Determination of the Activation Energy of Nitrocellulose Decomposition from UV-visible Spectroscopy of Thin Films

By

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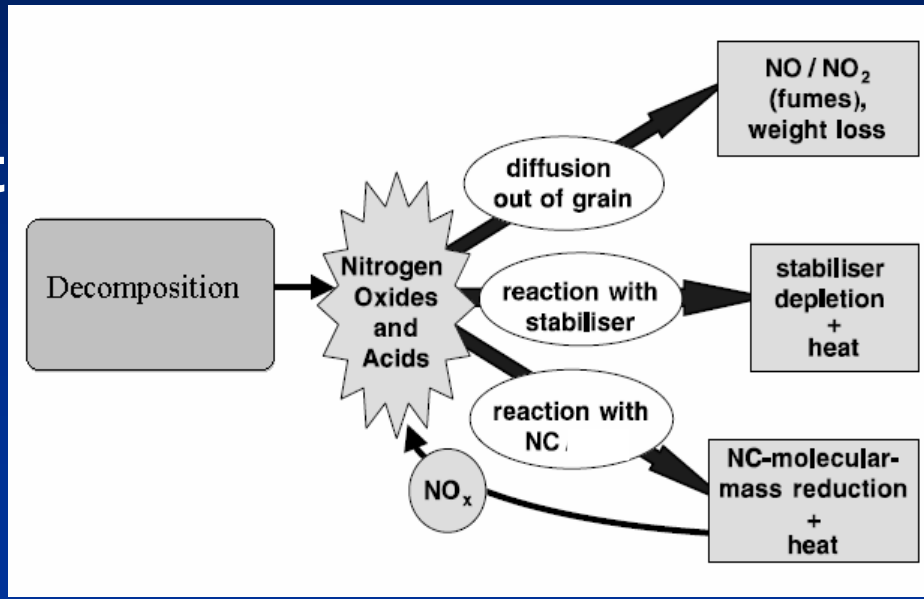
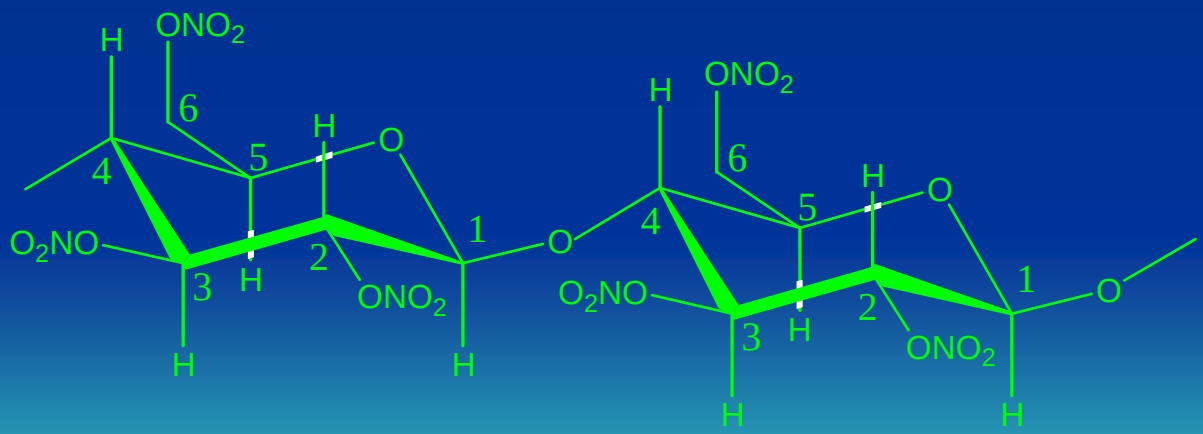
Introduction

- NC decomposes to give NO_x
- Causes autocatalysis
- Stabiliser added to prevent autocatalysis
- NC breakdown is usually monitored in a destructive way
  - By SEC, HPLC, DMA, TGA etc.



Nitrocellulose Structure

- **Fully nitrated NC has 3 nitrate ester groups**
  - Primary group at 6 position and two secondary groups at 2 and 3 positions
  - Reactivity: 3 $-ONO_2$ >2 $-ONO_2$ > 6 $-ONO_2$



Challenges

- Finding suitable dyes that act as stabilisers
- Following NC decomposition from the colour change of the dye
- Minimising the frequency of surveillance testing of NC

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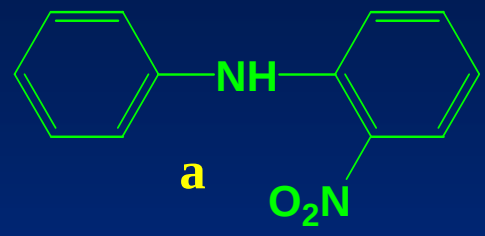
Aims

- To develop a technique for non-destructive monitoring of NC decomposition
- To validate the technique for monitoring NC decomposition in thin films
- To calculate activation energies associated with the breakdown of the three $-ONO_2$ groups

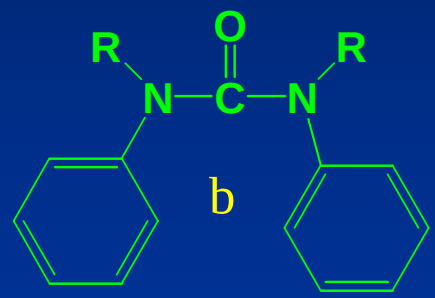
Conventional and Proposed stabilisers

- **Conventional stabiliser**
  a. Secondary amines
  b. Urea derivatives

- **Anthraquinone dye stabilisers**
  – UV-vis detects small colour change from dye/NOx reaction
  – Dye products do not absorb within the spectral region of parent dye



a



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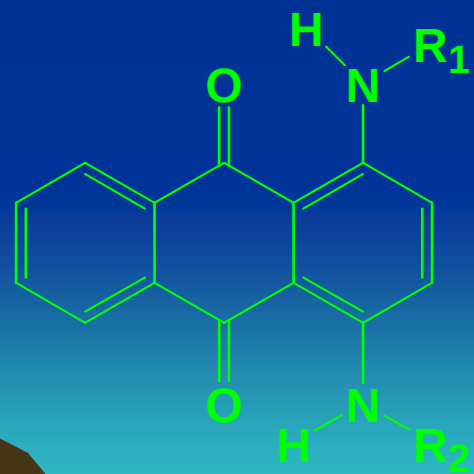
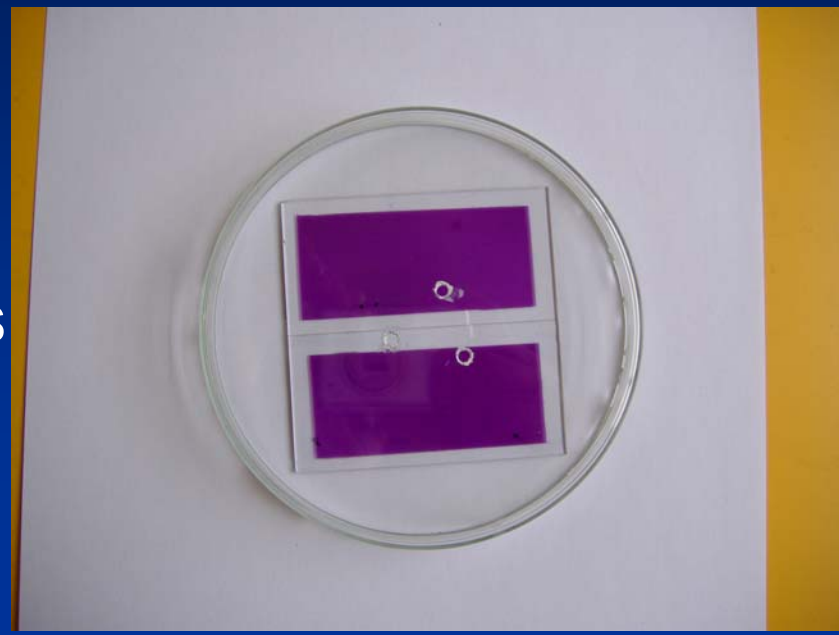


Experimental

- **Preparation of NC films (12 % N)**
  - Preparation of solution
    - Dye 2% *w/w* of NC
    - DOP 5% *w/w* of NC
  - Casting films on glass slides
- **Drying**
  - Ambient temperature
  - Under vacuum
- **Aging**
  - Aged at 40 ºC, 51 ºC, 60 ºC, 70 ºC



UV-visible measurements

- Zeiss, BLX 500/4 with a xenon flash lamp.
- Modified sample holder
- Spectra were taken at a particular position on aged and unaged films
- Multiple measurements on each film

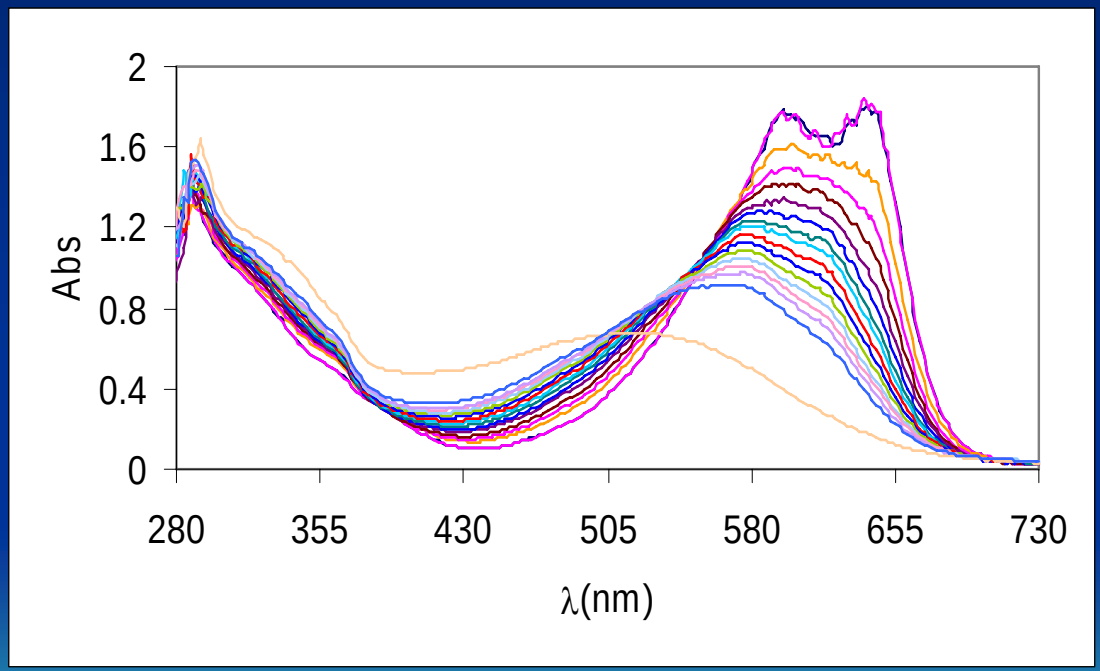
Results

Preparation of films

- Slow drying avoids the formation of rough surfaces
- No significant defects were observed
- Uniform thicknesses and homogeneous dye distribution
- Thickness ~ 40-50 μm

UV-visible spectra of an aged and unaged film with SB59 dye

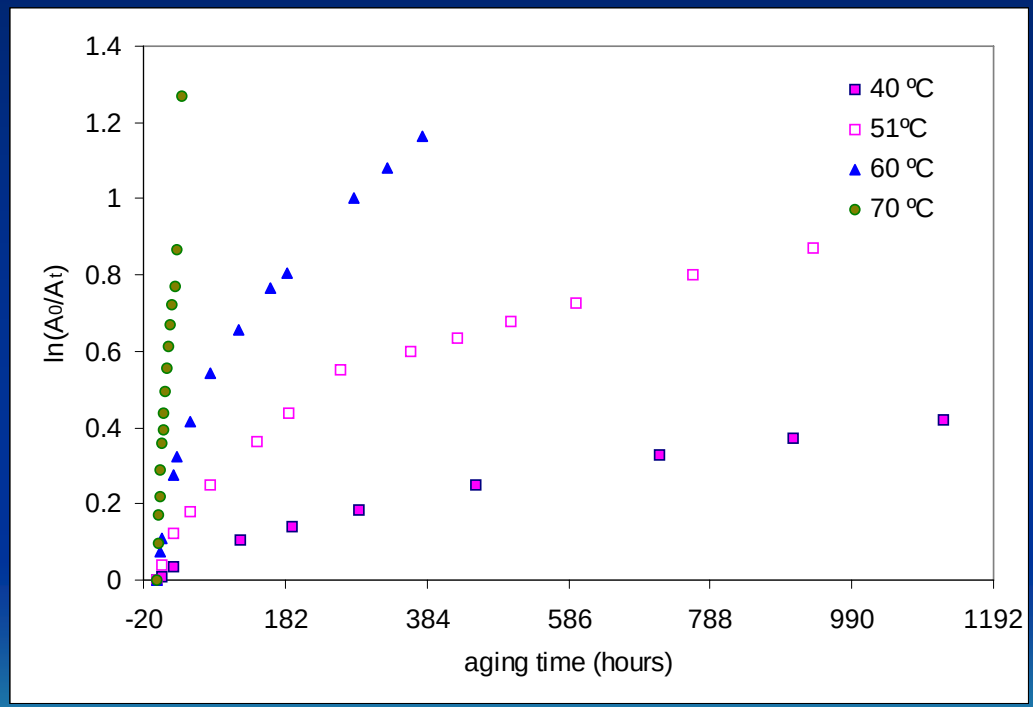
Spectra taken periodically during aging at 70°C



- **Dye depletion over 268 hours**
  - ~ 81% at 70°C
  - ~ 60% at 60°C
  - ~ 43% at 51°C
  - ~ 15% at 40°C

Rates of reaction at 40 - 70 ºC

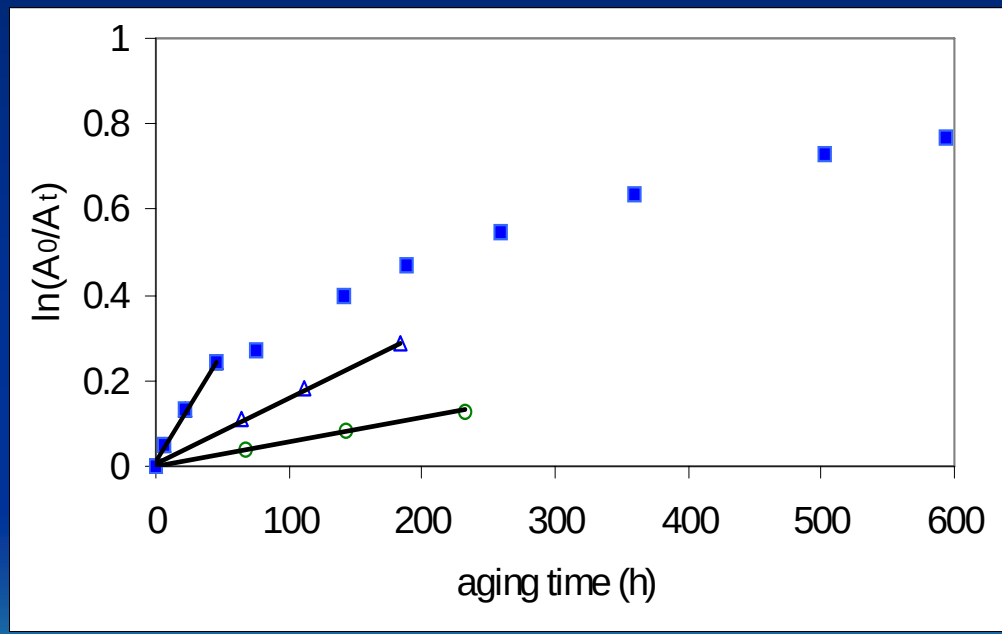
- 1st order plots are not single straight lines
- 3 Linear regions are observed



1st order reaction rates at 51 °C

- Absorbances at 600 nm were used to build plots
- Each linear region is thought to correspond to the breakdown of a different nitrate ester group (at positions 2, 3 and 6)

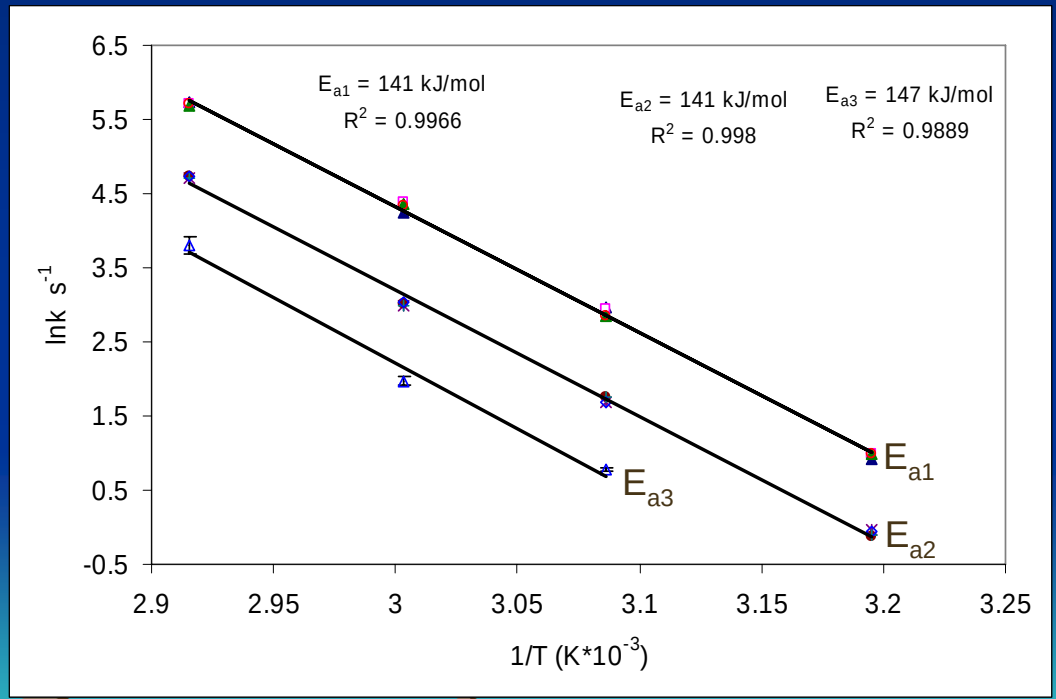
A plot of $\ln(A_0/A_t)$ vs aging time



E_a for NC decomposition

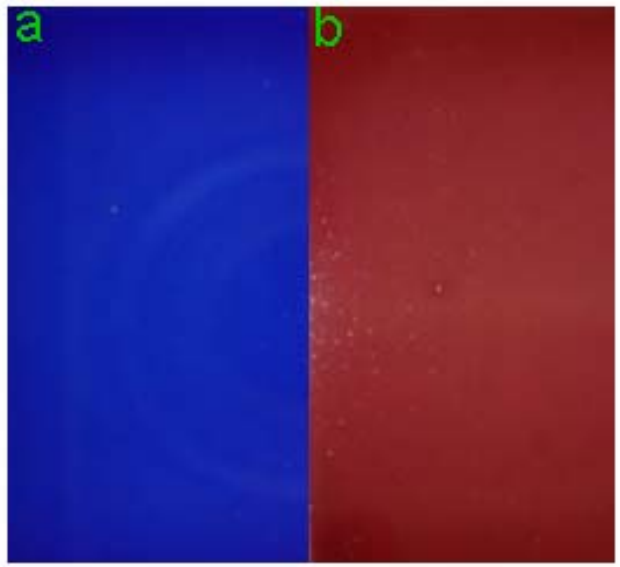
- **Activation energy for the $-ONO_2$ decomposition**
  - 141 $kJmol^{-1}$ - position 3
  - 141 $kJmol^{-1}$ - position 2
  - 147 $kJmol^{-1}$ - position 6

Arrhenius plots



Colour change of SB59 films

- Virgin films were blue
- Changed to red upon aging
- Colour change is attributed to the formation of dye derivatives
- Colour change is associated with the condition of NC



a- unaged film
b- aged film

Conclusion-1

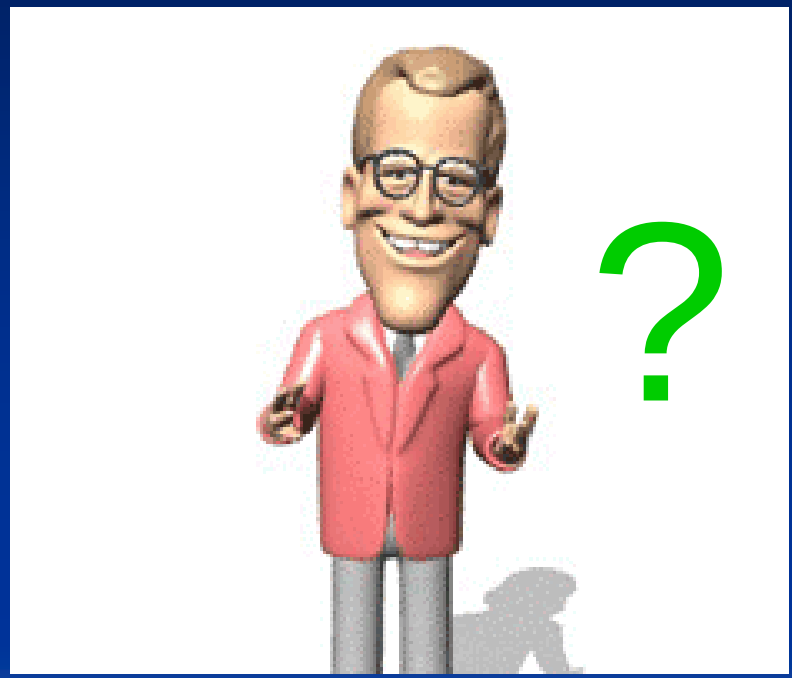
- Thin films of uniform thickness and homogeneous dye distribution were made
- An anthraquinone dye was the stabiliser
- UV-vis absorption spectroscopy was used to follow NC decomposition
- Daughter products of SB59 dye showed no absorption in the region of the parent dye

Conclusion-2

- Absorbance data fits three straight lines
- Three rate constants corresponding to three $-ONO_2$ decompositions were found
- Activation energy for each $-ONO_2$ group loss was determined

Acknowledgement

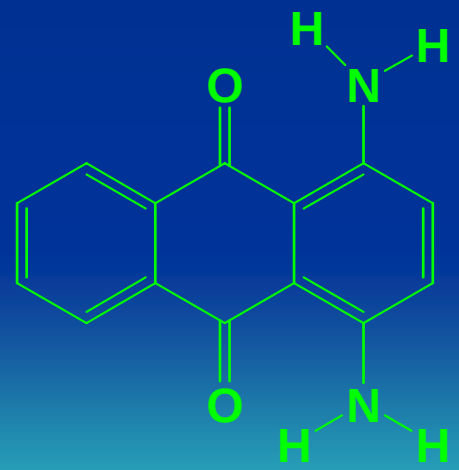
- This work was carried out under the remit of TTI work funded by DOSG
- We thank DOSG for their financial support
- We are also grateful to our colleagues for their support in various aspects of the project



Kinetics of SB59 and DAAQ dyes

- SB59 depletion was ~7 times faster than DAAQ which is a primary amine
- E_a from the first rate data of DAAQ work was 42 kJ/mol
- It corresponds to literature value of activation energy for NO_x desorption
- SB59 failed to detect E_a for NO_x desorption

SB59



DAAQ