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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 give mixing times of ≤ 70 s.
- 8 rows of photolysis lamps (Fig. 2).
- Uniquely pressure and temperature variable ($\sim 260 - 340$ K).



Fig. 1: The HIRAC laboratory.



Fig. 2: Photolysis lamps.

| Instrument | Species Detected | Detection limit | Time resolution |
|--|---|------------------|--------------------------------------|
| FAGE (Fluorescence Assay by Gas Expansion) | OH and HO ₂ | 0.1 - 0.02 pptv | 1 - 30 s |
| CRDS (Cavity Ring Down Spectroscopy) | NO ₃ | 6 pptv | 4 s |
| FTIR² (Fourier Transform Infra-Red) | O ₃ , CH ₃ CHO, CH ₄ , HCHO | 50 - 80 ppbv | 60 s |
| GC-FID (Gas Chromatography / Flame Ionisation Detection) | Organic species e.g.: CH ₄ , C ₂ H ₆ , C ₃ H ₈ , C ₃ H ₈ O ₂ | 0.01 - 0.05 ppmv | 20 s averages at 2 min resolution |
| Commercial Analysers | NO _x (=NO+NO ₂) | 50 pptv | 120 s |
| | O ₃ | 1 ppbv | 20 s |
| | H ₂ O | 2.5% RH | 10 s |

Table 1: Summary of HIRAC instrumentation with typical detection limits and time resolutions.

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, $\lambda = 590 - 650$ nm).
- Laser light at $\lambda = 623$ 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-200/240-3-15, 15 m) into the cavity.
- Light leaking out of the cavity was detected using a PMT (Hamamastu, H6780-20).
- Data were analysed using a Gage oscilloscope card (Gage, CS14105) coupled to custom-written LabVIEW software.

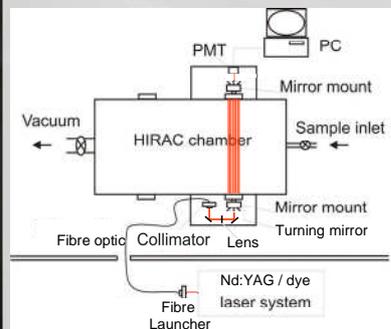


Fig. 3: Schematic of the HIRAC NO₃ CRDS setup.



Fig. 4: Picture of a mirror mounted on HIRAC.

- With an average background ring-down time (RDT) of 67.5 ± 0.5 μ s at atmospheric pressure, the detection limit for NO₃ in HIRAC was found to be ~ 6.1 pptv (averaging 1000 ring-down events, time resolution of 4 s).

4. Future work

- Development of a methodology to use the thermal decomposition of N₂O₅ (+ M \rightleftharpoons 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 ($\lambda \sim 440$ nm) for use in studies of the mechanism OH + aromatics and OH + alkyne.



Fig. 8: Installation of the HIRAC temperature control system.

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).

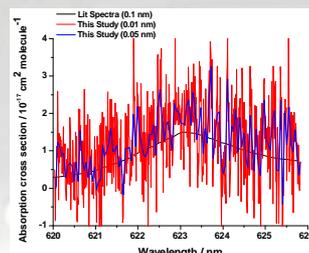


Fig. 5: NO₃ spectra measured in HIRAC by CRDS compared to literature spectra.

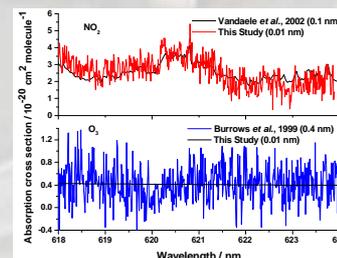


Fig. 6: NO₂ and O₃ spectra measured in HIRAC by CRDS compared to literature spectra.

- NO₂ and O₃ absorb in the same spectral region as NO₃.
- Relatively low [NO₂] (~ 10 s 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).

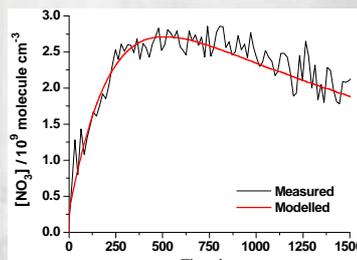


Fig. 7: Measured and modelled [NO₃] decay in the presence of propanal.

| Aldehyde | Average k_{exp} / molecule ⁻¹ cm ³ s ⁻¹ | k_{lit} / molecule ⁻¹ cm ³ s ⁻¹ (Atkinson et al., 2005) |
|----------|--|--|
| Methanal | (6.25 ± 0.38) × 10 ⁻¹⁶ | 5.5 ^{+3.2} _{-2.9} × 10 ⁻¹⁶ |
| Ethanal | (2.83 ± 0.59) × 10 ⁻¹⁵ | 2.7 ^{+0.1} _{-0.8} × 10 ⁻¹⁵ |
| Propanal | (7.17 ± 0.69) × 10 ⁻¹⁵ | 6.3 ^{+2.8} _{-0.8} × 10 ⁻¹⁵ |
| Butanal | (1.02 ± 0.10) × 10 ⁻¹⁴ | 1.1 ^{+0.5} _{-0.5} × 10 ⁻¹⁴ |

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).

References

- 1) D. R. Glowacki et al., Design and initial results from a Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC), *Atmos. Chem. Phys.*, 7, pp.5371-5390, 2007.
- 2) D. R. Glowacki et al., Design and performance of a throughput-matched, zero-geometric-loss, modified three objective multipass matrix system for FTIR spectrometry, *Applied Optics*, 46(32), pp. 7872-7883, 2007.