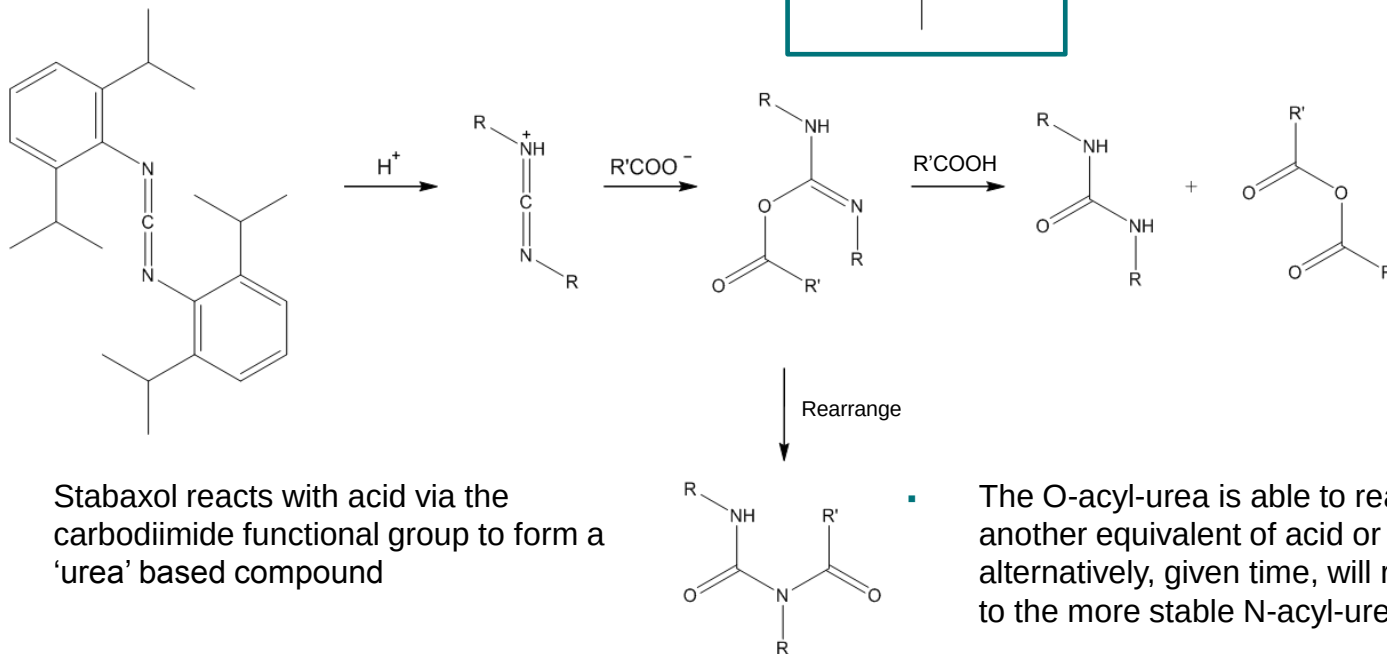


Stabilisers of Interest

Stabaxol I LF



- Acid scavenger
- Anti-hydrolysis
- Acid hydrolysis plays a larger contribution to NC degradation



- Stabaxol reacts with acid via the carbodiimide functional group to form a 'urea' based compound

- The O-acyl-urea is able to react with another equivalent of acid or alternatively, given time, will rearrange to the more stable N-acyl-urea

Method Development

- Samples of binder sheets were heated at a constant temperature within a controlled atmosphere in order to isolate the degradation reactions

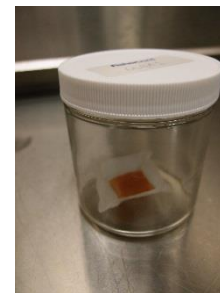
Humid

- Isolate the **hydrolysis** degradation reaction
- Samples present within desiccators above a NaCl saturated salt solution



Dry

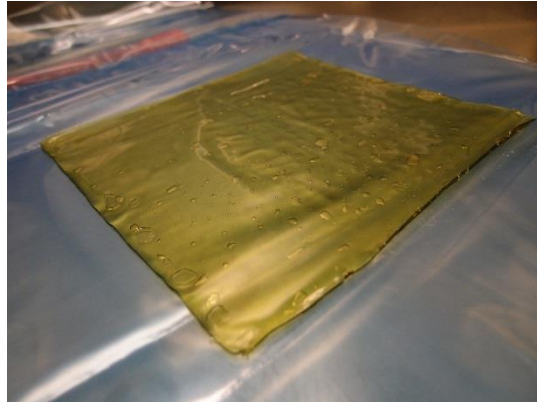
- Isolate the **oxidation** and peroxide formation degradation reaction
- Samples were dried prior to ageing
- Maintain a 21% oxygen atmosphere in headspace of samples



Method Development

Inert

- Act as a **reference** to the other environments
- Comparisons can be made then to assess how each individual stabiliser and the 'cocktail' behave under the two environments and their abilities to combat the degradation reactions



Unaged EC-stabilised binder sheet

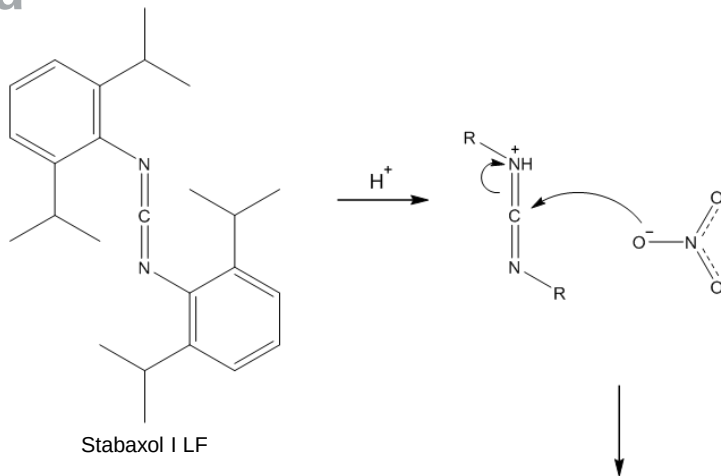
Results

Stabaxol Depletion Investigation

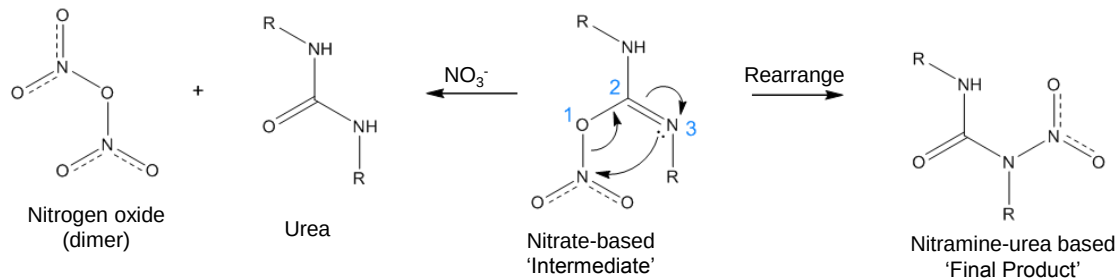
- HPLC analysis revealed absence of Stabaxol stabiliser in both aged samples and unaged samples
- Absence in unaged samples means that the Stabaxol has reacted up the residual acid present in the binder sheet immediately upon manufacture of the binder formulation
- Literature sources provide reaction mechanisms for Stabaxol reacting with Carboxylic acids, but predominant acids present in the binder are: **Nitric** (HNO_3), **Nitrous** (HNO_2) and **Sulfuric** acid (H_2SO_4)
- Investigation into possible mechanisms reinforced with computational molecular mechanics to determine viability

'Missing' Stabaxol

Nitric Acid



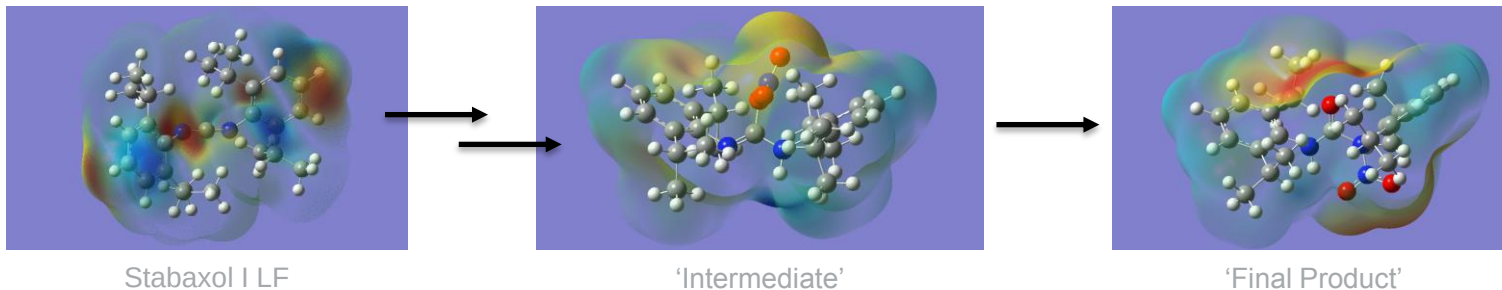
- Proposed mechanism for reaction with Nitric Acid, HNO_3
- Similar to that of carboxylic acid with the rearrangement of an 'intermediate' product to form the final 'Final Product': an Nitroamine-urea species



[4]

'Missing' Stabaxol

Nitric Acid – Modelling Data



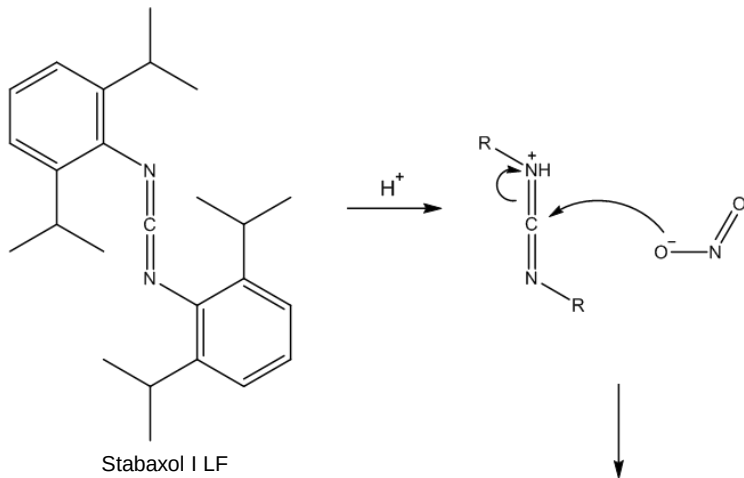
		ΔH°	ΔG° (kJmol^{-1})
$\text{HNO}_3 + \text{Stab}$	$\longrightarrow$ $\text{H}^+\text{Stab} + \text{NO}_3^-$	-73.9445749	-28.92250522
$\text{NO}_3^- + \text{H}^+\text{Stab}$	$\longrightarrow$ 'Intermediate'	-26.0187025	-11.24501542
'Intermediate'	$\longrightarrow$ 'Final Product'	-133.711451	-131.408888
Overall		-233.674729	-171.576409

[5]

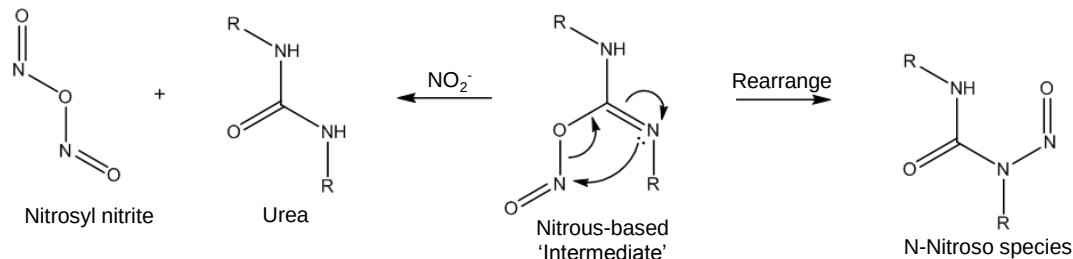
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'Missing' Stabaxol

Nitrous Acid



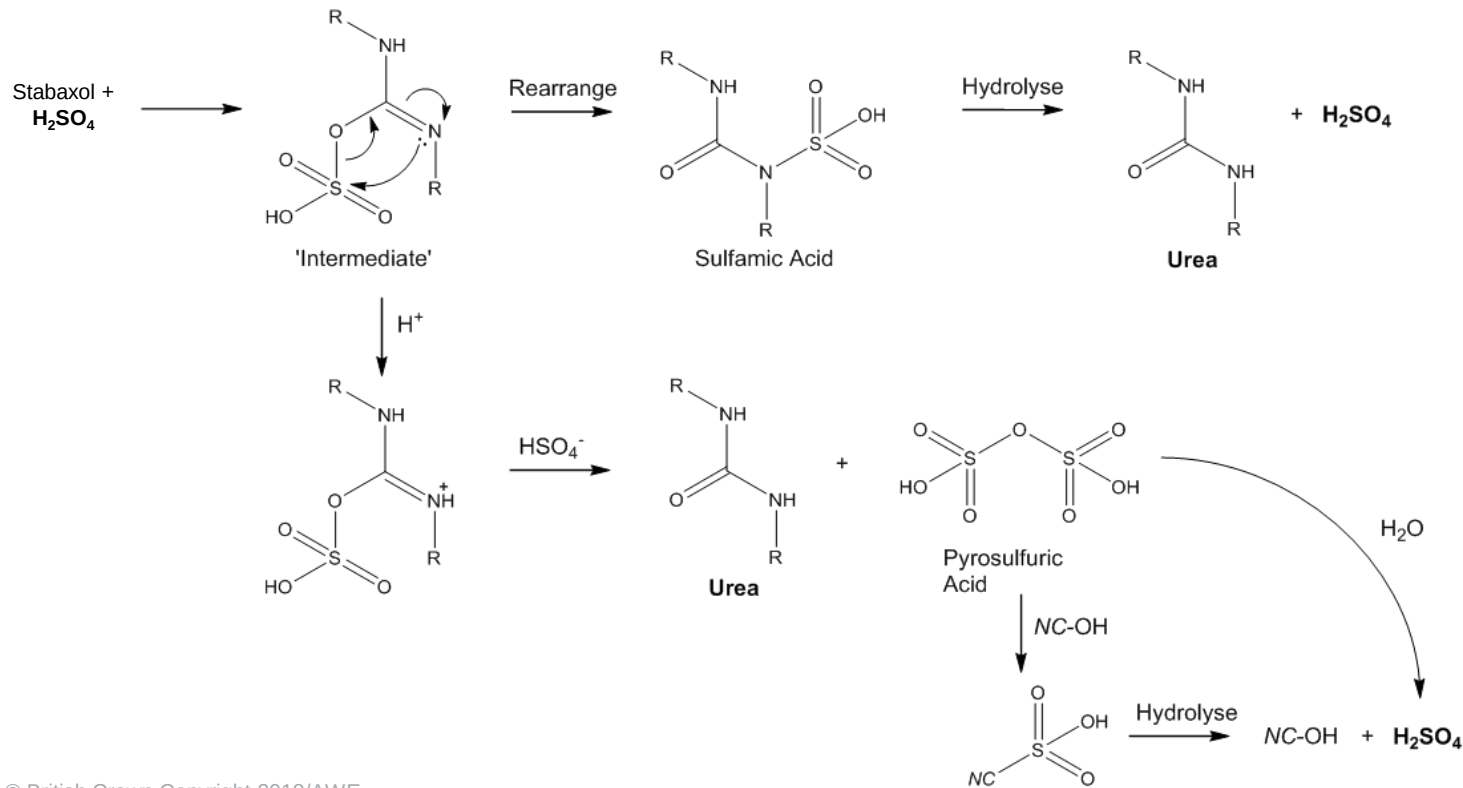
- Proposed mechanism for reaction with Nitrous Acid, HNO_2
- Same mechanism as proposed for reaction with Nitric Acid
- 'Intermediate' structure is now a nitrous-based species which rearranges to the N-Nitroso product



'Missing' Stabaxol

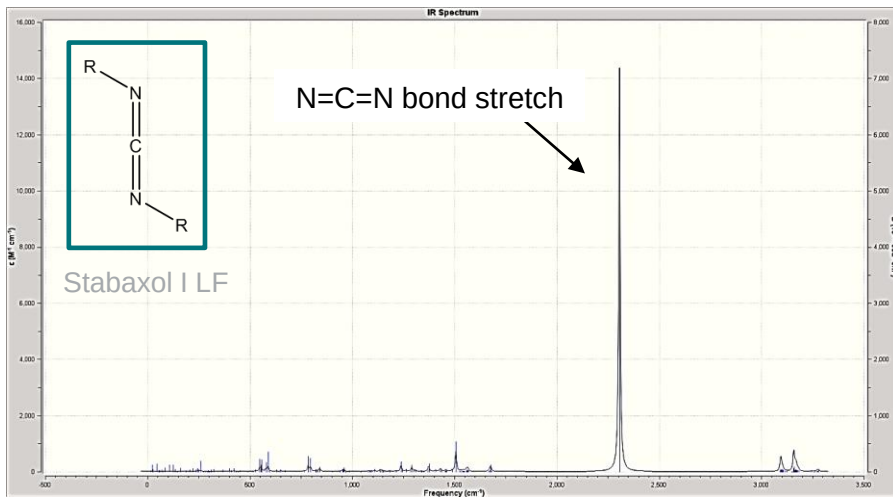
- Proposed mechanism for reaction with Sulfuric Acid, H_2SO_4

Sulfuric Acid

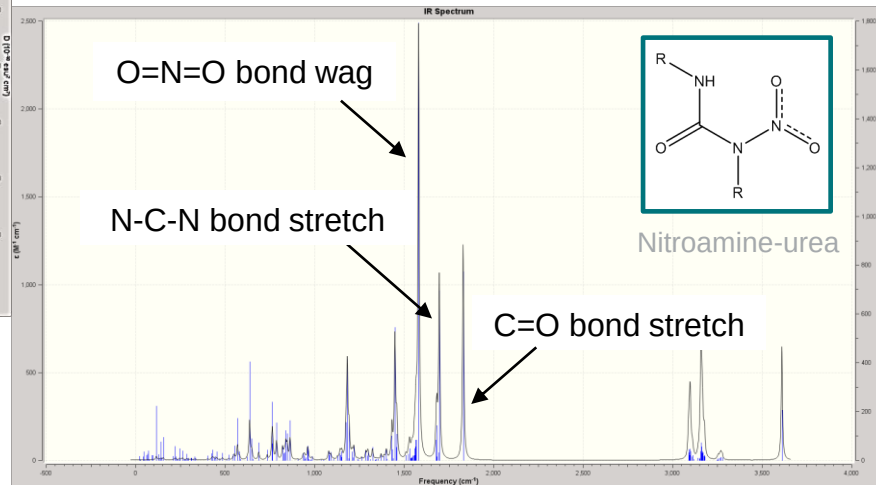


'Missing' Stabaxol

Predicted IR Spectra

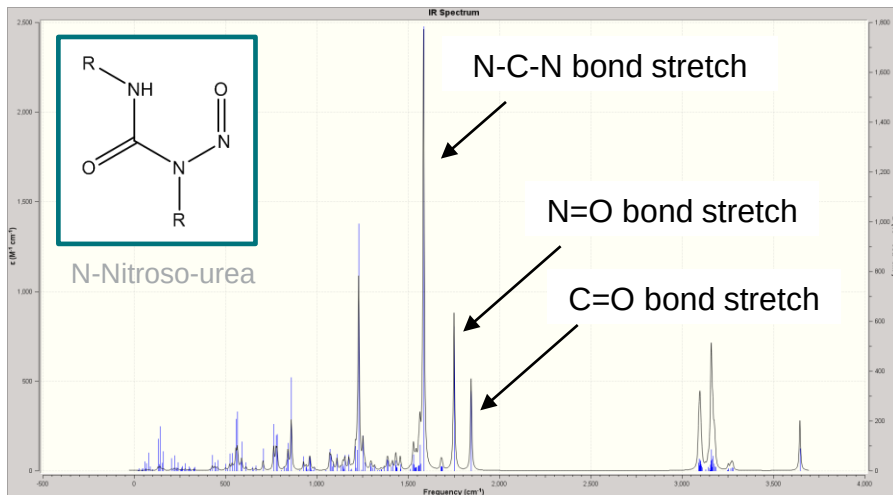


- Predicted Spectra generated from vibrational modelling data for Stabaxol ILF and the Nitroamine-urea species

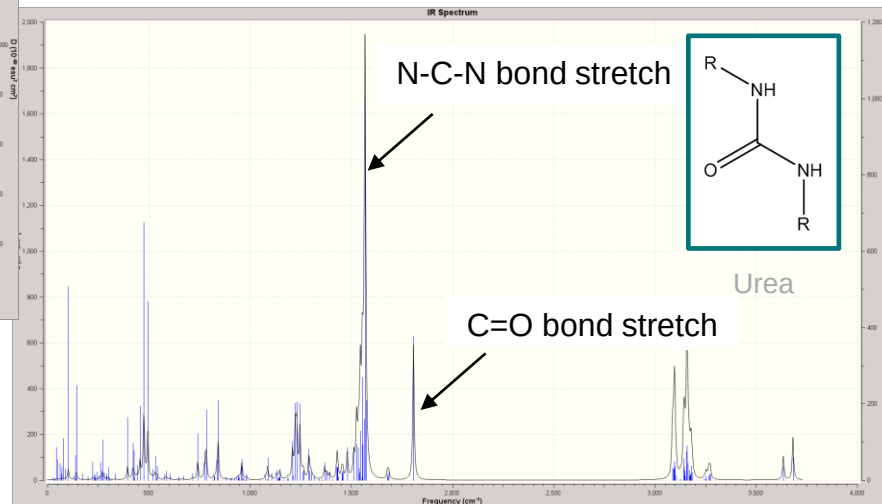


'Missing' Stabaxol

Predicted IR Spectra

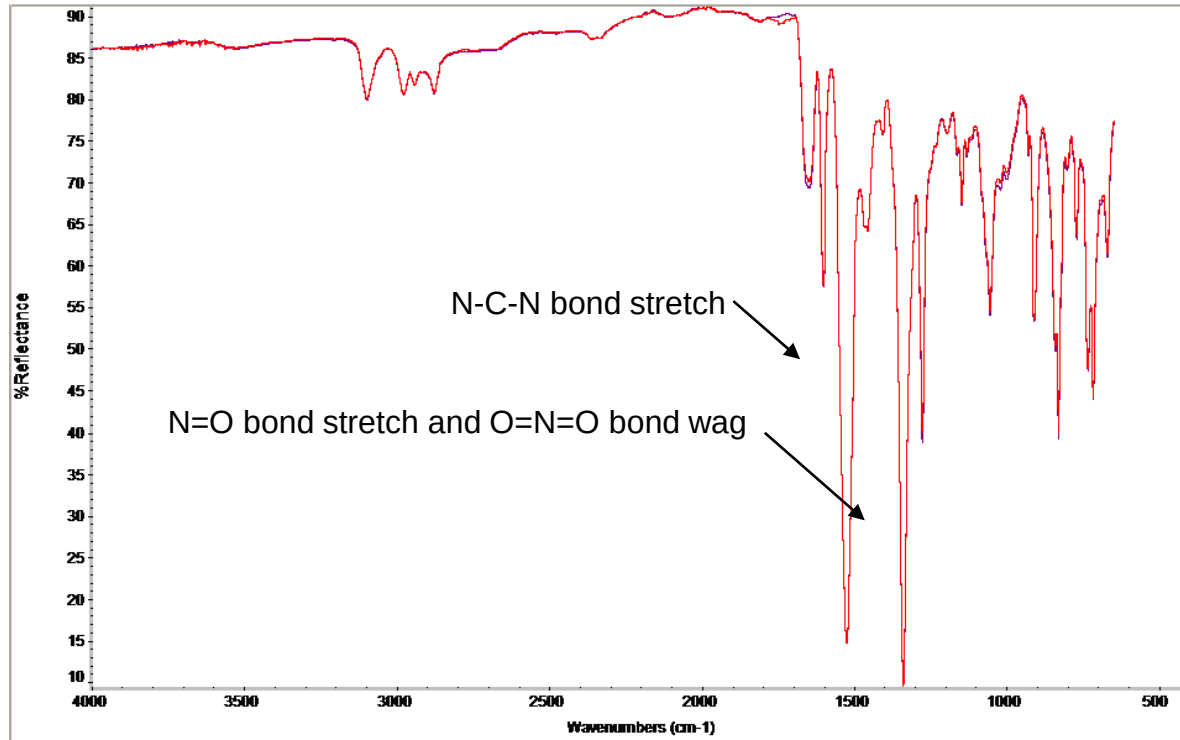


- Predicted Spectra generated from vibrational modelling data for the N-Nitroso-urea species and the Urea species



'Missing' Stabaxol

NC Binder Sheet (Unaged) IR Spectra



Ongoing work

- Continuation of ageing experiments and analysis of sample withdrawals by GPC and HPLC to assess the effectiveness of each stabiliser individually and as a collective 'cocktail'
- Should any stabilisers prove ineffective in their roles then alternative stabilisers can be suggested

Acknowledgements

- Dr Scott Connors, Dan Lewis, Dr Peter Jenkins and the rest of the Life and Mechanical Assessment Team
- Chemists and Analytical scientists in the lab building

Thank you for listening

References

- [1] *Polymer Degradation and Stability*; M. Moniruzzaman, J.M. Bellerby and M.A. Bohn; 2014; **102**; 49 – 58
- [2] *Propellants, Explosives, Pyrotechnics*; **13, 14** J. Kimura, 1988; and **22**; T.B. Brill and P.E. Gangwer 1997
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