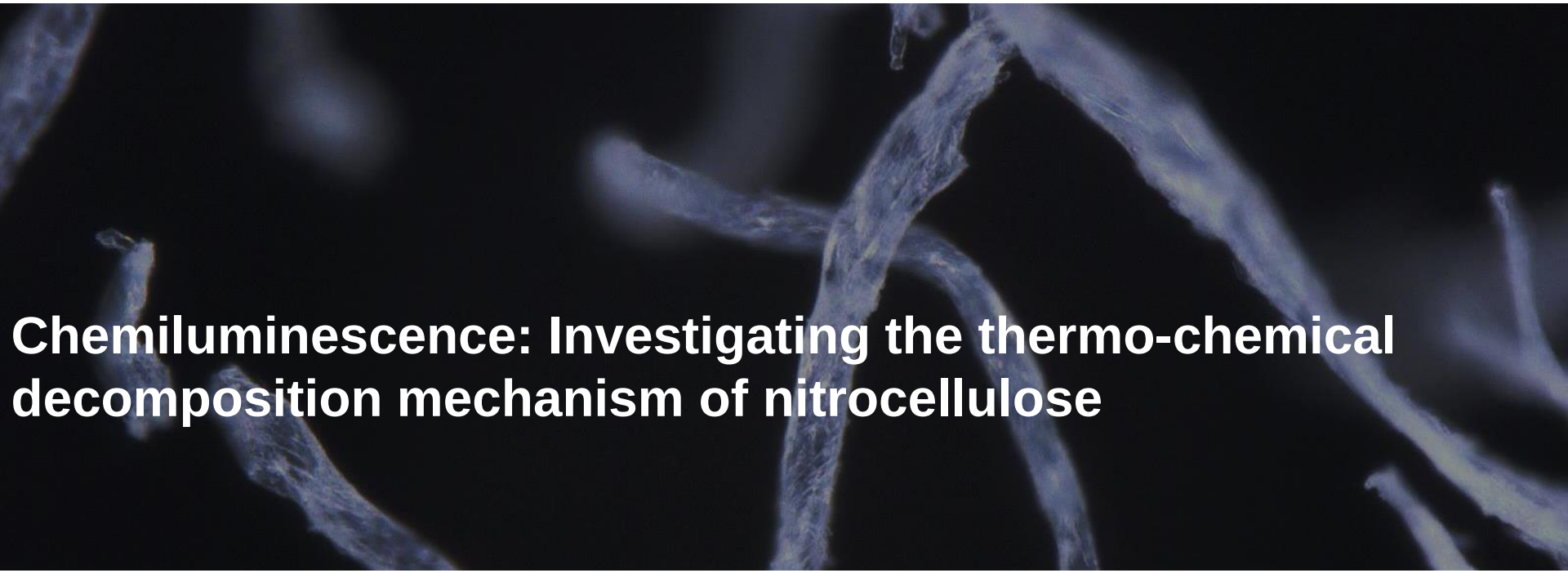

Chemiluminescence: Investigating the thermo-chemical decomposition mechanism of nitrocellulose

8th NC Symposium, Bergerac, 5th – 7th June 2018

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Agenda

Background

Detection and Techniques

Chemiluminescence Theory

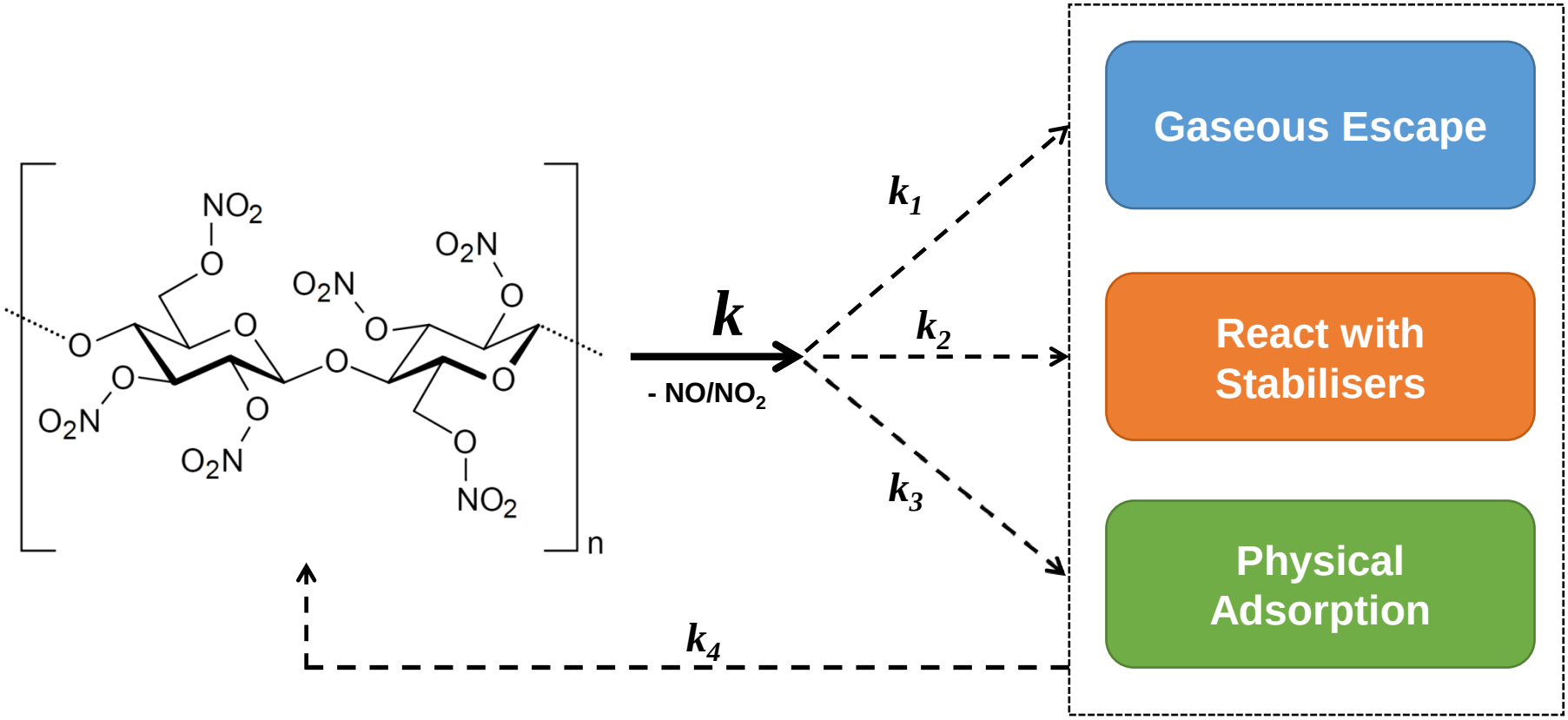
Experimental

Chemiluminescence Results

Summary

Chemiluminescence Future Work

Background – Nitrocellulose Degradation

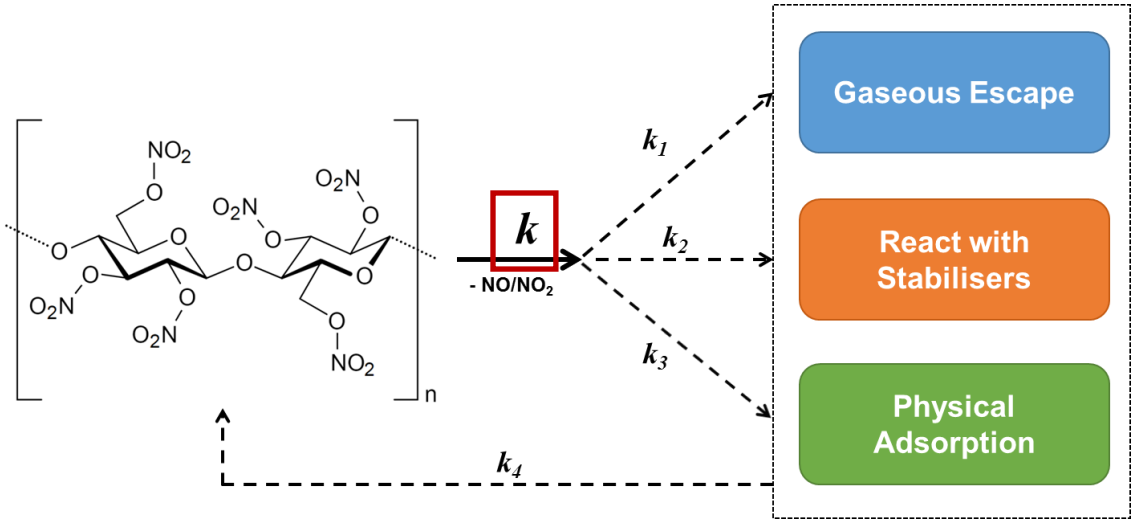


Detection and Techniques

Tests

- Mass Loss
- Bergmann-Junk Test
- Methyl Violet Test
- Abel Heat Test
- Vacuum Stability

- Stabiliser Depletion



Measurements of k_1-k_4 are typically non-intrinsic

Degradation Mechanisms

Thermolysis vs Hydrolysis

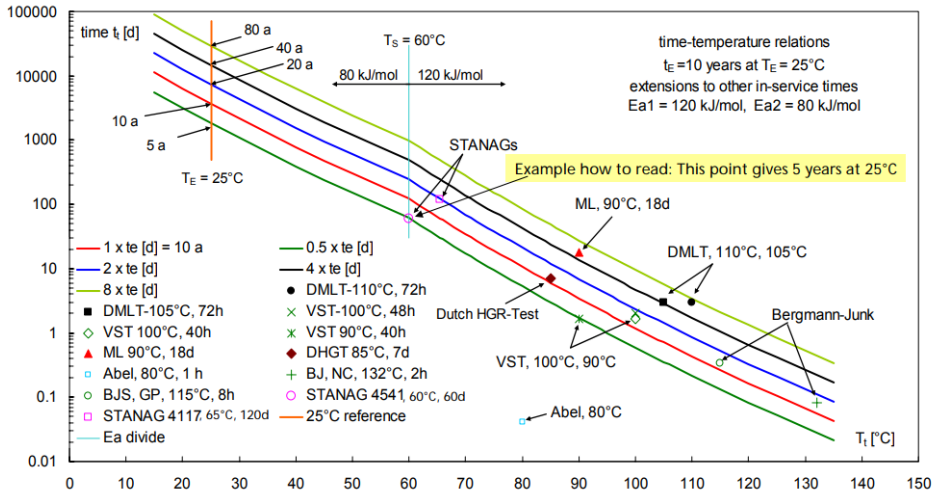
- Decomposition follows 2 pathways:

Thermolysis of CO-NO_2 groups

E_a = 160 – 170 kJ mol^{-1}

Hydrolysis of CO-NO_2 groups

E_a = 80 - 120 kJ mol^{-1}



Non-intrinsic measurements

M. A. Bohn, J. Thermal Analysis and Calorimetry, 2001, 65, 103

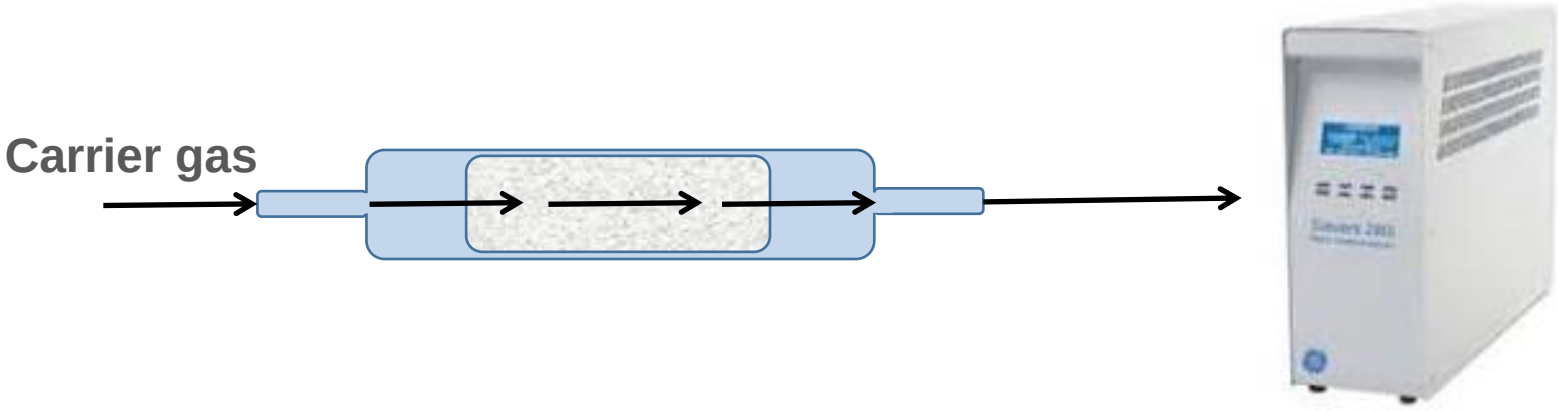
M. A. Bohn, 3rd Nitrocellulose Symposium, Aldermaston, 2007

Chemiluminescence Method

Chemiluminescence Theory

$$NO + O_3 \rightarrow NO_2^* + O_2$$

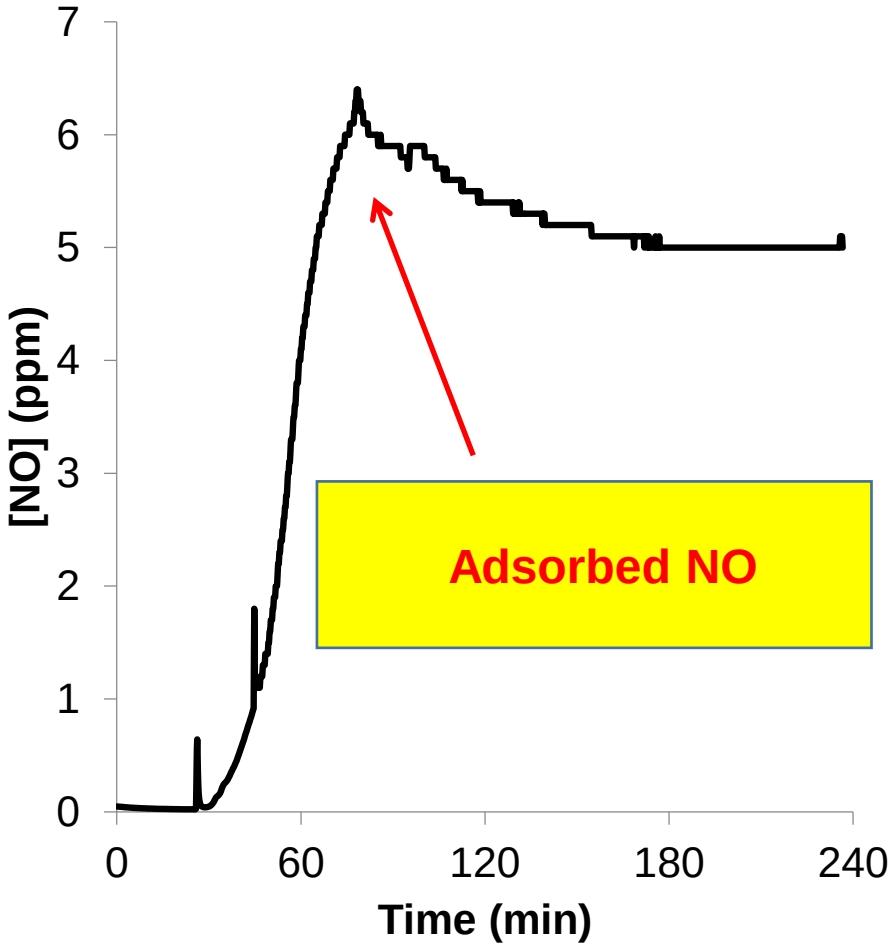
$$NO_2^* \rightarrow NO_2 + h\nu$$



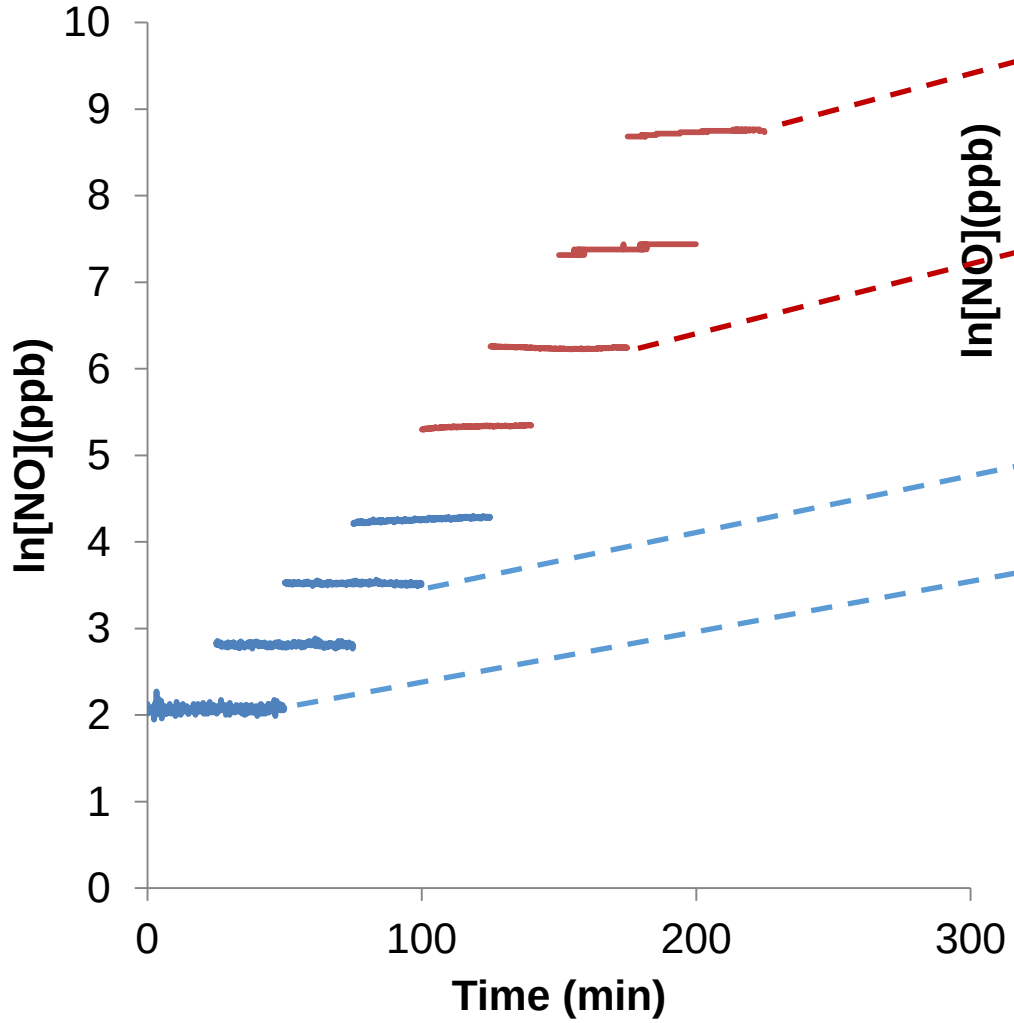
Experimental

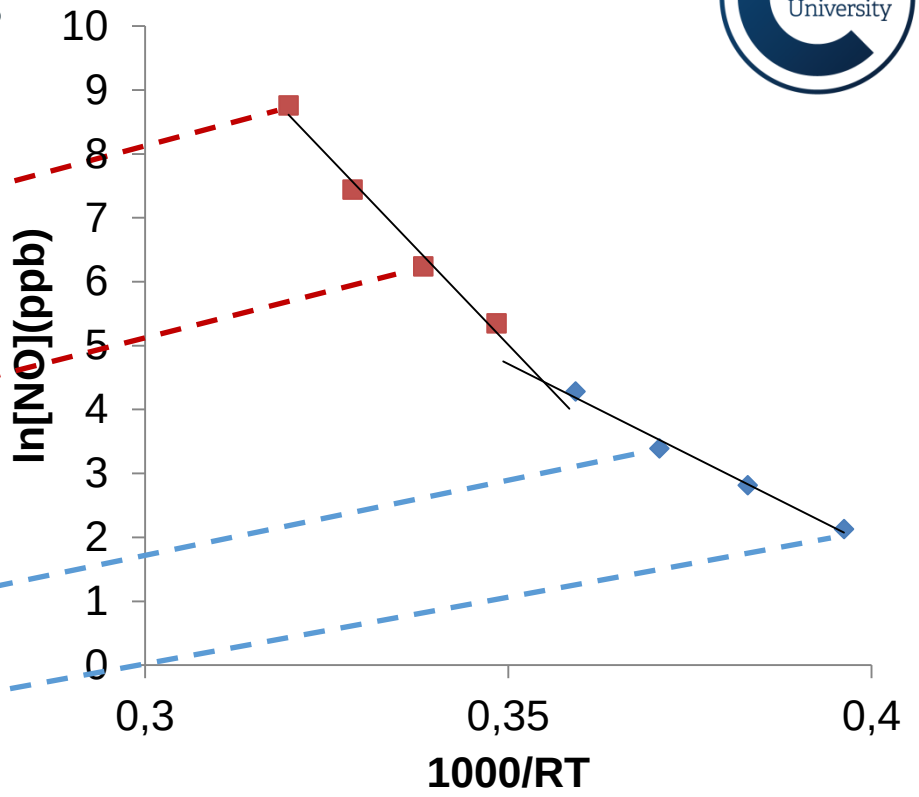
Method

- Sample – 12.7 N%
- Sample dried at 60 °C to ambient under constant vacuum for 4 hours
- Pre-conditioned at 100 °C for 4 hours
- NO measured from 30 - 100 °C
- 2.5 hour per temp, measured at equilibrium

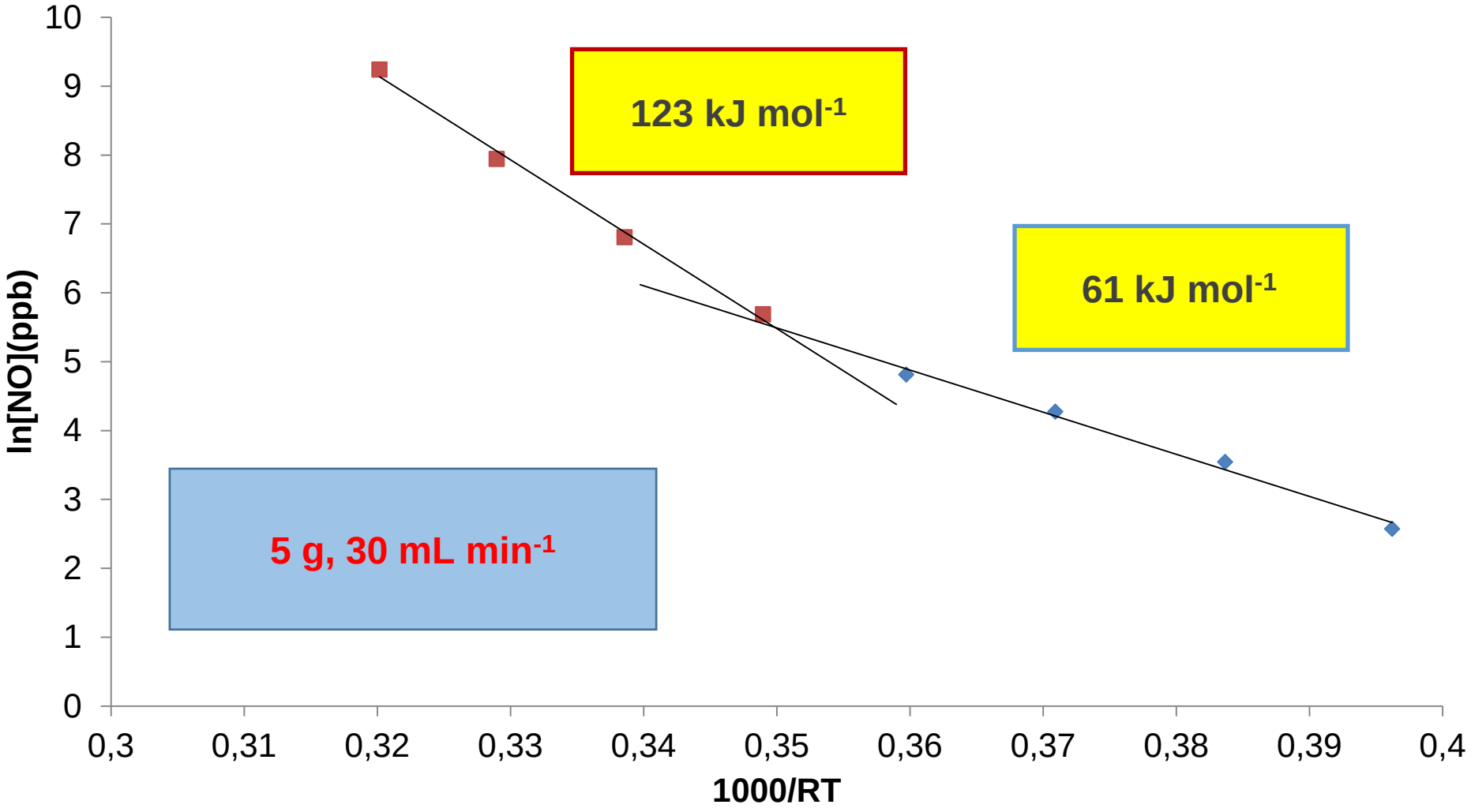


Chemiluminescence Results

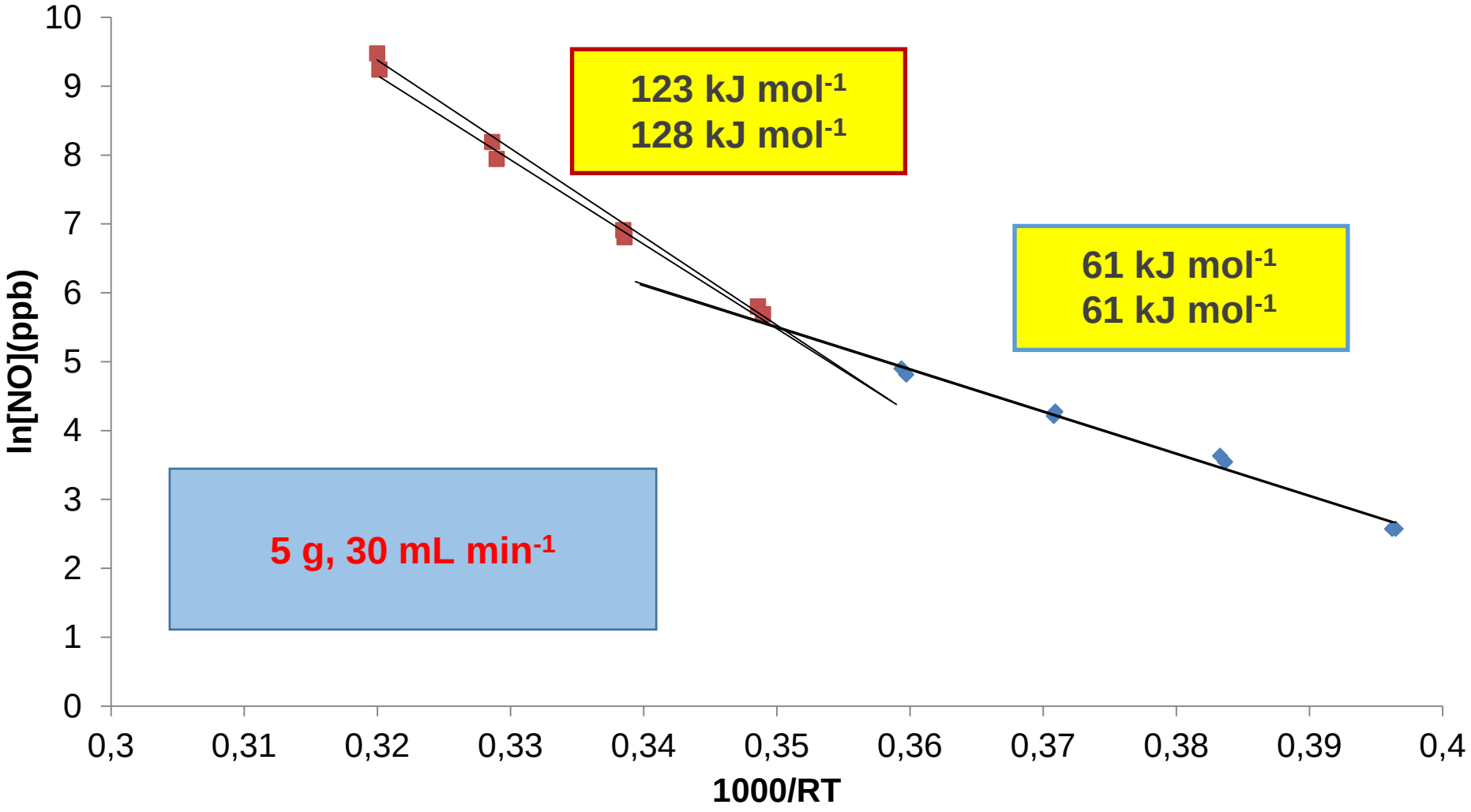




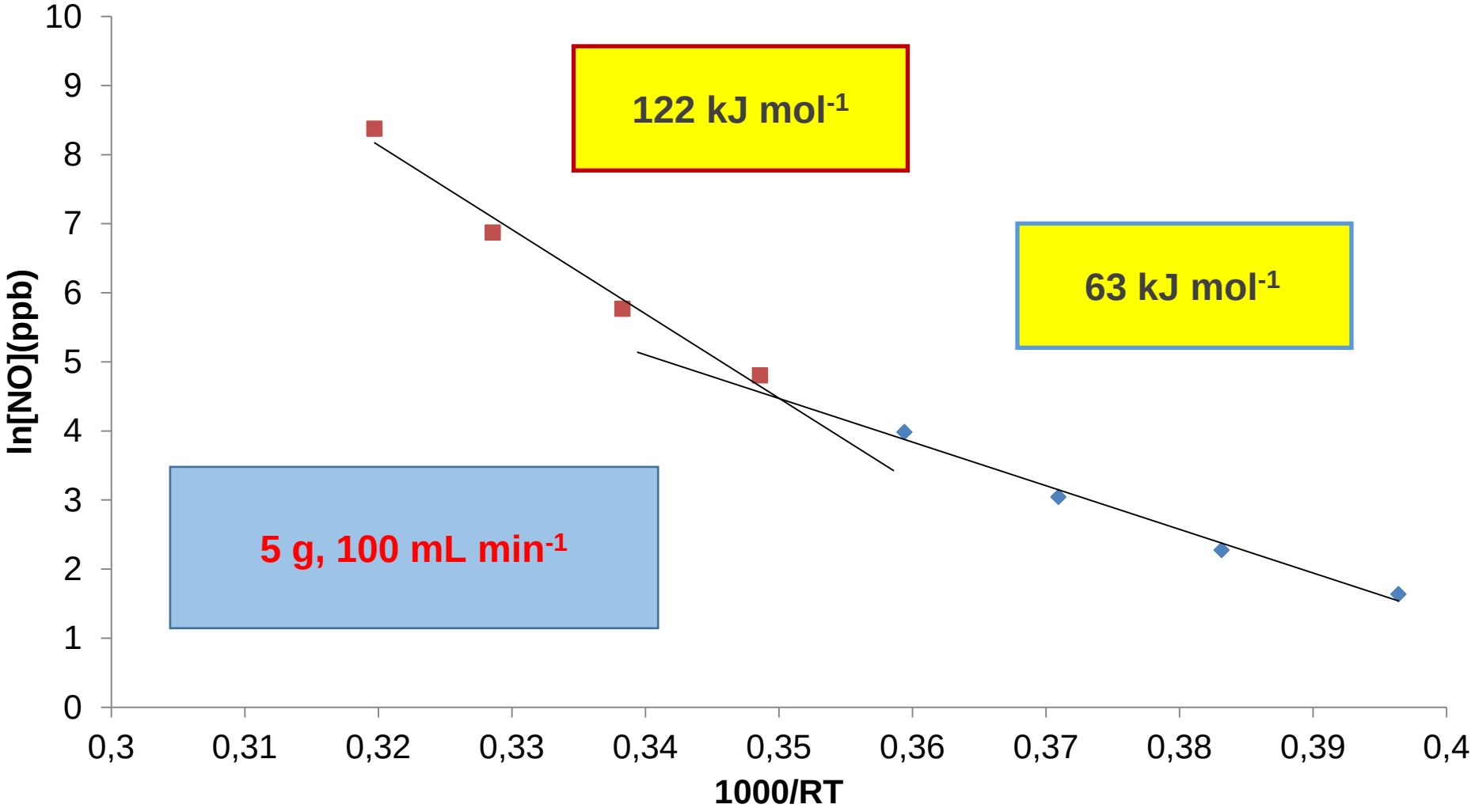
Chemiluminescence Results



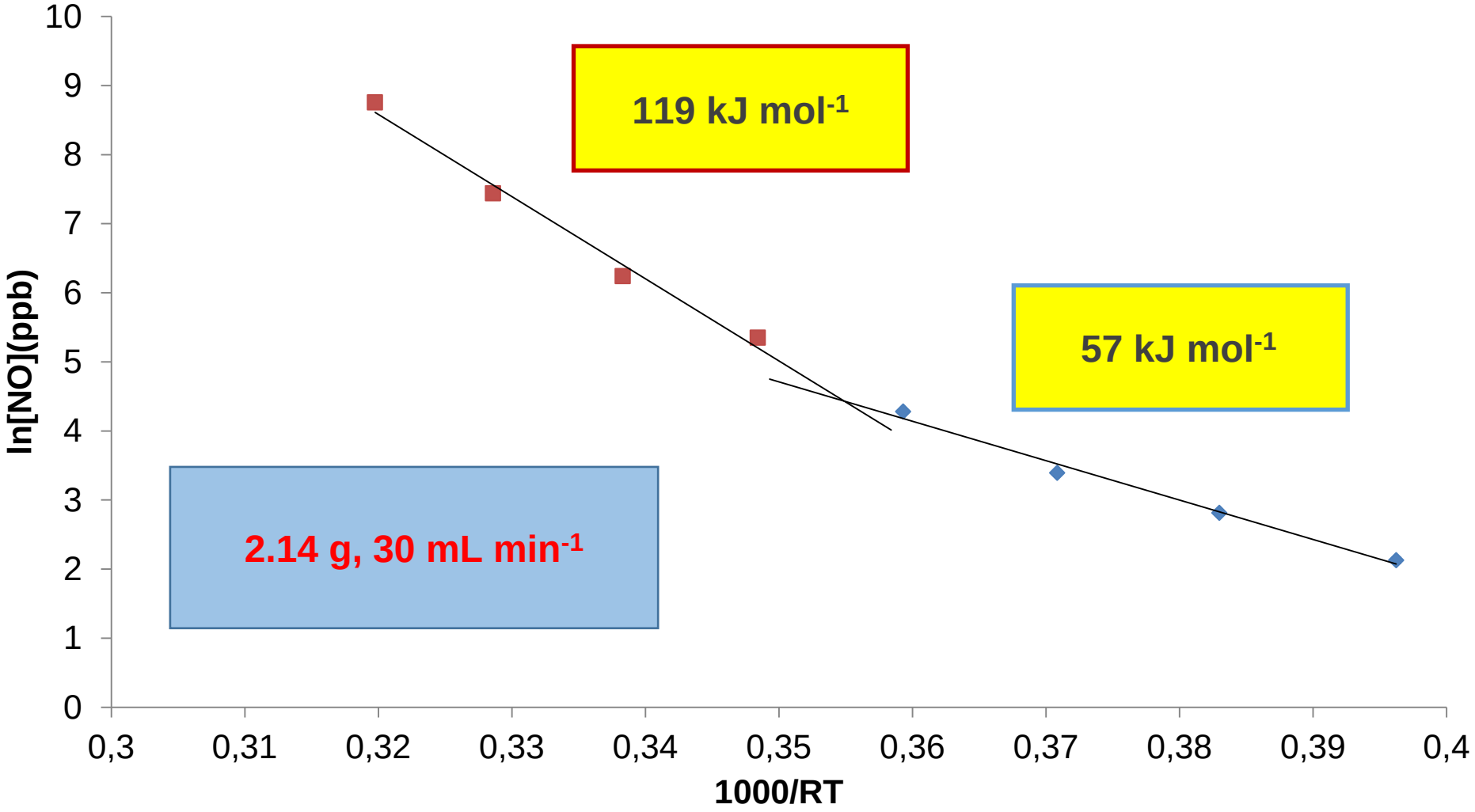
Chemiluminescence Results



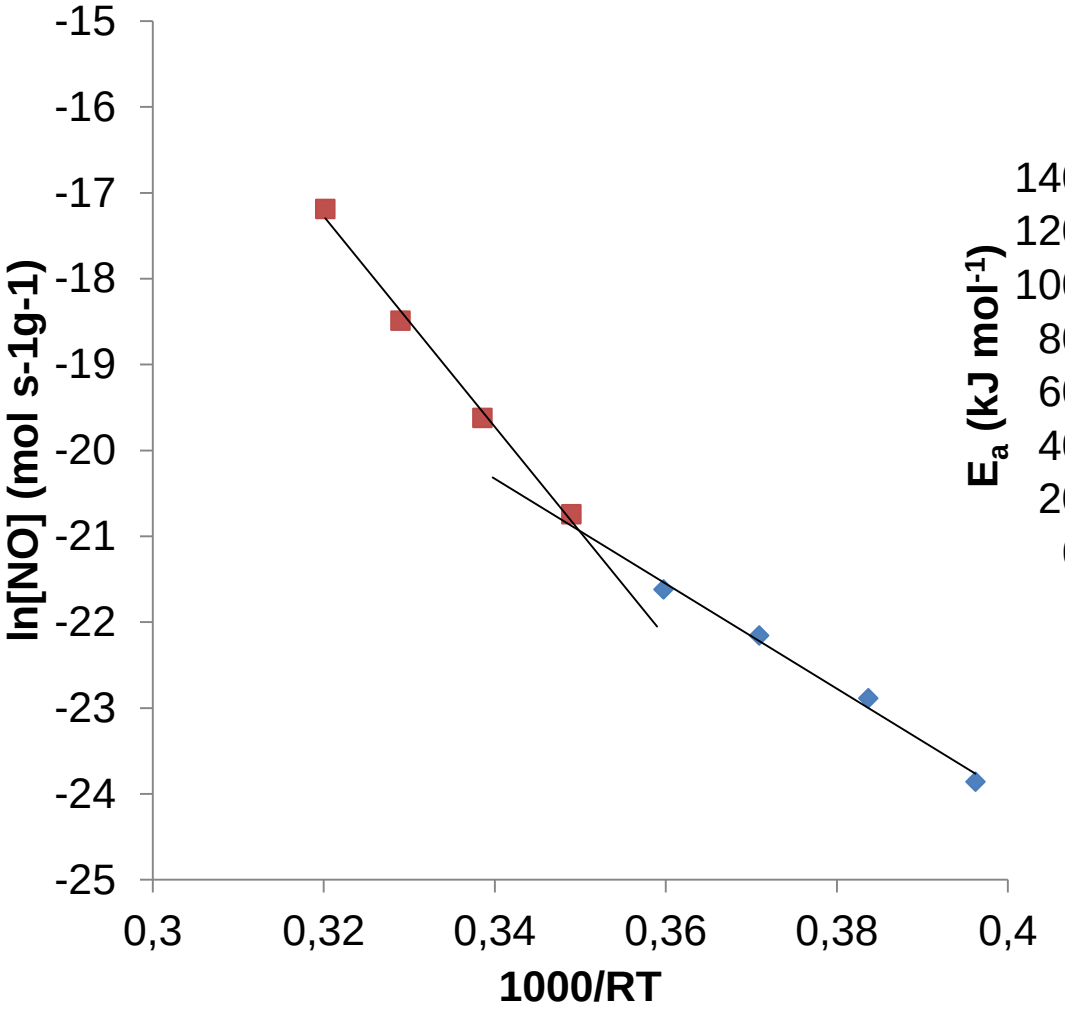
Chemiluminescence Results

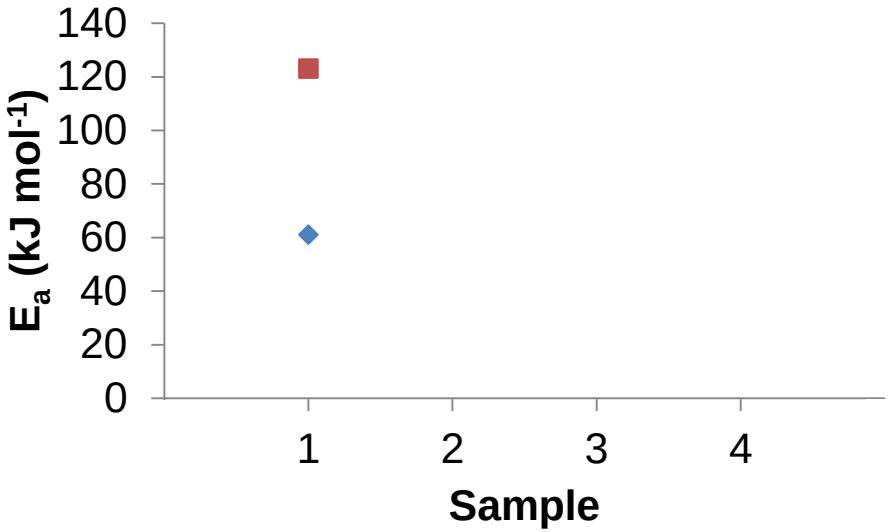


Chemiluminescence Results

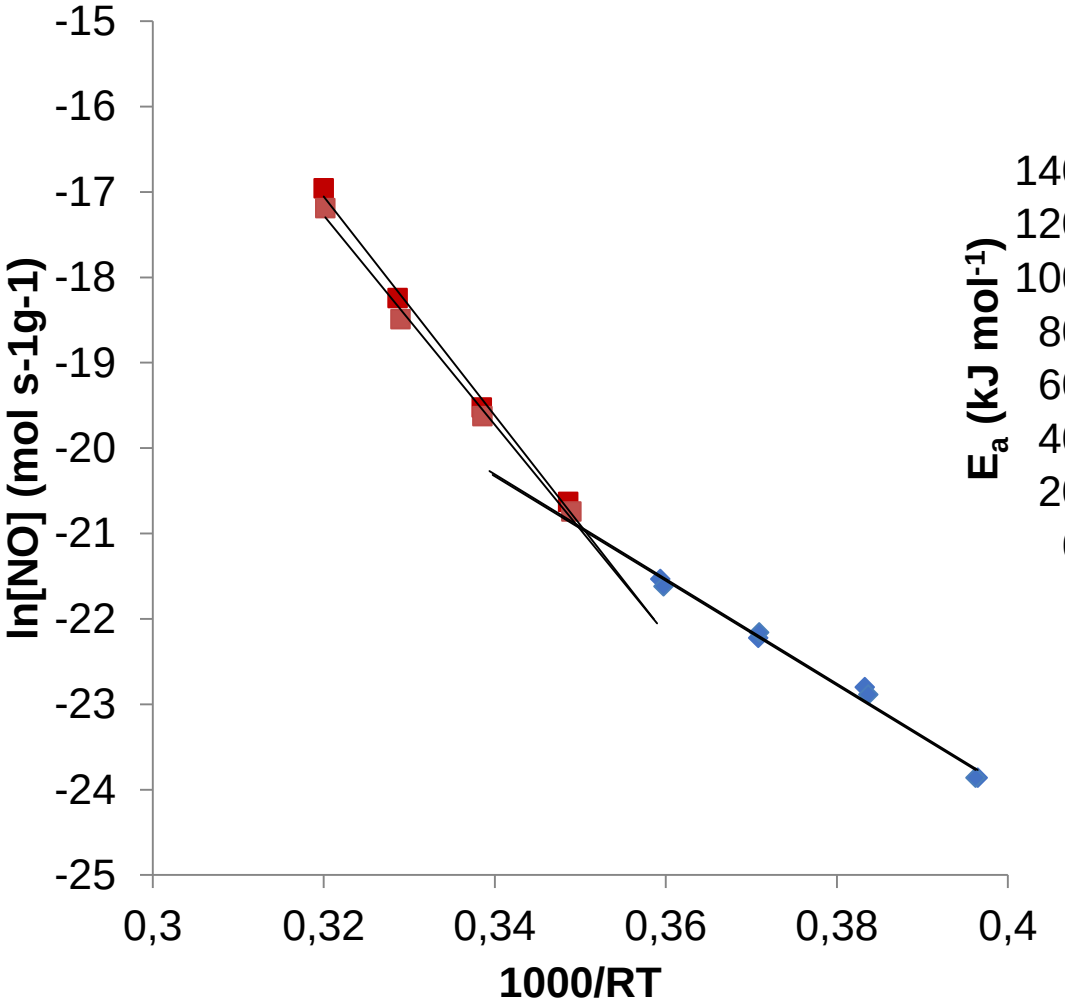


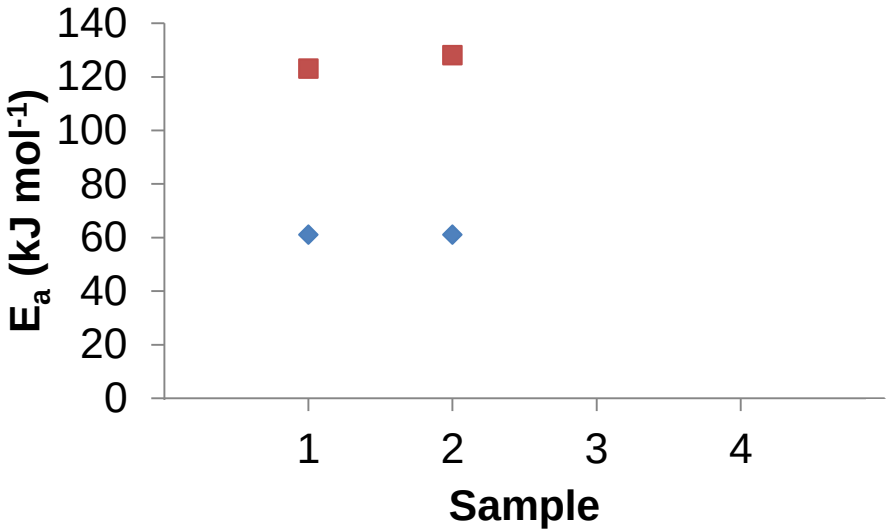
Chemiluminescence Results





Chemiluminescence Results





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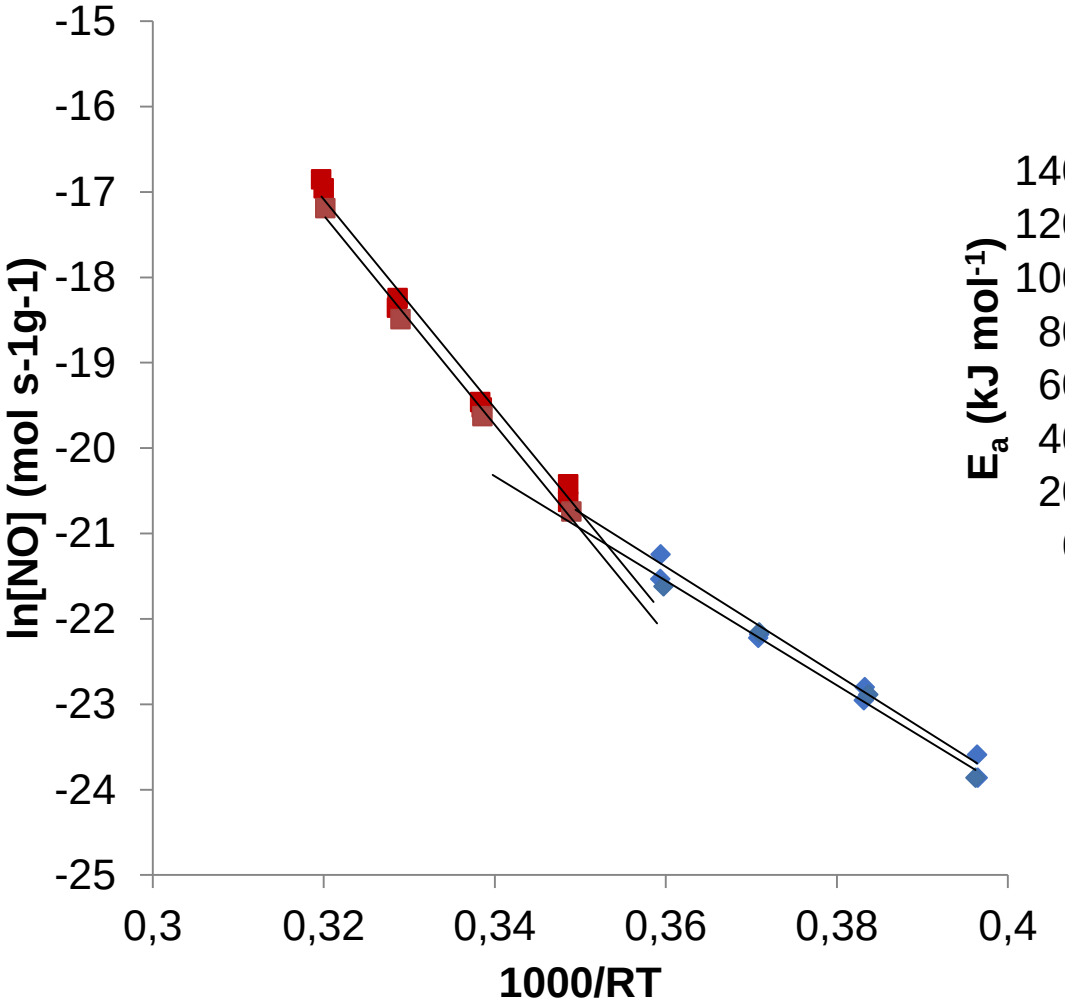
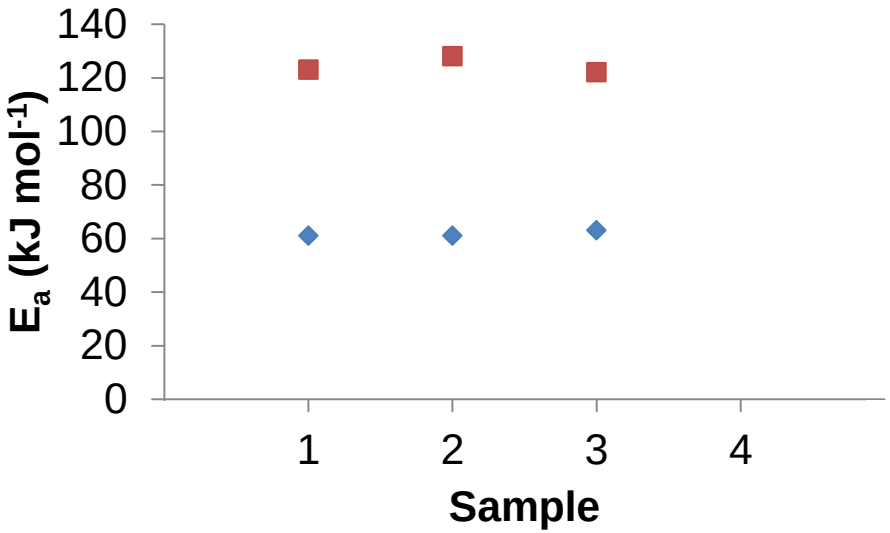
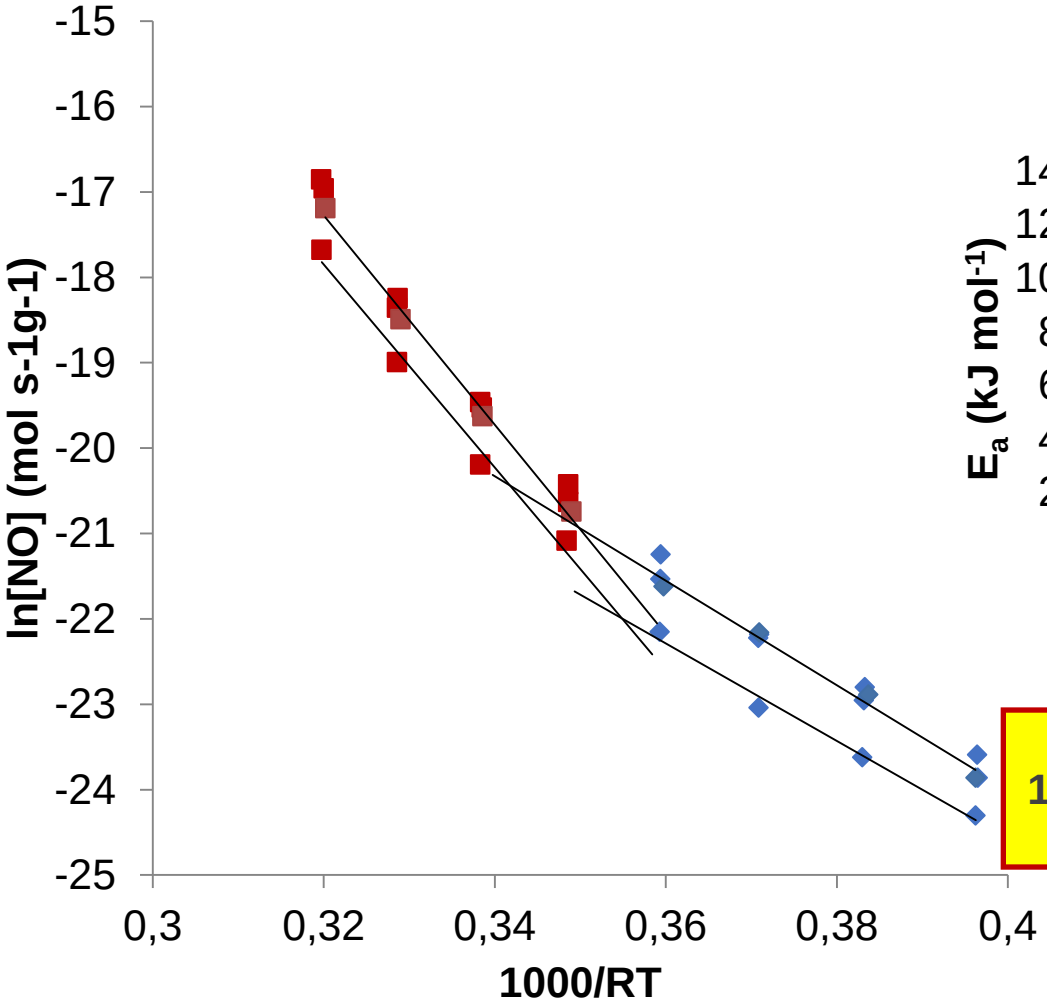
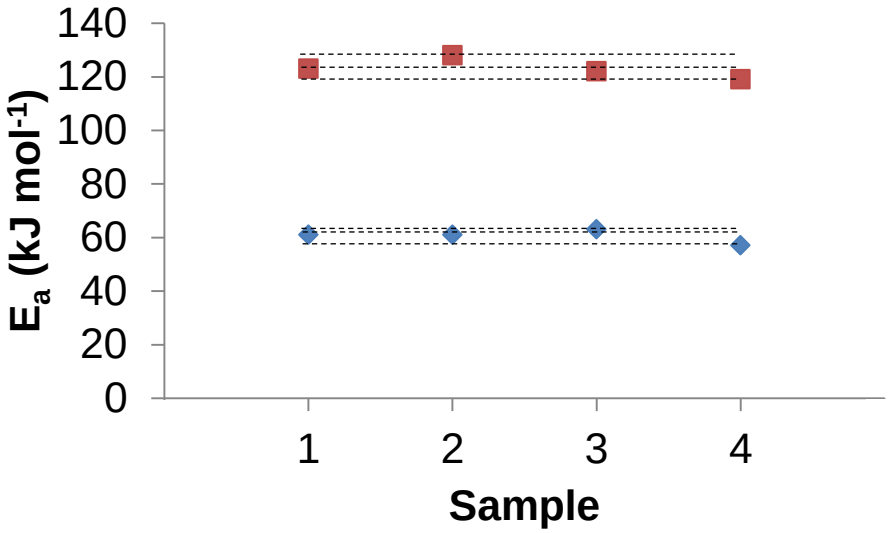




Chemiluminescence Results





123 ± 3.7 kJ mol^{-1}

60.5 ± 2.5 kJ mol^{-1}

Results Summary

Sample	Mass (g)	Flow Rate (mL min^{-1})	Ea 30 – 60 °C (kJ mol^{-1})	Ea 70 – 100 °C (kJ mol^{-1})
1	5	30	61 ± 4.7	123 ± 6.3
2	5	30	61 ± 4.9	128 ± 6.1
3	5	100	63 ± 5.2	122 ± 12.0
4	2.1	30	57 ± 4.5	119 ± 9.6

Conclusions

- Chemiluminescence is a reliable, robust tool for investigating the intrinsic decomposition of NC

- Demostrates intrinsic decomposition
  - 30 – 60 °C ~ 60 kJ mol^{-1}
  - 70 – 100 °C ~ 120 kJ mol^{-1}

- Robust, relatively quick test for investigating NC/propellant/stabilisers
  - < 1 week for 30 – 130 °C

Chemiluminescence Future Work

Experiment Types

Swept

Flow rate

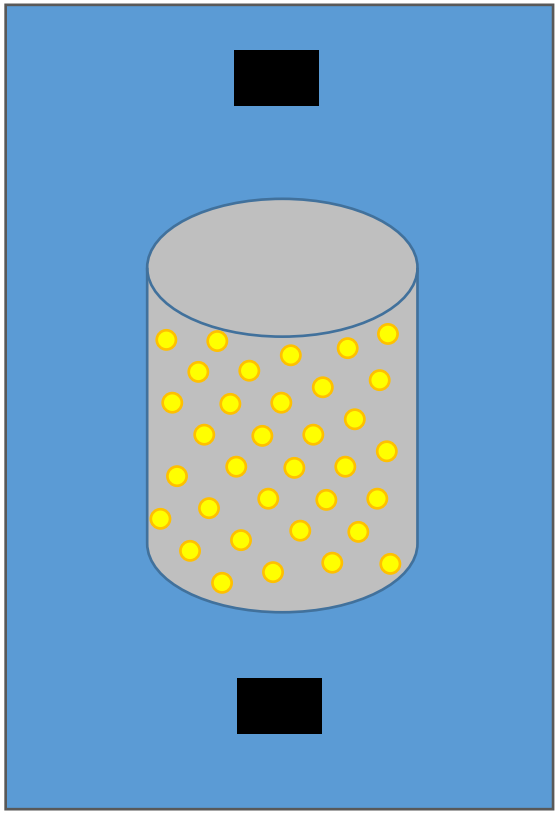
Sample geometry

Sample density

Humidity

NC Type

Propellant (trapping)



Chemiluminescence Future Work

Experiment Types

Closed

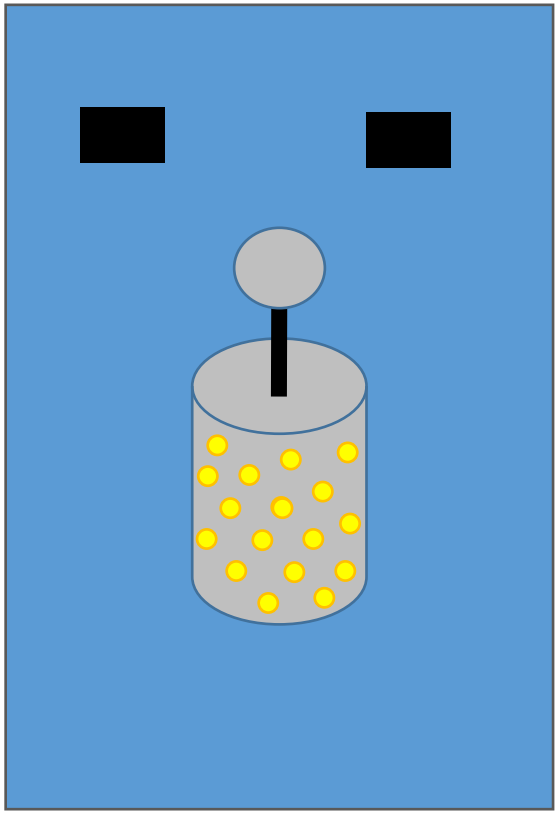
Sealed systems

10 µL/temp

NC/propellants

Temperature

Humidity



Chemiluminescence Future Work

Experiment Types

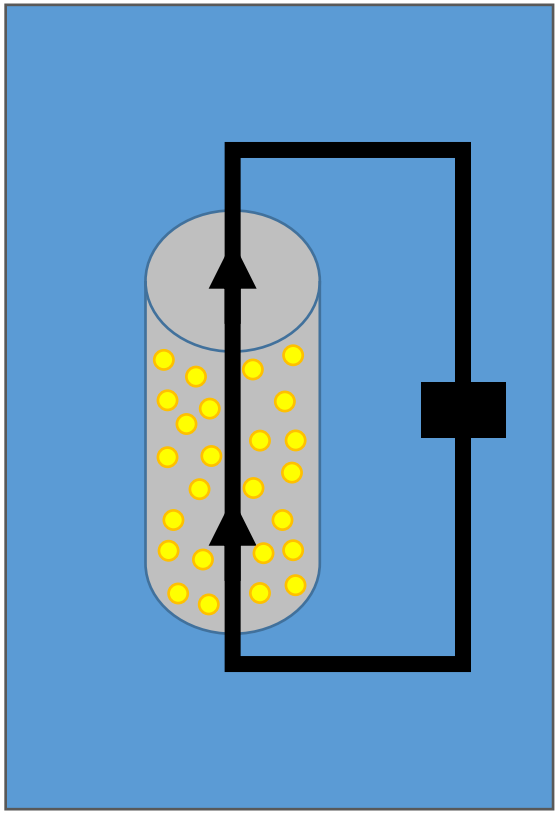
Looped

Reactivity of NO/NO_2

NC

Stabilisers – new, green

Plasticisers



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Questions?