1. Introduction

HIRAC

The Highly Instrumented Reactor for Atmospheric Chemistry, HIRAC, 1 is a NERC funded atmospheric simulation chamber which utilises a range of instrumentation based on a variety of techniques (see Table 1) to study atmospherically relevant gas phase chemical reactions.

Design

• 2.25 m³ stainless steel drum (Fig. 1).
• 4 mixing fans giving mixing times of ≤70 s.
• 8 rows of photolysis lamps (Fig. 2).
• Uniquely pressure and temperature variable (~260 – 340 K).

NO₃ radicals

Night-time chemistry is dominated by the nitrate radical, NO₃, formed by the reaction NO₂ + O₃ → NO₃ + O₂. The influence of NO₃ on the oxidation rates of certain species at night has been suggested to be comparable to the hydroxyl radical is during the day. Accurate knowledge of the kinetics of NO₃ radicals is therefore vital to our understanding of night-time chemistry. A CRDS instrument for the measurements of NO₃ radicals has been setup in the HIRAC chamber in order to study the kinetics of NO₃ with a variety of VOC and to develop temperature dependent Structural Activity Relationships (SAR).

2. Instrument Design

An optical cavity was formed across the chamber diameter (1.4 m) using two highly reflective mirrors (Los Gatos Research, R = 99.995%, ROC = 1.0 m, λ = 590 – 650 nm).

• Laser light at λ = 623 nm, produced by a Nd:YAG (Litron Nano TRL, 250 Hz) pumped dye laser (Lambda Physik FL3001) was fibre coupled (OZ optics, QMMJ-55-UVVIS-

Fig. 2: Photolysis lamps.

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3. Results

Spectra

NO₃ radicals were generated in HIRAC using the reaction NO₂ + O₃ → NO₃ + O₂ and spectra were recorded at 0.01 nm resolution (Fig. 5 and 6).

Fig. 5: NO₃ spectra measured in HIRAC by CRDS compared to literature spectra.

• NO₂ and O₃ absorb in the same spectral region as NO₃.
• Relatively low [NO₃] (~10s ppbv) resulted in no interfering absorption signal.
• Reductions in the RDT due to absorption by O₃ were observed due to the relatively high [O₃] (~500 ppbv).
• Data taken during kinetic studies were corrected for the changing contribution of O₃ to the measured RDT.

Kinetic Study

A kinetic study of NO₃ with a series of aldehydes (C1 to C4) was used to test the HIRAC CRDS system. The decay in [NO₃] was observed in the presence of each aldehyde (Fig. 7). Rate coefficients were determined by fitting the measured data using a simple box model based on the MCM (7 species, 30 reactions).

Table 2: Comparison between NO₃-aldehyde rate constants measured by CRDS and those from literature.

All of the experimentally determined NO₃ + aldehyde rate constants were found to be within error of literature values (Table 2).

4. Future work

• Development of a methodology to use the thermal decomposition of NO₂O₅ (+ M = NO₃ + NO₂ + M) as an NO₃ source in HIRAC.
• Temperature dependent kinetic study of NO₃ + alkene reactions and Structural Activity Relationship development.
• Development of a laser induced fluorescence (LIF) based NO₃ instrument and intercomparison with the HIRAC CRDS system and other optical cavities for NO₃ detection.
• Development of a CRDS system for detection of glyoxal (λ ~ 440 nm) for use in studies of the mechanism OH + aromatics and OH + alkynes.

References