



Thermal decomposition mechanism of nitrocellulose investigated by **CHEMILUMINESCENCE**

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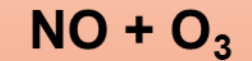
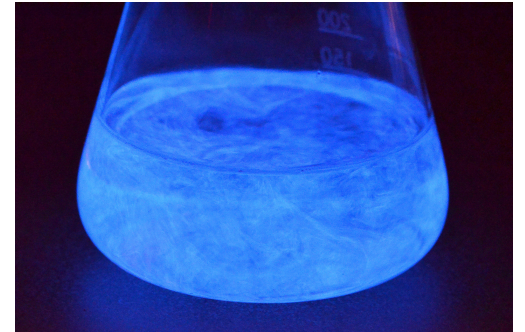
Part1.

1. Chemiluminescence NOx analysis. What is it?
2. Swept experiments – reactivity of NO₂
3. Understanding Abel heat test results – prompt NOx
4. Compatibility
5. Swept experiment – Kinetics

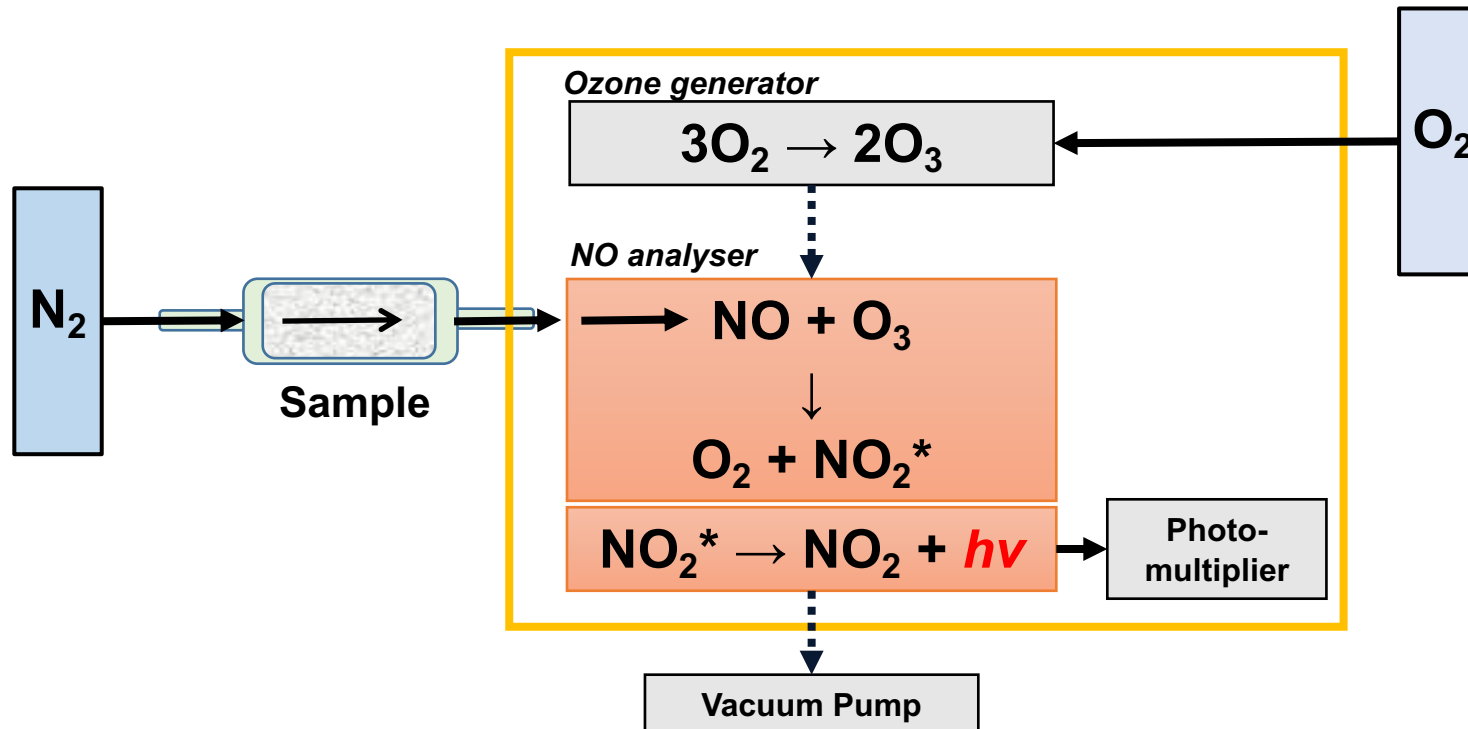
Part 2.

1. NC degradation phenomenological description
2. Chemiluminescence NOx analysis – setup
3. Swept – Kinetics evaluation
4. Effect of Moisture
5. Future
6. Conclusions

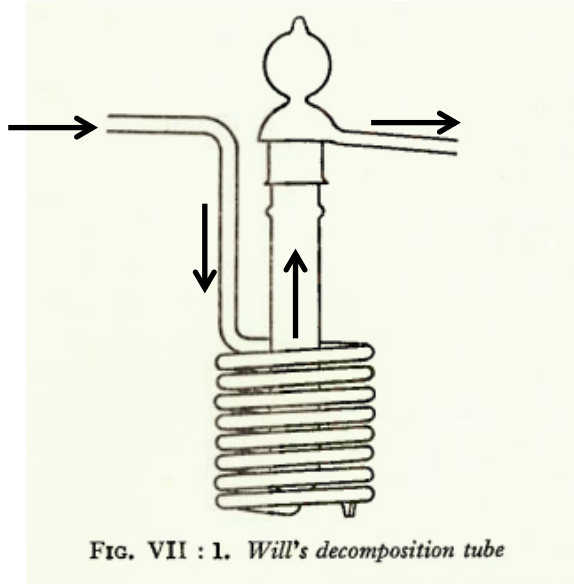
Chemiluminescence



(1) What is Chemiluminescence?



(2.1) Swept experiment



Flow of gas through NC is important [Ref 1]

- too high the gas is not preheated (135 °C)
- too low the products of decomposition are not removed

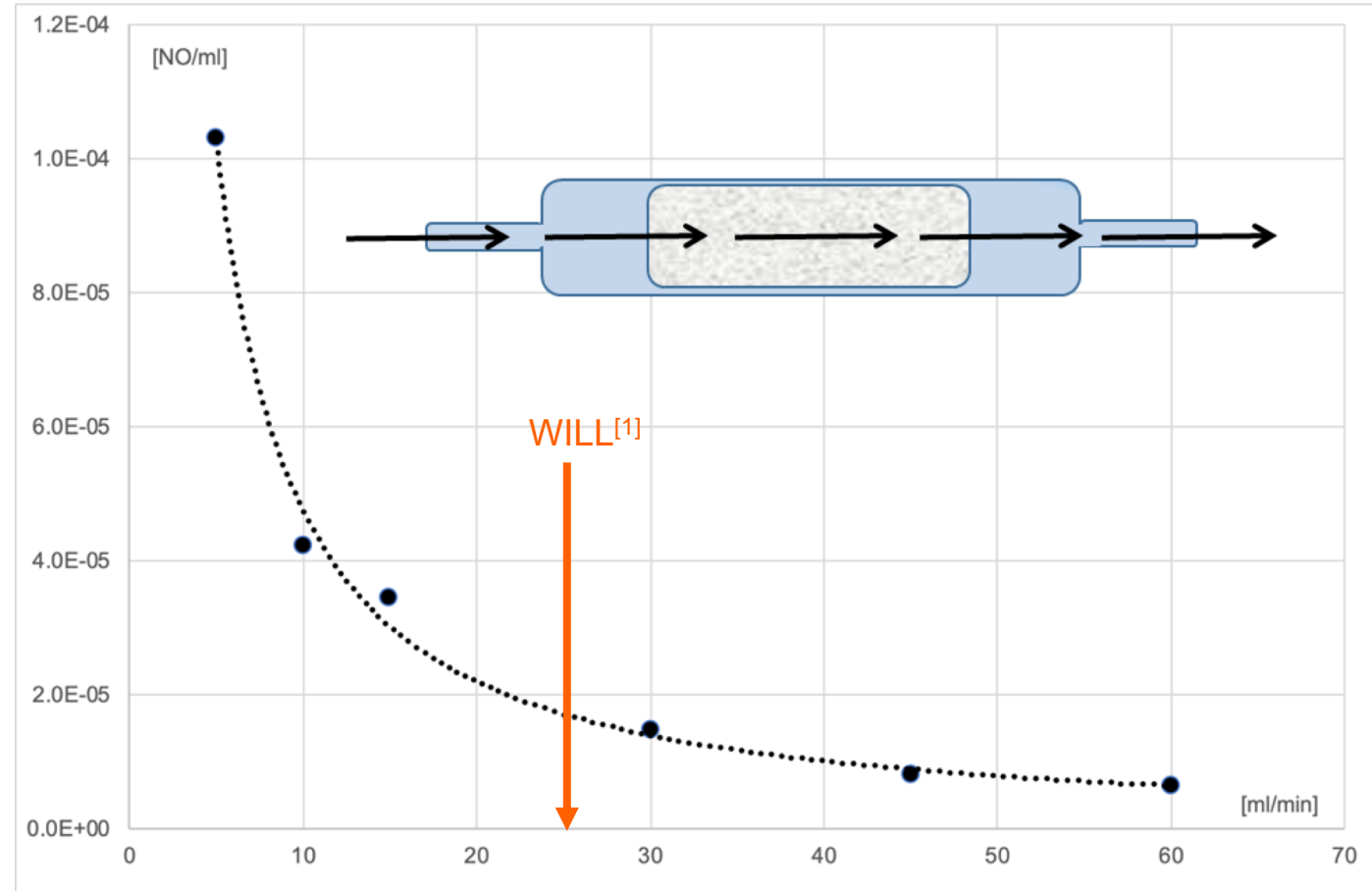


Fig 1. Swept NO concentration as a function of N₂ gas flow.
5 g NC sample. 25 mm diameter tube, 12.6 %N, 100 °C, <10 ppm [H₂O]

(2.2) Swept Experiment

NO_2/NO_x ratio - Effect of sweep rate

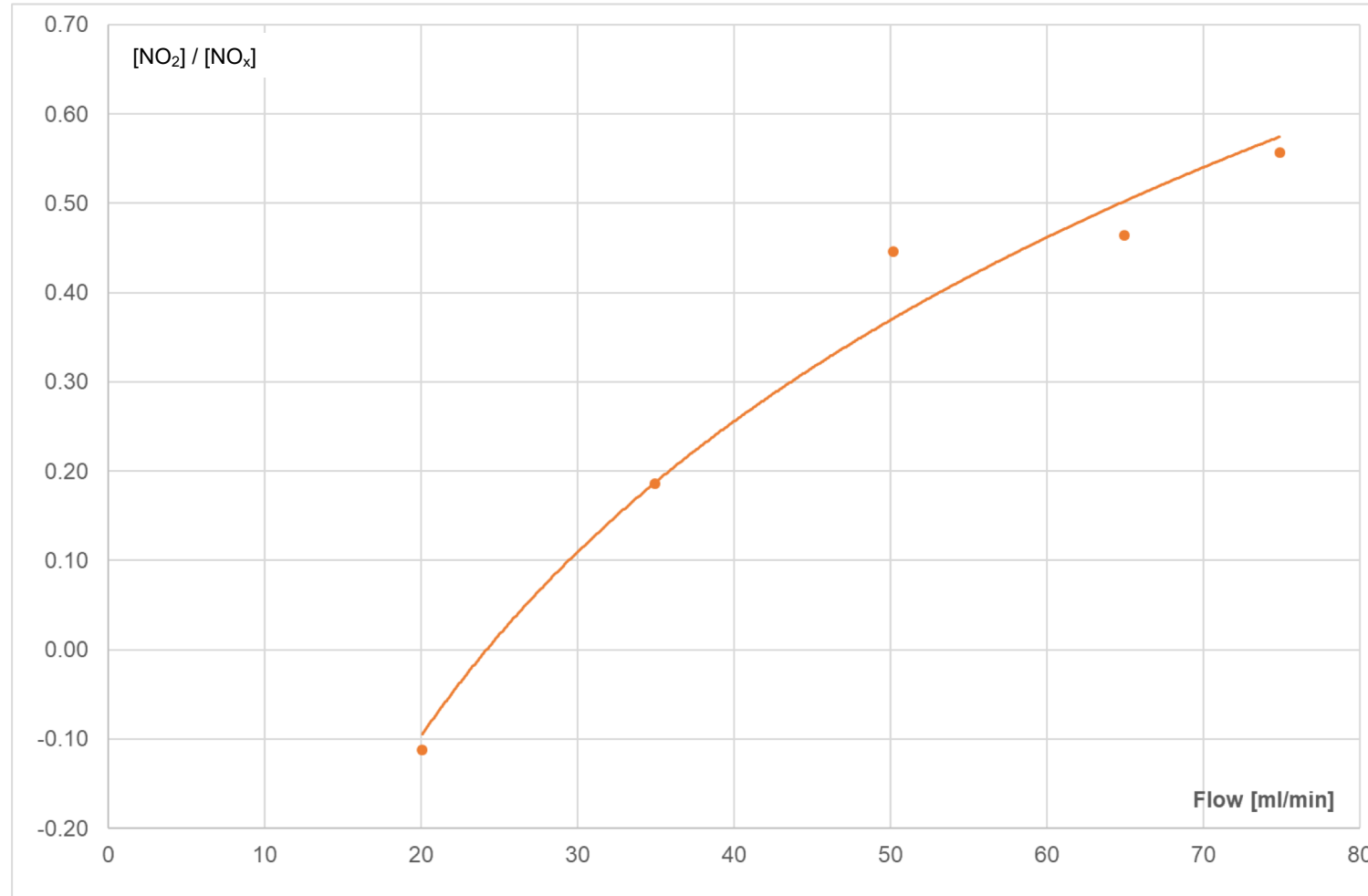


Fig 2. Effect of sweep rate on NO_2/NO_x ratio. 2.5 g NC at 30 °C. [new data]

(2.3) Swept Experiment

NO/NO_x ratio - Effect of pressure

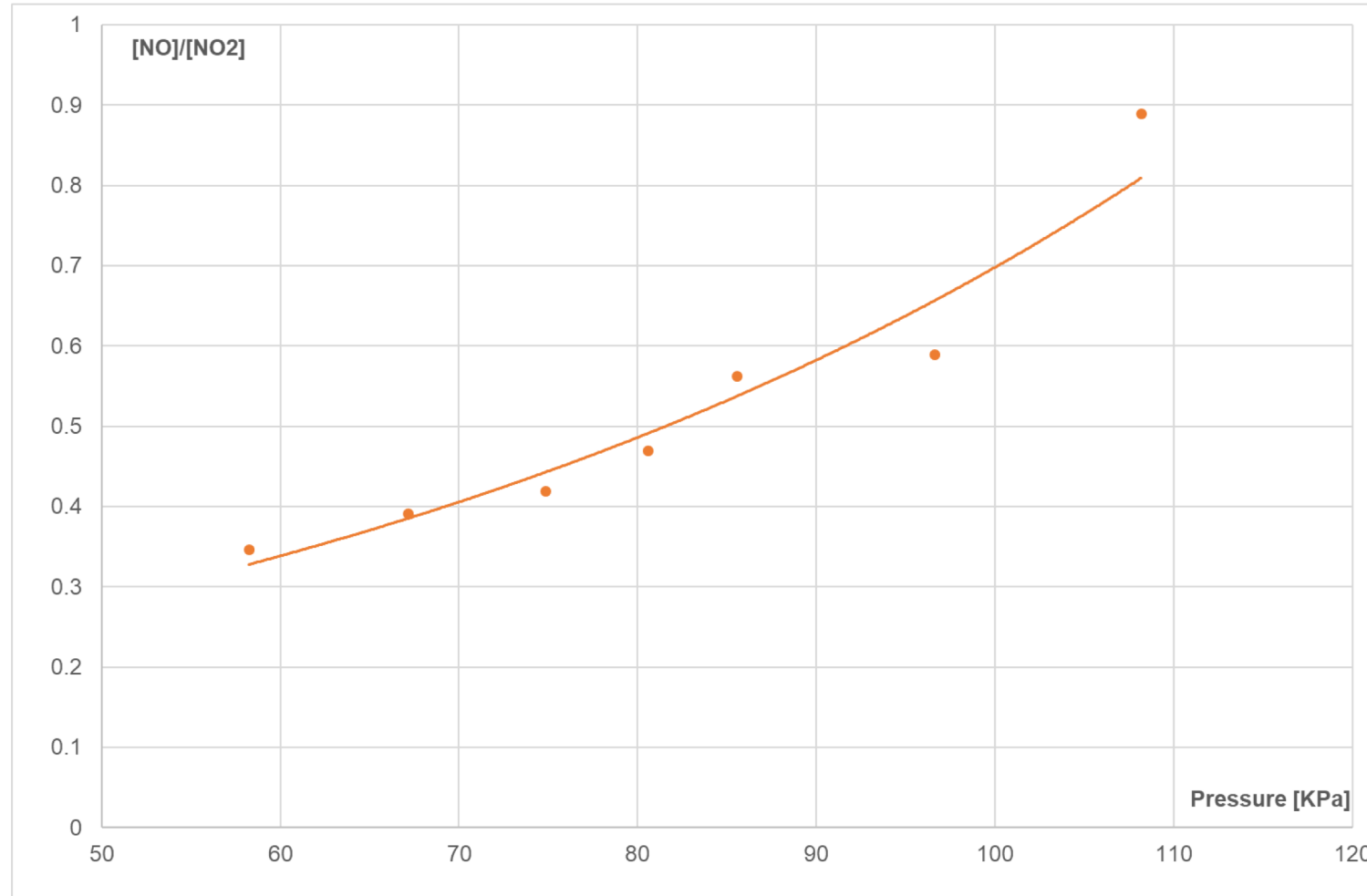


Fig 3. Effect of pressure on NO/NO₂ ratio. 0.5 g NC at 100 °C. 60 ml/min N₂ gas. [new data]

(3) Prompt NO_x – Effect of sample storage/age Constant Temperature

Anomalous Abel Heat Test Results

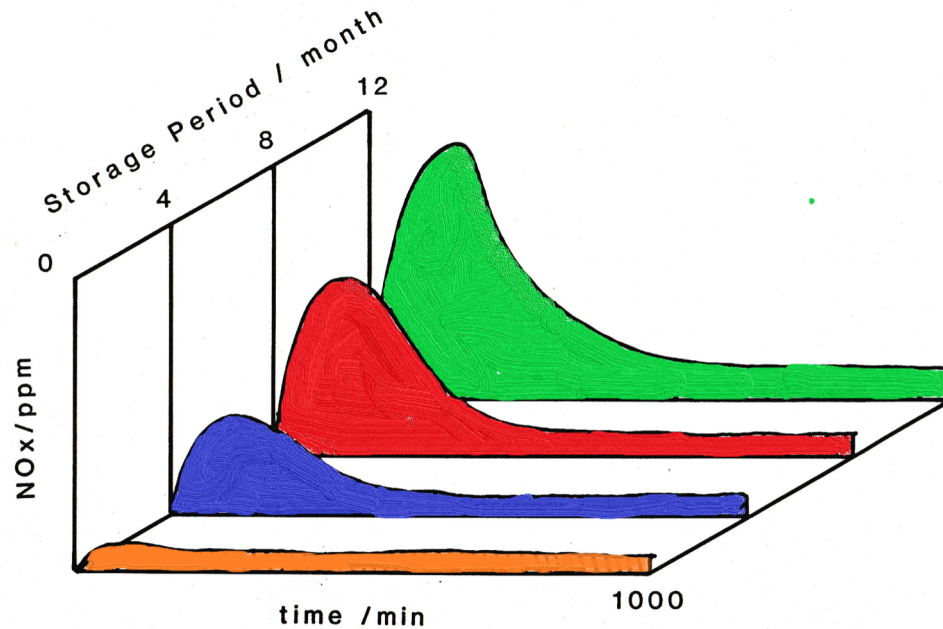
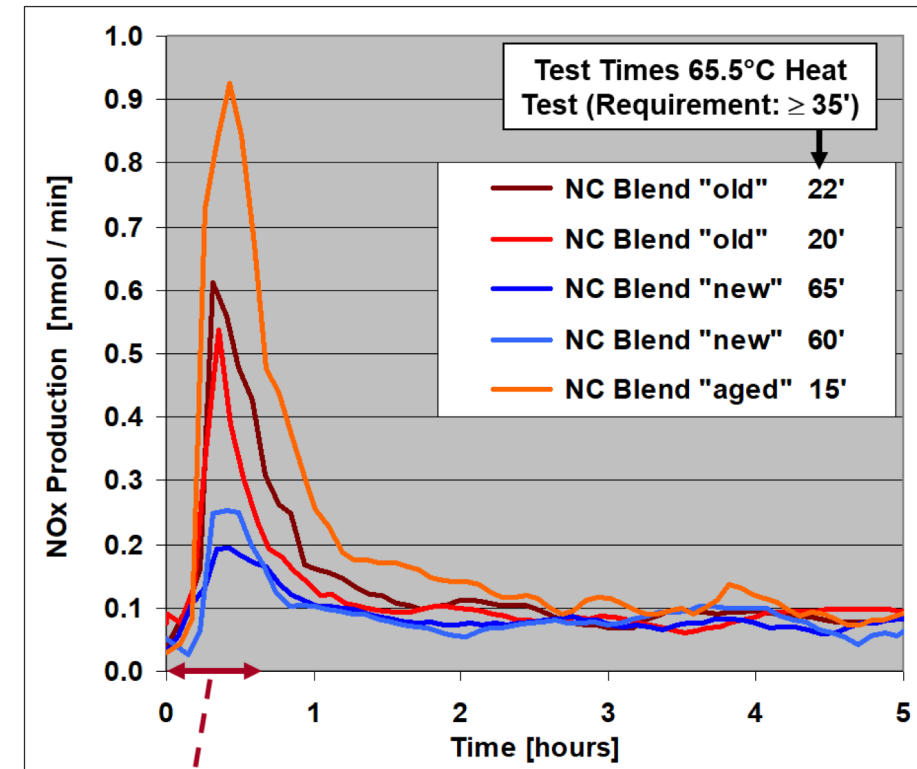


Fig 4. Effect of Storage Time on NO_x Evolution at 70 °C. [Ref 3]



35' = Abel Heat Test Time

Fig 5. NO_x-Production at Abel Heat Test Temperatures [Ref 4]

(4.1) Compatibility – Constant Temperature

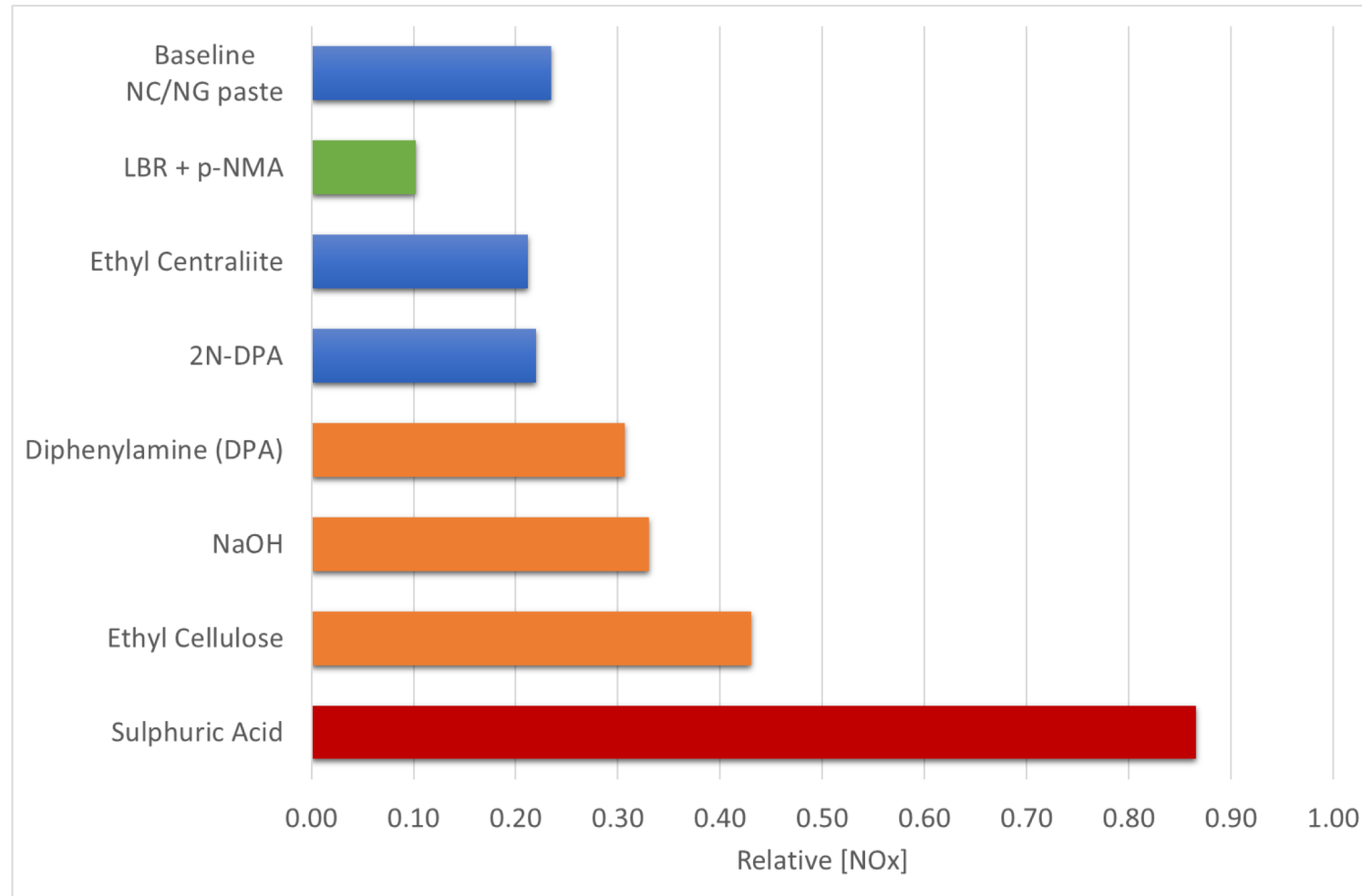


Fig 6. NOx Evolution rate from NC/NG Paste + additives at 80 °C. [Ref 5]

(4.2) Compatibility – Constant Temperature

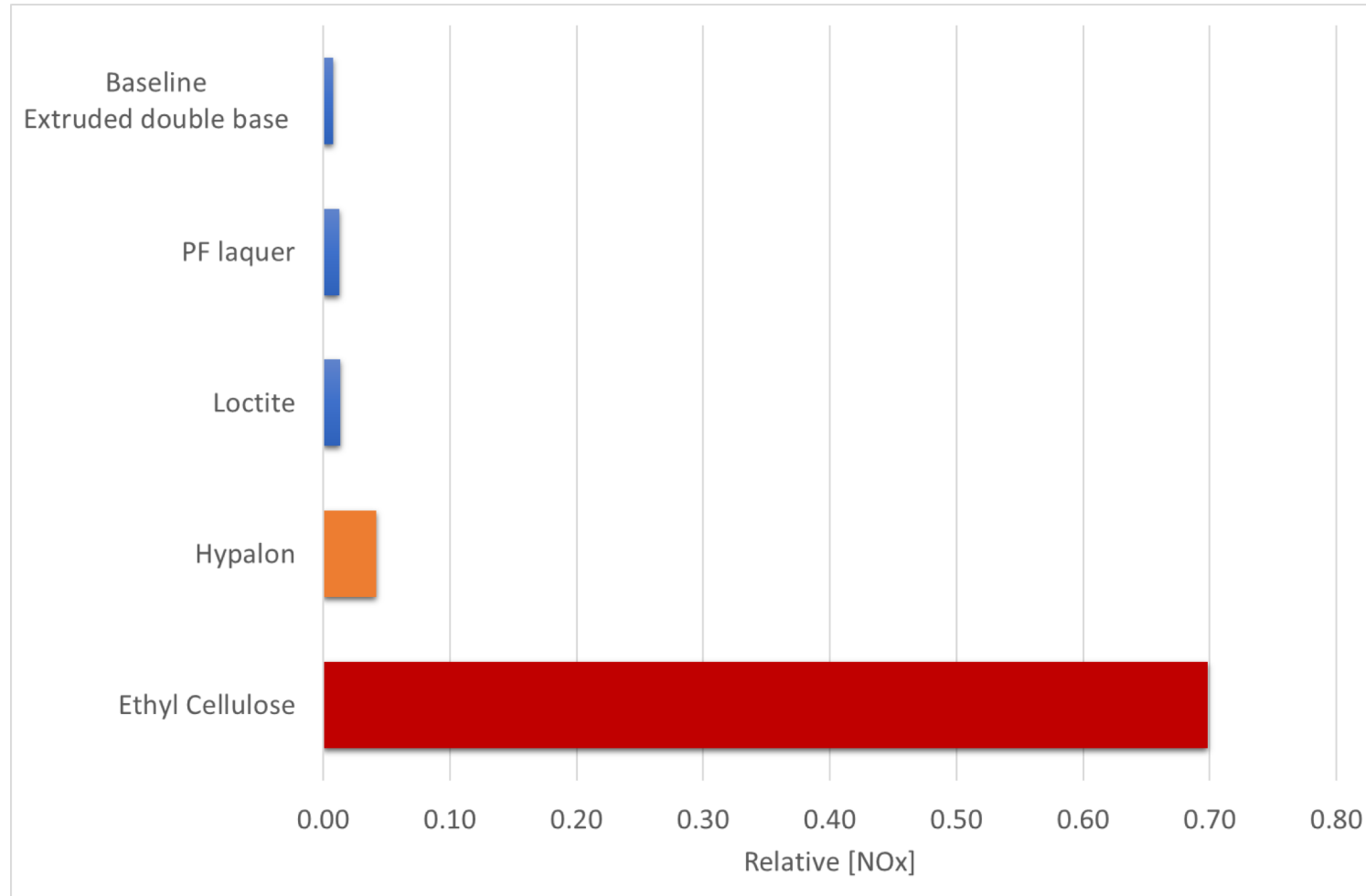


Fig 7. NO_x Evolution rate from EDB propellant + additives at 80 °C. [Ref 5]

(5) Swept Experiments – Variable Temperature

Year	NC (%N)	Temp (°C)	Ea (kJ/mol)	Ref
1980	12.6	30-80	50.6	6
		80- 130	152.3	
1980	12.2	40-70	62.8	7
		70-100	129.7	
1981	12.2	40-80	106.7	1
		80-130	179.9	
2018	12.6	30-60	60.5 (± 2.5)	8
		70-100	123 (± 3.7)	

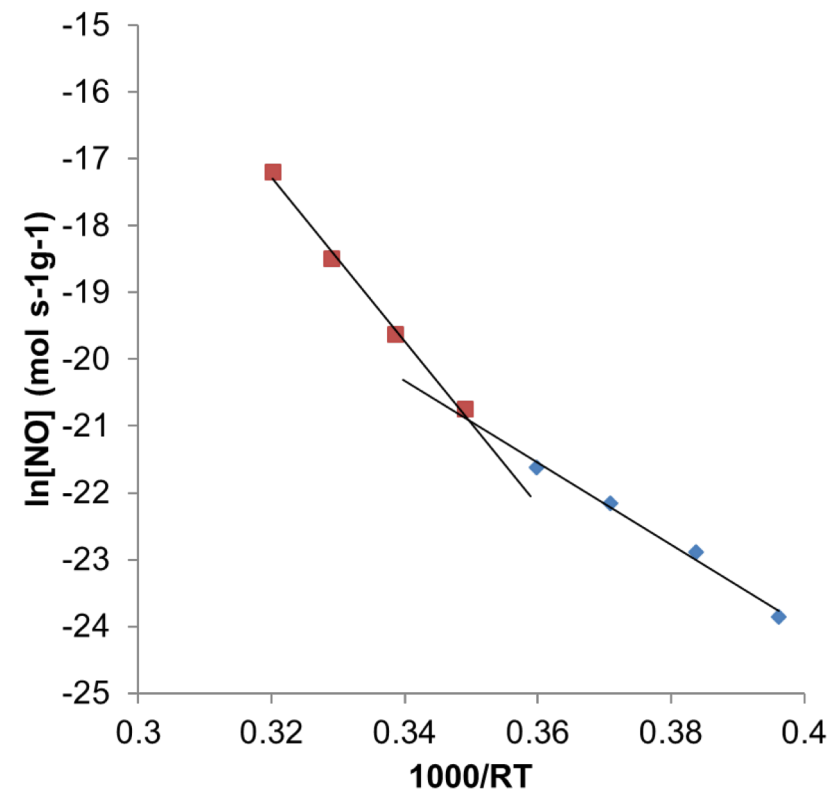
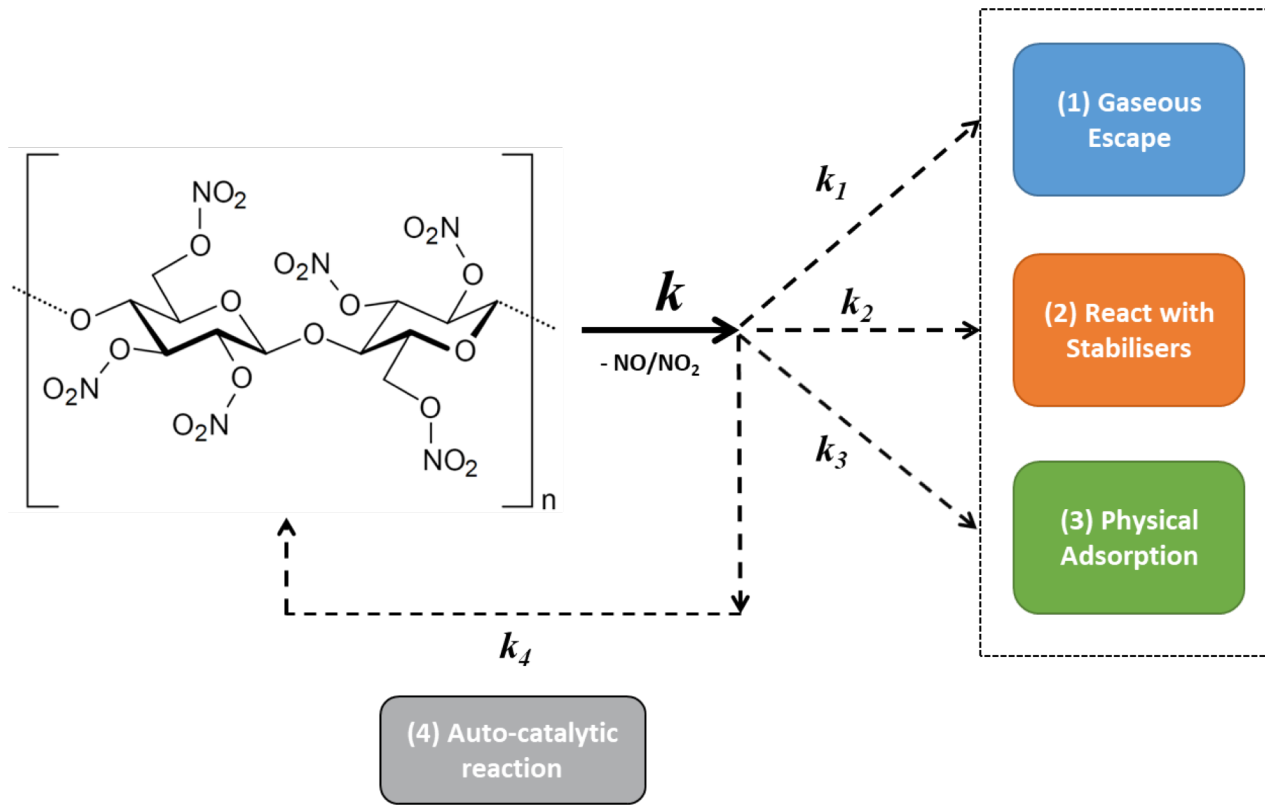


Fig 8. Arrhenius plot NO. 5 g NC. 100 ml/min flow of N₂ gas. [Ref 8]

(6) NC degradation phenomenological description



Literature: decomposition k follows 2 pathways:

Thermolysis of CO-NO₂ groups

$$E_a = 160 - 170 \text{ kJ mol}^{-1}$$

Hydrolysis of CO-NO₂ groups

$$E_a = 80 - 120 \text{ kJ mol}^{-1}$$

Fig 9. Simplified scheme for the chemical ageing of propellants. [Ref 9]

(7) Chemiluminescence – swept experiment

- Dry NC (5 g) was loaded into a glass reaction chamber (0.25 g/cm³, 25 mm diameter) and swept with N₂ gas (5-60 ml/min) and heated at 3 °C/h (20-120 °C).
- NO gas was quantified with an Analytix Sievers 280i chemiluminescence nitric oxide (NO) analyzer, fitted with a NOx/NO converter (JNOX-CV, AMCS Analytical Specialists).
- Humidity was measured with Vaisala DMT152 Dew Point Transmitter and controlled with molecular sieves and water permeation tubes.

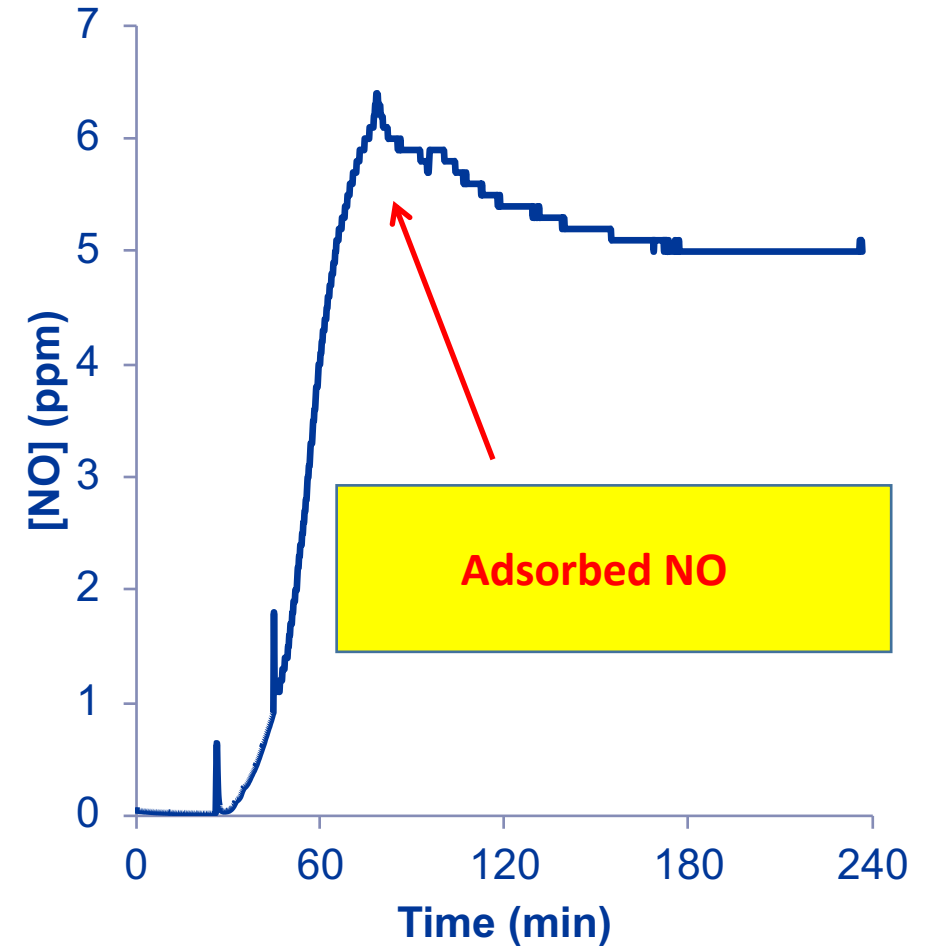
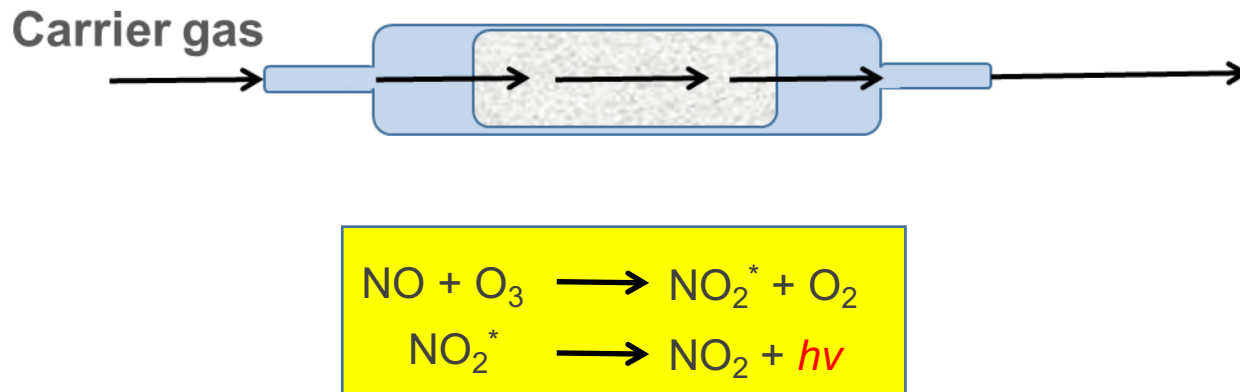


Fig 10. Example prompt NO evolution from swept exp.

(8.1) Kinetics of decomposition

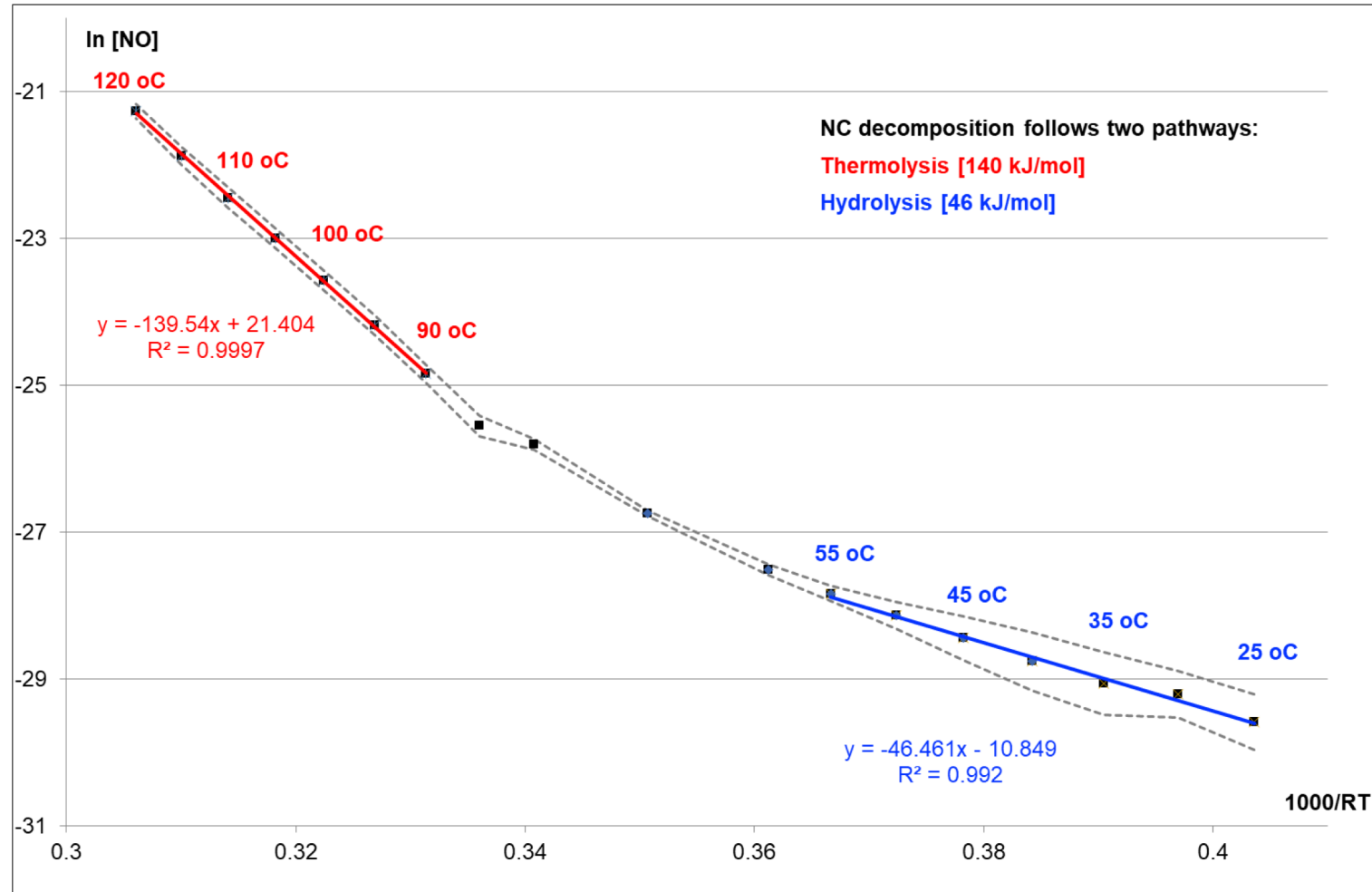


Fig 11. Arrhenius plot of nitric oxide (NO) decomposition gas concentration. NC (12.6 %N), 60 ml/min flow of N₂ gas containing <10 ppm water, heating rate 3 °C/h (20-120 °C). Error bars x1 SD of 4 replicate analysis.

(8.1) Kinetics of decomposition

Year	NC (%N)	Temp (°C)	Ea (kJ/mol)	Ref
1980	12.6	30-80	50.6	6
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		80-130	179.9	
2018	12.6	30-60	60.5 (±2.5)	8
		70-100	123 (±3.7)	
2023	12.6	25-55	46	New
		90-120	140	

(8.1) Kinetics of decomposition

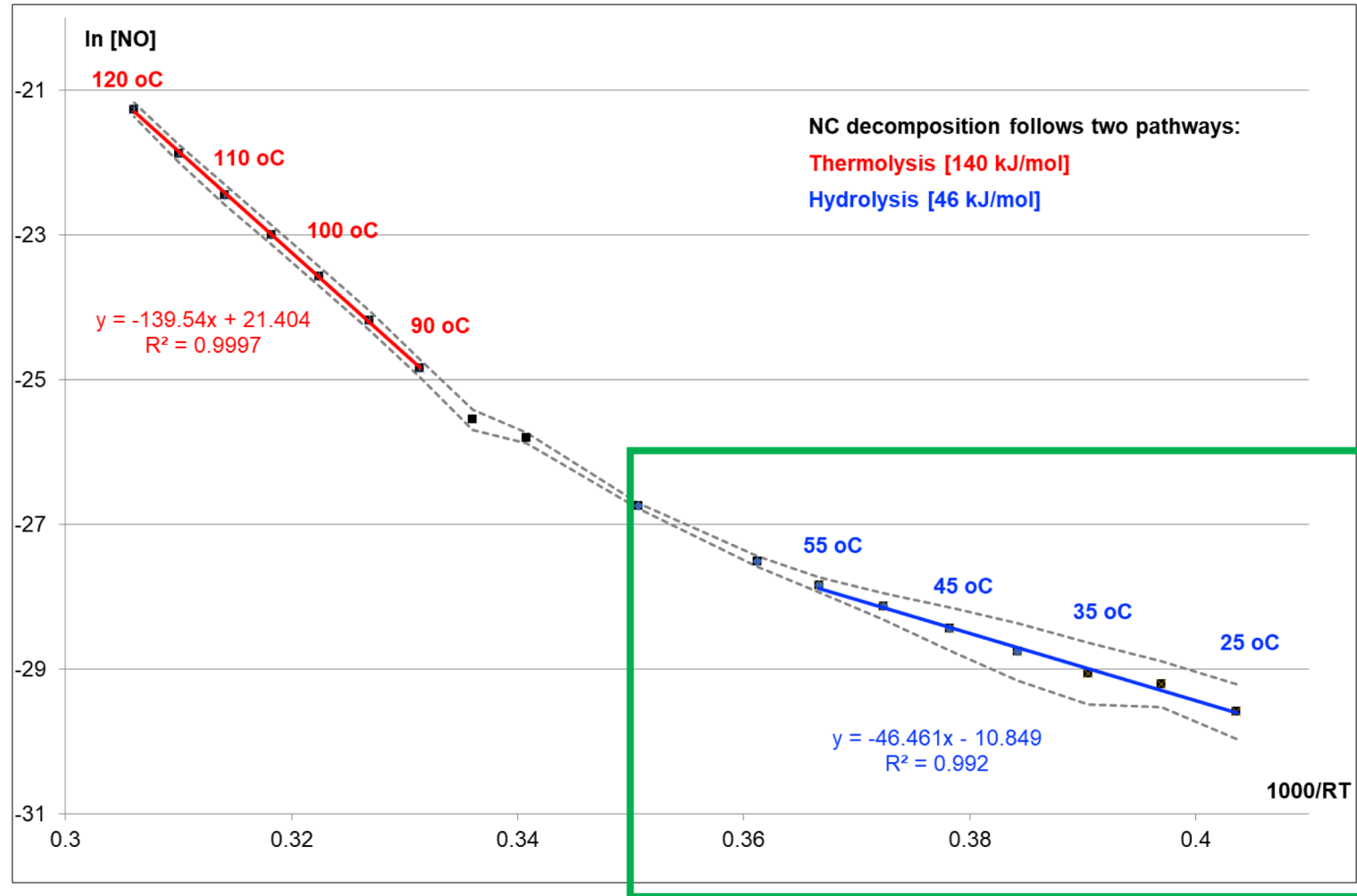


Fig 11. Arrhenius plot of nitric oxide (NO) decomposition gas concentration. NC (12.6 %N), 60 ml/min flow of N₂ gas containing <10 ppm water, heating rate 3 °C/h (20-120 °C). Error bars x1 SD of 4 replicate analysis.

(8.2) Kinetics of decomposition

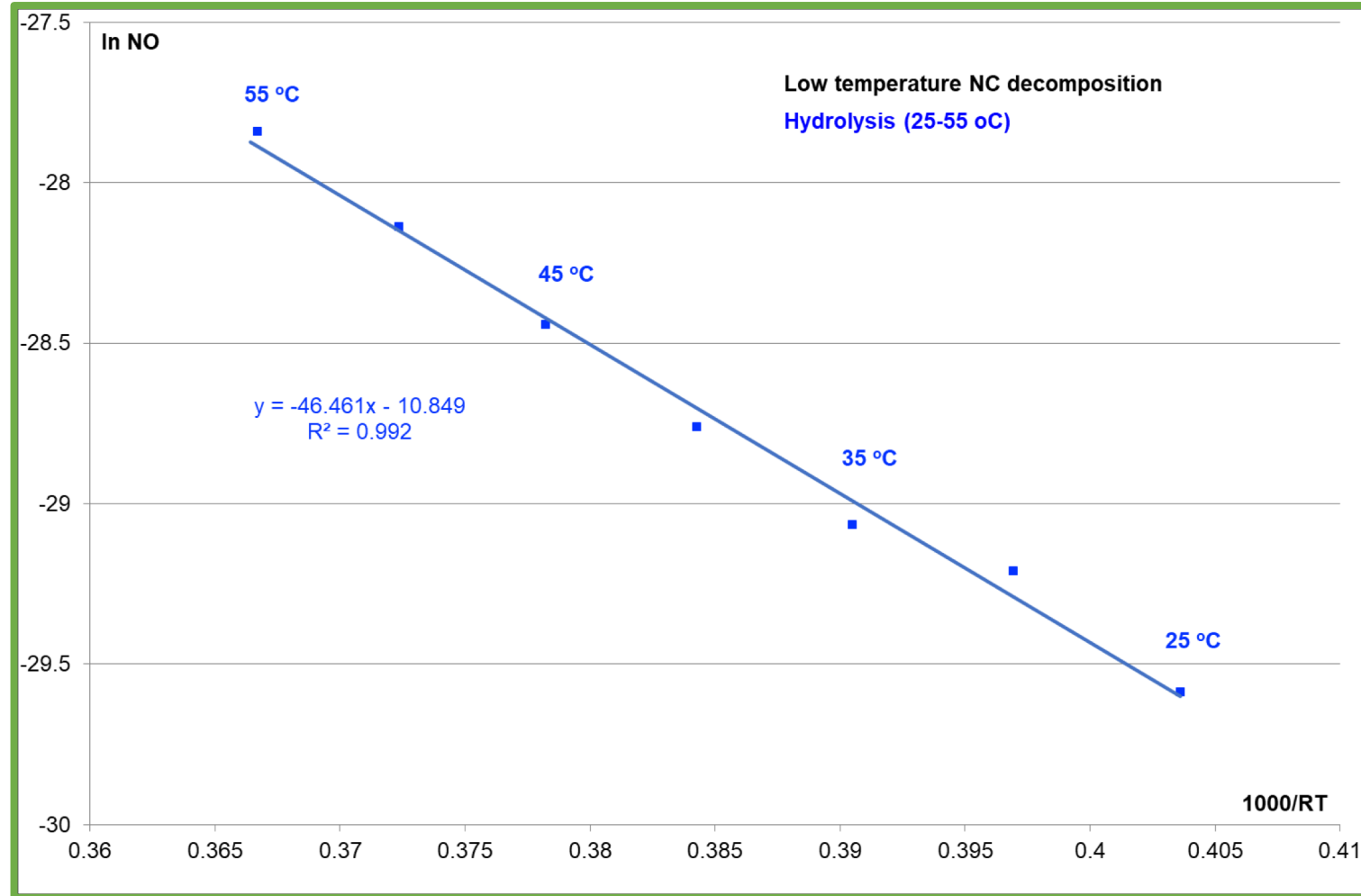


Fig 12. Arrhenius plot of nitric oxide (NO) decomposition gas concentration. NC (12.6 %N), 60 ml/min flow of N₂ gas containing <10 ppm water, heating rate 3 °C/h (25-55 °C). Average of 4 replicate analysis.

(8.3) Kinetics of decomposition

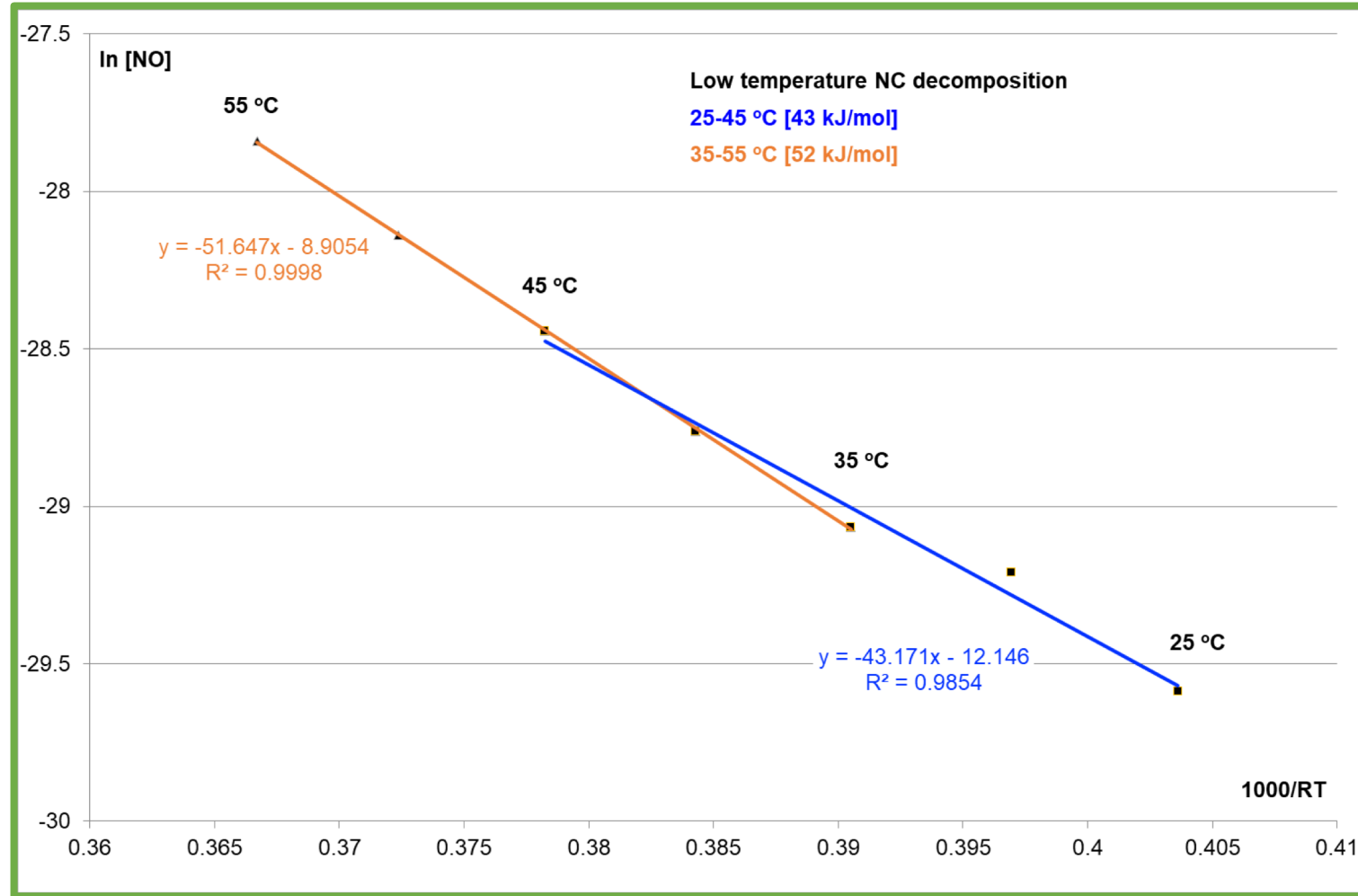


Fig 13. Arrhenius plot of nitric oxide (NO) decomposition gas concentration. NC (12.6 %N), 60 ml/min flow of N₂ gas containing <10 ppm water, heating rate 3 °C/h (25-55 °C). Average of 4 replicate analysis.

(9) Swept experiment - Influence of water/humidity

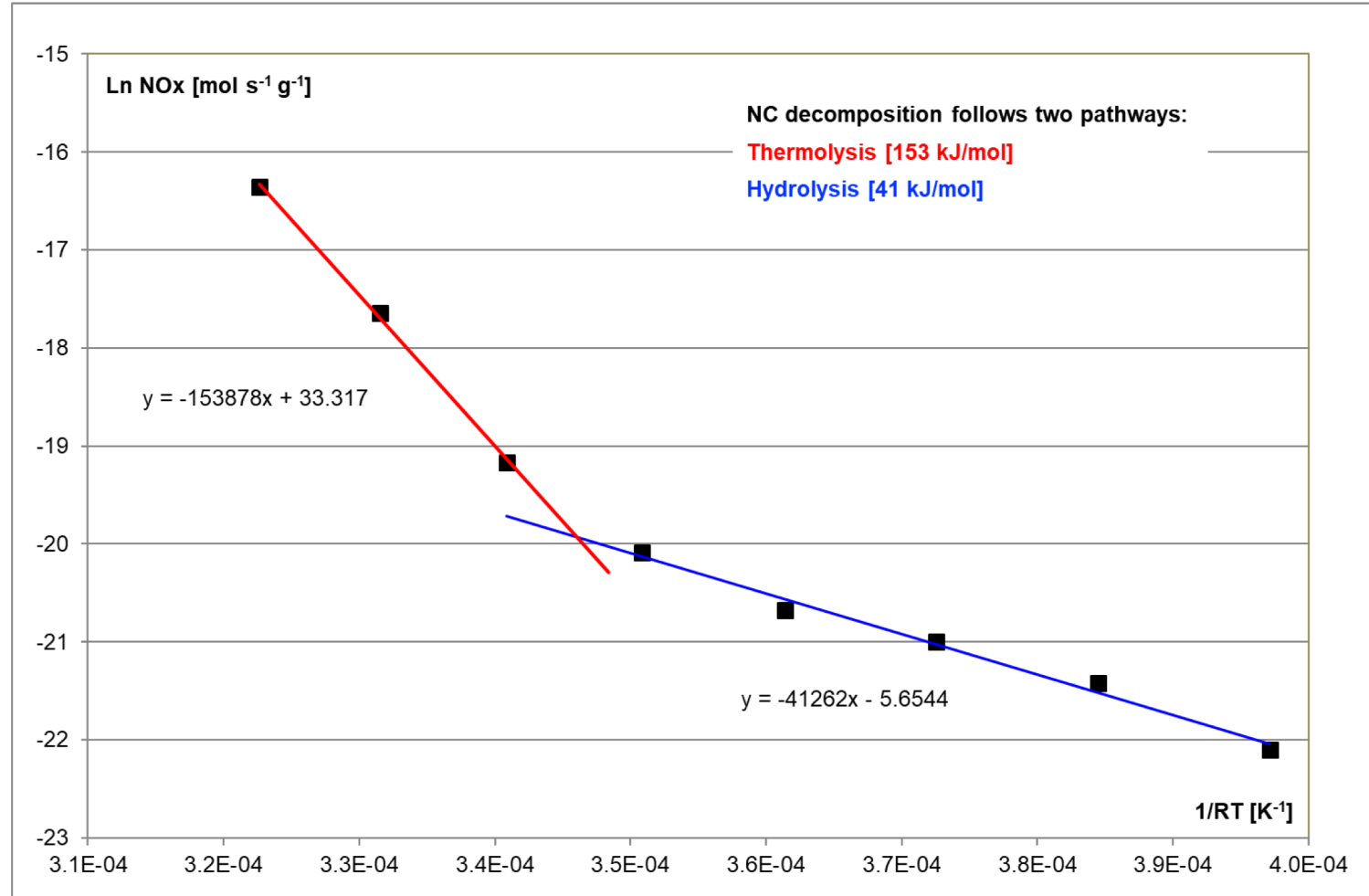


Fig 14. Arrhenius plot of nitric oxide (NO) decomposition gas concentration. NC (12.6 %N), 60 ml/min flow of N₂ gas containing, Stepped experiment 30-100 °C). [Ref 8]

(9) Swept experiment - Influence of water/humidity

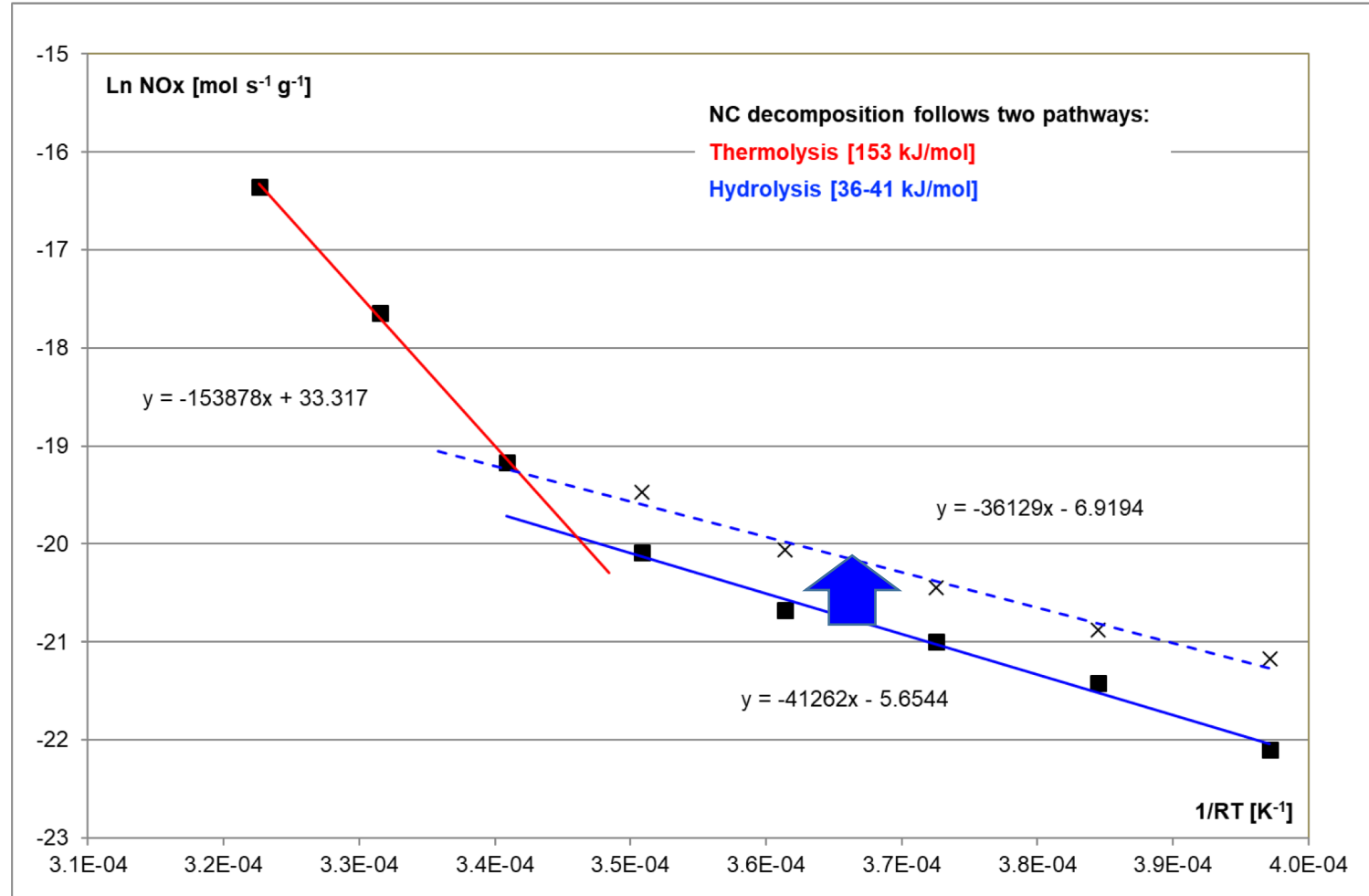


Fig 14. Arrhenius plot of nitric oxide (NO) decomposition gas concentration. NC (12.6 %N), 60 ml/min flow of N₂ gas containing, Stepped experiment 30-100 °C). [Ref 8]



(10.1) Future

Flow/Swept Experiments

Kinetics of NC decomposition

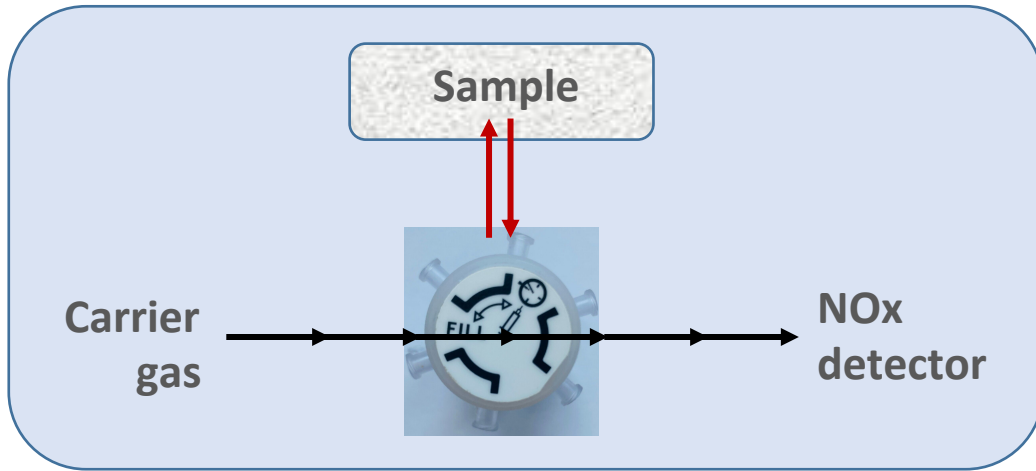
- Nitrocellulose N%
- NC/Cellulose sources
- Crystallinity
- Gelatinized/Fiber
- NC/NG paste
- Chemical stabilizers
- Ballistic modifiers
- Moisture/humidity

N₂O/CO/CO₂ – analysis (IR)

Closed Loop Experiments

Compatibility method

(10.2) Future. Closed loop applications



- Closed loop or stop flow setup experiment
- Sample sealed.
- 10-100 μl periodically sample and
- NO/NO_x (ppb) analysed

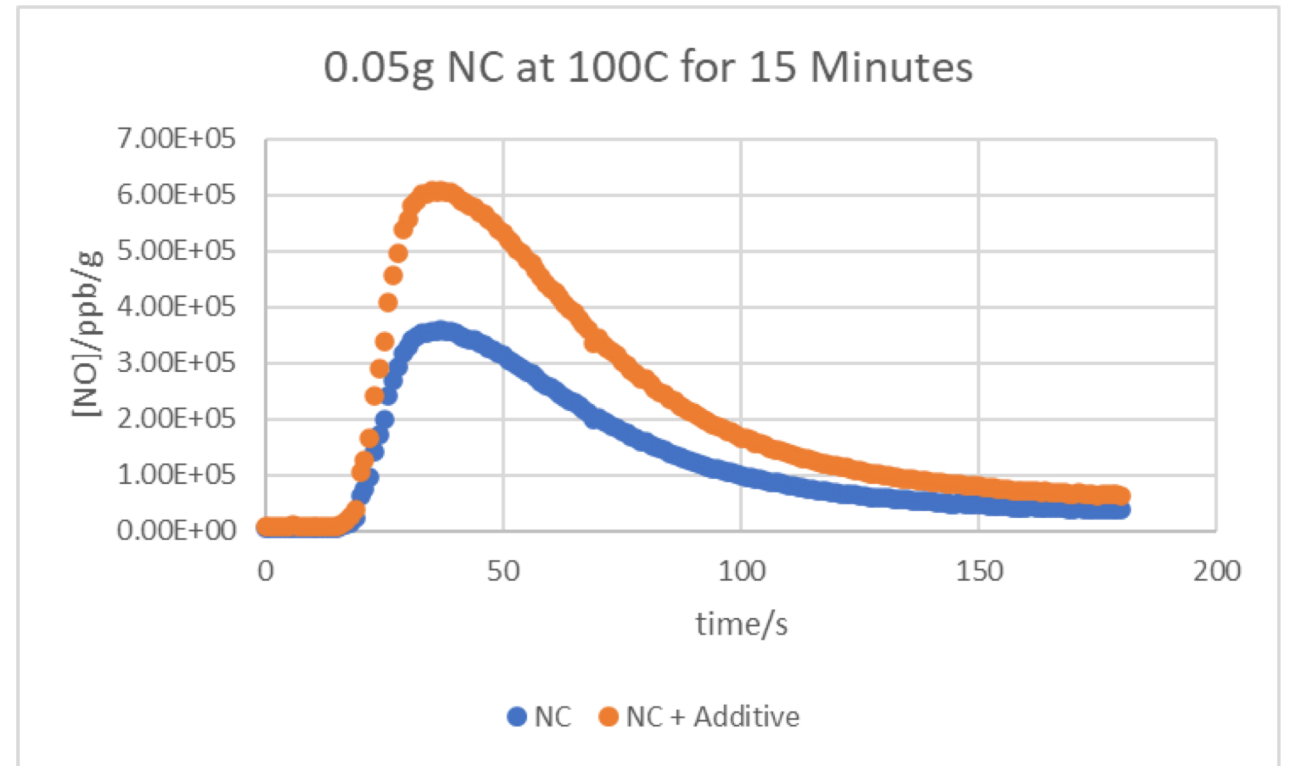


Fig 15. NO decomposition gas concentration. 0.5 g NC (12.6 %N), 100 °C, 15 min stop flow experiment [new data]

(10.1) Future

Flow/Swept Experiments

Kinetics of NC decomposition

- Nitrocellulose N%
- NC/Cellulose sources
- Crystallinity
- Gelatinized/Fiber
- NC/NG paste
- Chemical stabilizers
- Ballistic modifiers
- Moisture/humidity

$\text{N}_2\text{O}/\text{CO}/\text{CO}_2$ – analysis (IR)

Closed Loop Experiments

Compatibility method

Kinetics of NC decomposition

Kinetics of propellant decomposition

- Single/Double/Triple base
- Chemical stabilizers
- Ballistic modifiers
- Moisture
- Plasticizers
- Filler (RDX/HMX/NQ)



(11) Conclusions

- Chemiluminescence is a reliable, robust tool for investigating the intrinsic decomposition of nitrate esters such as nitrocellulose
- Swept experiment investigates the intrinsic decomposition
 - 20 – 60 °C ~ 40-60 kJ mol⁻¹
 - 70 – 100 °C ~ 160-170 kJ mol⁻¹
- Robust, quick test for life assessment and compatibility of NC/propellant
 - 20 – 120 °C in less than 48 hours
 - Single temperature compatibility 2-3 hours
- Closed loop experiments
 - compatibility mg samples in a few minutes
 - (storage life) in hours



References

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Questions?

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