NATURAL ENVIRONMENT RESEARCH COUNCIL

HIRAC – the Highly Instrumented Reactor for Atmospheric Chemistry

UNIVERSITY OF LEEDS

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A21-0206

1. HIRAC

The Highly Instrumented Reactor for Atmospheric Chemistry, HIRAC,[1] is a new NERC funded atmospheric simulation chamber developed to bridge the divide between the study of elementary reactions in the lab, and large scale field work. HIRAC has been used to study an number of atmospherically relevant reactions. In this poster we present examples of studies relating to the 3 major HIRAC objectives.

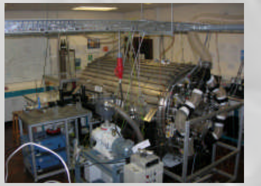

Fig. 1: *The HIRAC laboratory.*

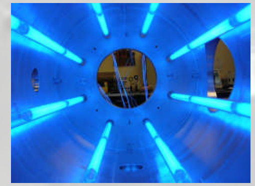

Fig. 2: *Photolysis lamps.*

Fig. 3: *FTIR mirrors.*

Design

- 2.25 m^3 stainless steel drum (Fig. 1).
- 4 mixing fans give mixing times of ≤70 s.
- 8 rows of photolysis lamps (Fig. 2).
- Uniquely pressure and (soon) temperature variable (~200 – 350 K).

Instrumentation

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 1 - 30 s
CRDS *(Cavity Ring Down Spectroscopy)*	NO_3	6 pptv	4 s
FTIR [2] (Fig. 3) *(Fourier Transform Infra-Red)*	O_3, CH_3CHO, CH_4, HCHO	50 - 80 ppbv	60 s
GC-FID *(Gas Chromatography / Flame Ionisation Detection)*	*Organic species e.g.:* CH_4, C_6H_{12}, C_5H_8, $C_3H_6O_2$	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	1ppbv	20 s
	H_2O	2.5% RH	10 s

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

3. Kinetics and SAR development – *Cl+acetates by relative rate*

- Accurate kinetic data for Cl+ester reactions are required to analyse data from chamber experiments in which Cl atoms are used to initiate the oxidation of organic compounds.
- Relative rate studies of the reaction of Cl atoms with a series of acetates have been carried out inside of HIRAC using GC-FID and FTIR spectroscopy.
- Table 3 shows a comparison between values determined in this study and those calculated using the Structural Activity Relationship (SAR) method. In the SAR method the calculation of the overall rate coefficient is based on the estimation of CH_3, CH_2 and CH group rate coefficients which depend only on the identity of the substituents bonded to the group.

Compound	$k_{expt}/10^{-11}$ cm^3 molecule^{-1} s^{-1}	k_{calc} ^{a}/ 10^{-11} cm^3 molecule^{-1} s^{-1}	k_{calc} ^{b}/ 10^{-11} cm^3 molecule^{-1} s^{-1}
Methyl Acetate	0.206 ± 0.043	0.199	0.199
Ethyl Acetate	1.68 ± 0.29	2.922	1.69
n-Propyl Acetate	6.02 ± 0.41	9.48	6.39
n-Butyl Acetate	15.8 ± 1.31	14.7	12.2
t-butyl Acetate	1.69 ± 0.15	4.44	1.65
Ethyl Formate	0.95 ± 0.05	2.79	1.56

Table 3: *Summary of measured rate coefficients for Cl+acetate reactions along with values calculated using the SAR method. Calculated using factors ^{a}F(-CO) and ^{b}F(-C(O)O-).*

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.

3) T. L. Malkin et al., Measurements of OH and HO_2 yields from the gas phase ozonolysis of isoprene, *Atmos. Chem Phys. Discuss.*, 9, pp.17579-17631, 2009.

2. Mechanism development – *OH and HO_2 yields from O_3+isoprene*

OH radicals are the major oxidant of volatile organic compounds (VOCs) in the atmosphere. Ozone alkene reactions are a non-photolytic source of HO_x radicals (especially forested) air. Pressure dependent (100 – 1000 mbar) OH yields from O_3+isoprene have been measured both directly and indirectly in HIRAC (Fig. 4).[3]

Indirect measurements

- ***Scavenger technique:*** Using cyclohexane as an OH scavenger, the yield of cyclohexanone was measured using GC-FID along with the concurrent loss rate of isoprene.
- ***Kinetic technique:*** Kinetics studies using cyclohexane. A 10 fold excess O_3 over isoprene was used to ensure that the decay of isoprene was pseudo-first order. The consumption of isoprene was monitored using both FTIR and GC-FID.

Direct measurements

OH and HO_2 yields were measured using FAGE for chamber pressures between 300 and 1000 mbar (Fig. 5 and Table 2).

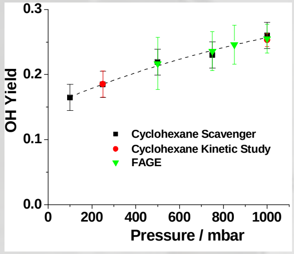

Fig. 4: *Pressure dependent OH yields determined by indirect and direct techniques.*

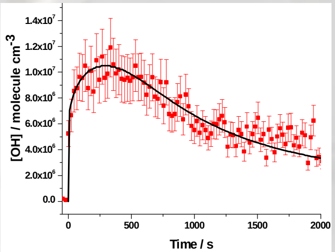

Fig. 5: *Direct FAGE OH measurements from O_3+isoprene at p = 1000 mbar (red squares) with modelled data (black line) giving an a OH yield of 0.26±0.02.*

Pressure / mbar	Overall HO_2 yield
1000	0.257 ± 0.025
850	0.263 ± 0.026
750	0.260 ± 0.027
500	0.255 ± 0.026
300	0.253 ± 0.026

Table 2: *Pressure dependent HO_2 yields determined directly using FAGE.*

4. Instrument development – *NO_3 Cavity Ring-Down Spectroscopy*

HIRAC has been used to carry out the first calibration of a FAGE HO_x instrument over a range of external pressures. Find out more at poster A21-0197.

Cavity Ring Down Spectroscopy, CRDS, is a sensitive and absolute technique used to measure a variety of atmospheric species. In HIRAC, a CRDS instrument has been set up across the chamber diameter to measure NO_3 radicals using laser light at λ = 623 nm (250 Hz Nd:YAG pumped dye laser) (Fig. 6). NO_3 radicals were produced in HIRAC by $NO_2+O_3 \rightarrow NO_3+O_2$. The NO_3 detection limit was 6 pptv (time resolution = 4 s (average of 1000 shots) and p = 1000 mbar).

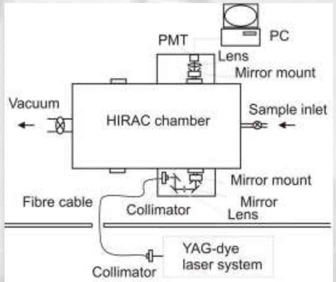

Fig. 6: *Schematic of the HIRAC NO_3 CRDS setup.*

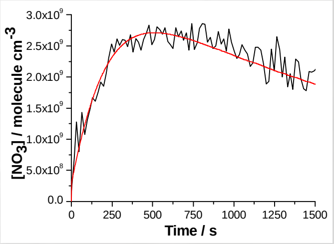

Fig. 7: *Example data set of measured decay in $[NO_3]$ from reaction with propanal.*

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) x10^{-16}	$5.5^{+3.2}_{-2.0} \times 10^{-16}$
Ethanal	(2.83 ± 0.59) x10^{-15}	$2.7^{+0.1}_{-0.8} \times 10^{-15}$
Propanal	(7.17 ± 0.69) x10^{-15}	$6.3^{+2.6}_{-1.8} \times 10^{-15}$
Butanal	(1.02 ± 0.10) x10^{-14}	$1.1^{+0.5}_{-0.3} \times 10^{-14}$

Table 4: *Comparison between NO_3+aldehyde rate constants measured by CRDS and those from literature.*

A study of the rate of NO_3 with a series of aldehydes was used to test the system (Fig. 7). All of the experimentally determined NO_3+aldehyde rate constants were found to be within error of literature values (Table 4). The CRDS system will now be used to study NO_3+alkene rate constants and SARs. We also plan to measure glyoxal by CRDS in HIRAC.

See poster A21-0197 and www.chem.leeds.ac.uk/HIRAC for more information about HIRAC

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