Effect of Humidity on the Real-Time, Low Temperature, Nitrocellulose Degradation by Chemiluminescence

Cranfield UNIVERSITY

C. O'Keeffe, I. Wallace
and P. P. Gill

Introduction

Chemiluminescence is an extremely sensitive technique for the detection of NOx gas. Many conventional explosives contain nitro or nitrate ester groups that on decomposition evolve oxides of nitrogen. The rate of evolution of these gases can be used as a means of assessing the rate of decomposition of these explosives. A number of researchers have used chemiluminescence analysis to measure low temperature decomposition of explosives and their constituents.

An advantage of this technique is its capability to measure parts per billion levels of NO and NO_2 at temperatures similar to those encountered by explosives in service. The technique has been successfully used to determine the temperature dependence of the decomposition of nitrocellulose (NC) and it has been used to establish the activation energy for the decomposition mechanisms (thermolysis and hydrolysis) of NC.

Activation energies were determined by examining the levels of NO and NO_2 gas evolved at varying humidity levels and temperatures of dry NC (5 g, 12.6% N content). Within the continuously swept technique (N_2 gas, 30 ml min^{-1}) the humidity levels generated ranged from 4 ppm to 938 ppm using water permeation tubes. This poster describes the investigation of the effect of humidity on the nitrocellulose degradation in real-time at conditions similar to those experienced in operational and storage conditions.

Figure 1. Glass reaction chamber

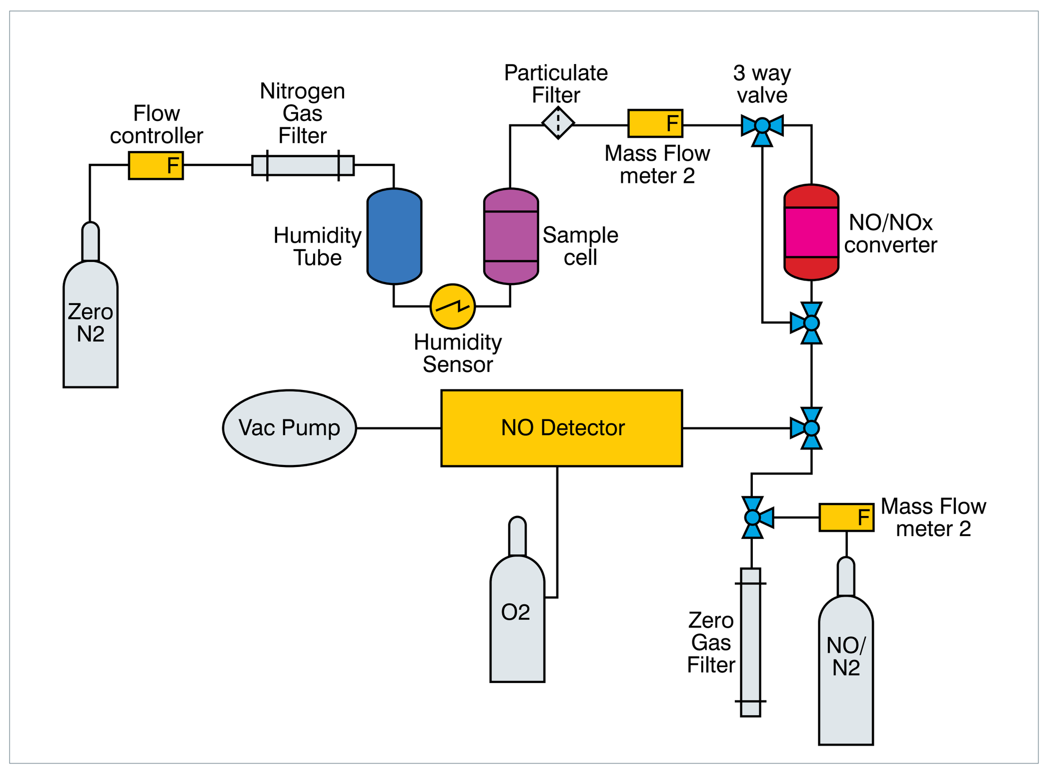

Figure 2. Experimental equipment and layout

Results and Discussions

Figure 3 shows the rate of NO/NO_2 gas evolution of NC at 50°C as a function of humidity. It is apparent that from 4 ppm to 938 ppm humidity the NO_x evolution approximately doubled. Also observed was that the NO concentration was higher than NO_2 at lower humidity, this relationship switched at higher humidity.

Figure 4 shows how at lower temperatures (30°C - 70°C) the rate of NC decomposition increased when moisture was present, with the concentration of the NO_x gas evolution approximately doubling. The temperature at which the reaction mechanism changes from thermolytic decomposition to hydrolytic shifted 5°C higher at higher humidity conditions.

The activation energy for the NO_x evolution at 80°C -100°C (154 kJ mol^{-1}) was similar for low and high humidity conditions, and was indicative of thermolytic decomposition of NC. A lower activation energy (Ea = 37-41 kJ mol^{-1}), indicative of hydrolysis, was observed at 30°C -70°C.

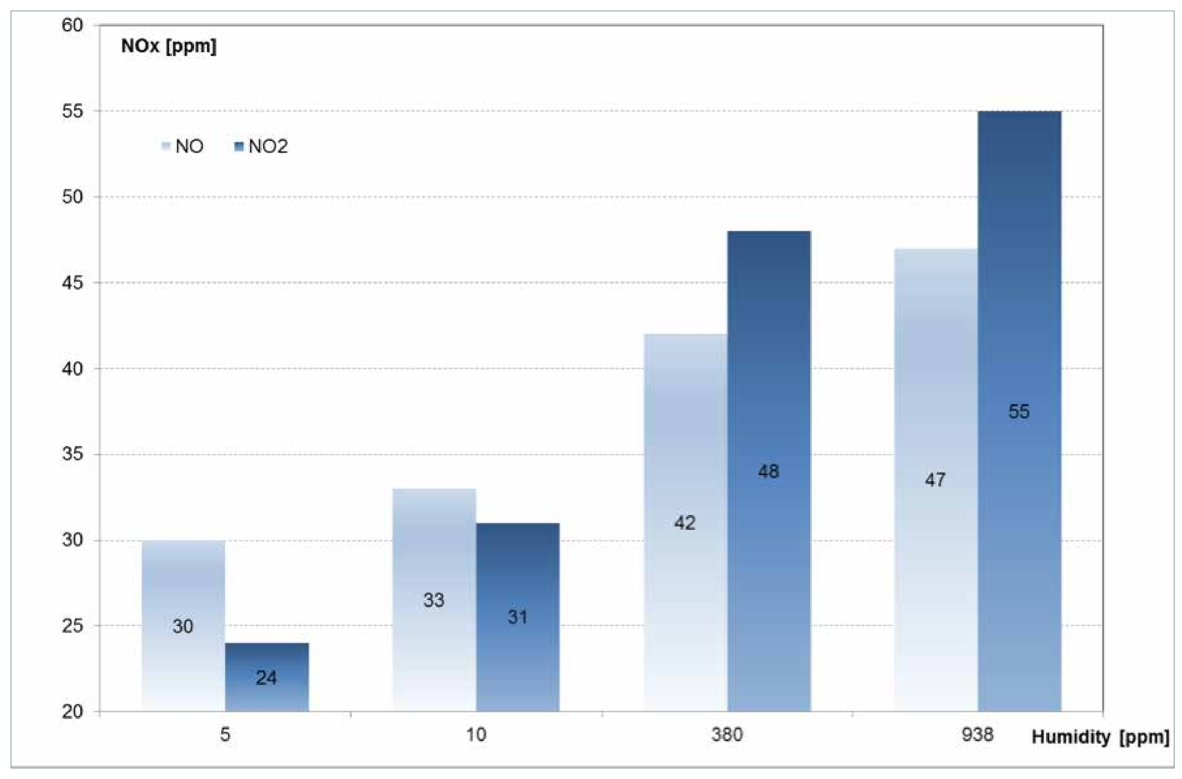

Figure 3. NO_x evolution rate as a function of humidity. 5 grams of 12.6% N NC; N_2 flow 0.47 ml s^{-1}; temperature 50°C

Conclusions

This present work confirms the value of this method for NC stability testing. It allows the decomposition to be observed at low temperatures, more akin to those under which the NC formulations are stored and used.

- The rate of decomposition at lower temperatures increased significantly when moisture was present.
- At higher temperatures, high humidity imparts little obvious effect on degradation. It appears that the dominant degradation mechanism is thermolytic, whereas hydrolytic degradation imparts a more obvious effect at lower temperatures.
- The NO concentration was higher than NO_2 at low humidity, but this relationship switched at higher humidity. This implied there was a change in the reaction mechanism as the humidity increased.

The swept style of experiment described here solely looks at the primary decomposition reactions. Although considered, it discounts the effects of nitrate ester interactions as well as secondary reactions between degradation products and the propellant or explosive constituents. However the experimental set-up could easily be configured to a closed loop system and enable the investigation of the secondary (autocatalytic) decomposition mechanisms. Although we have studied pure NC during this work, the high sensitivity of this technique means it might effective for propellants and explosive formulations containing low levels of NC.

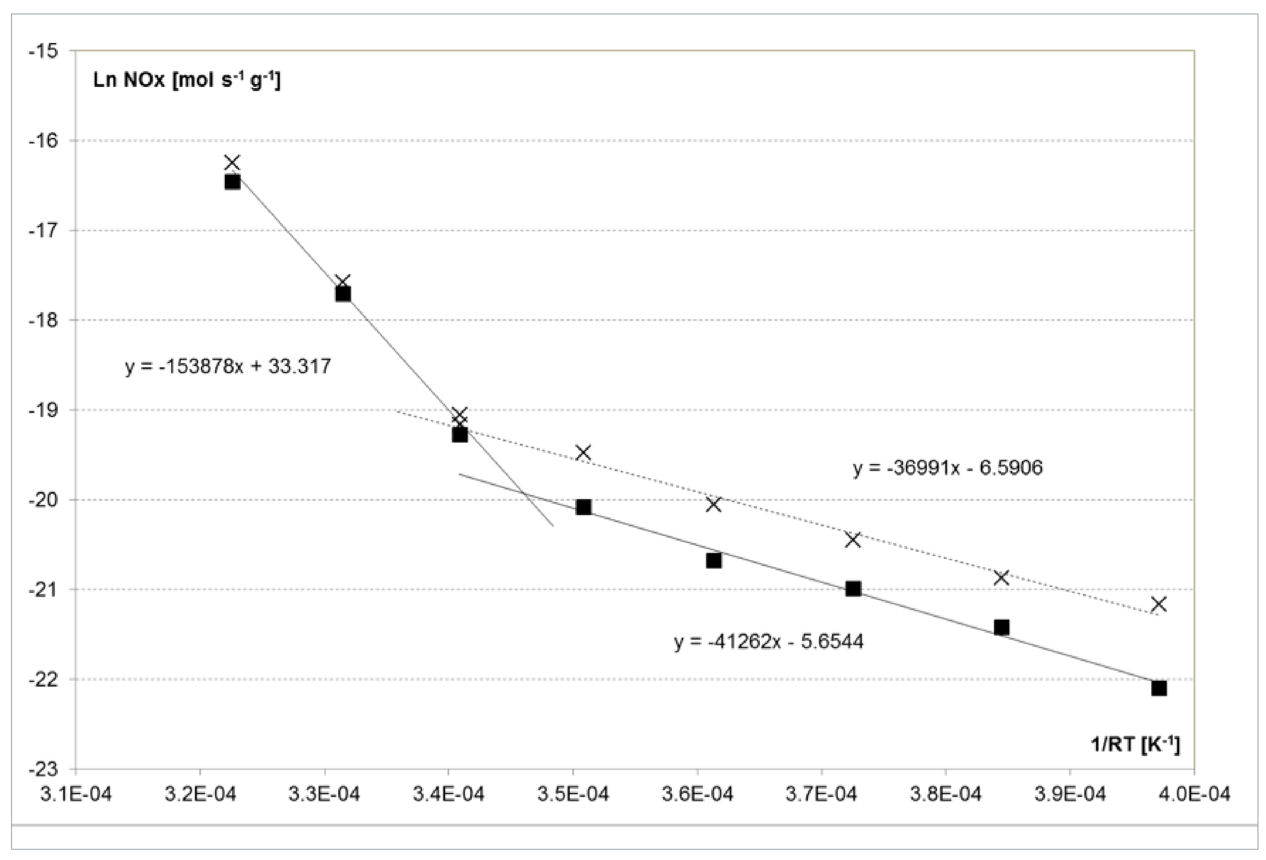

Figure 4. NO_x evolution rate as a function of humidity and temperature. 5 grams of 12.6% N NC; N_2 flow 0.47 ml s^{-1} at STP.
Key: ■ 2 ppm humidity; x 906 ppm humidity.
Best fit curve for 80 -100°C data has been averaged for the two experiments

www.cranfield.ac.uk/cds

Centre for Defence Chemistry, Cranfield University
Defence Academy of the United Kingdom, Shrivenham, Swindon, SN6 8LA, UK

Acknowledgements

This work was carried out as part of a research program funded by AWE plc.