HIRAC-A Highly Instrumented Reactor for Atmospheric Chemistry

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1. Introduction

Environmental chambers are an important part of an integrated and multifaceted approach to understanding chemical processes in the atmosphere, bridging the gap between laboratory measurements of individual elementary reactions and the complexity of the real atmosphere.

Existing chambers have limitations affecting their utility and the range of conditions for mechanism evaluation. The HIRAC chamber was developed to address these limitations. The highly instrumented chamber will allow control of the conditions of temperature, pressure and photolysis rate which are important variables affecting the rate of processes in the atmosphere.

Our approach to chamber design has been to develop an instrument capable of operation over a wide range of conditions and in which we can monitor both free-radical and stable reactants, products and intermediates. HIRAC will be utilised for kinetic and mechanistic studies and also in the development and calibration of field apparatus.

This poster describes the design, construction and validation of HIRAC, and initial results for relative rate kinetic studies and OH yields from ozone alkene reactions.
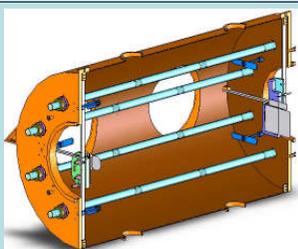
2. Design

A stainless steel chamber (2 m^3) was chosen because it permits the system to be temperature variable and to operate at low pressures (Fig. 1). The design necessitates mounting the photolysis lamps inside the chamber.

HIRAC contains 24 lamps (Phillips Actinic 05 40 Watt blacklamps) housed in 8 cylindrical 2 mm thick quartz tubes that run the length of the chamber. Inside of the tubes are thermocouples, and the ends of the tubes are coupled to fans, in order that the temperature within the tubes can be maintained at the optimum lamp operation temperature (36-38°C). Care was taken to optimise the positioning of the lamps to maximise the volume of relatively uniform intensity and hence photolysis frequency (Fig. 2). The gas inside the chamber is mixed with up to 6 fans.

Fourier Transform Infra-red spectrometry (FTIR) (Bruker IFS 66), Gas Chromatography (GC) (HP6890) and commercial analysers (NO$_x$/O$_3$/CO/H$_2$O vapour) are the main tools for monitoring stable species (Table 1). A long path (~150 m) for FTIR is obtained using a modified Chernin configuration for the field and far mirrors (Fig. 3) [Glowacki et al. 2007]. GC and analyser samples are obtained from moveable probes to check for any concentration gradients across the chamber.

OH and HO$_2$ radicals are measured via the Fluorescence Assay by Gas Expansion (FAGE) technique as used by FAGE group at Leeds [Heard, 2006]. FAGE is a technique based on laser induced fluorescence at low pressure. Radical concentrations will be more susceptible to non-uniform photolysis, wall loss and mixing effects, therefore the inlet has also been designed to be moveable to probe concentration gradients within the chamber.

Figure 1 – Schematic of HIRAC chamber showing lamps and position of FTIR mirrors

Technique	Species Monitored
FAGE	OH, HO$_2$
Multipass FTIR	Stable species e.g. Acetylaldehyde
GC-HID	Formaldehyde
GC-FID	Hydrocarbons
O$_3$ Analyser	O$_3$
NO$_x$ Analyser	NO$_x$
CO Analyser	CO
Hygrometer	Water Vapour

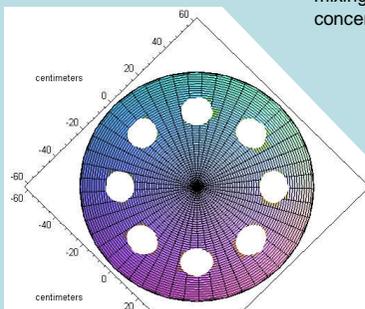*Table 1 – Techniques coupled to HIRAC and species monitored*

Figure 2 : Modelled light intensity within ± 15% of the mean. Volume covered >85%
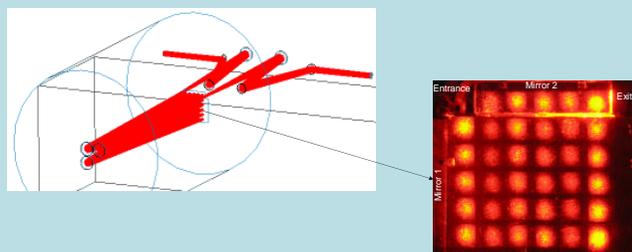

Figure 3 : Modified Chernin configuration for the multipass FTIR optics. The arrangement depicted above features 36 spots on the field mirror, for a total of 72 passes, or a path length of 144 m.
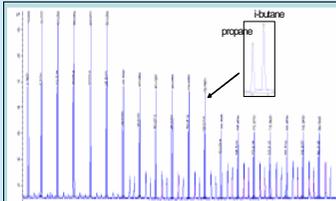
3. Relative rate measurements of rate coefficients

Relative rate measurements using a reference compound with a well established rate coefficient are widely used for determining rate coefficients for gas-phase reactions.

The quantitative performance of HIRAC for the measurement of rate coefficients was characterised by a relative rate method with gas chromatography; mainly via Cl atom + alkane experiments. High lamp intensities cause rapid reactions and step changes in concentrations of reagents and products. (Fig. 4) Under less intense conditions the real time decay of hydrocarbons can be observed giving excellent kinetic results (Figs.5 and 6). Ozone and OH initiated reactions have also been observed using a GC.
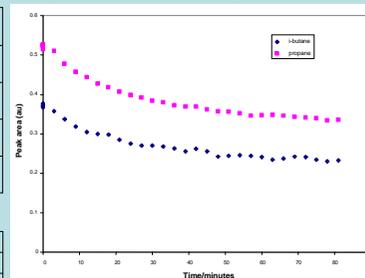

Figure 4 : Isothermal GC with 3 minute duty cycle

Concentration of alkanes and Internal standard (DCM)	Source of Cl	Experiment al ks/kr
10 ppm Propane, 10 ppm i-butane, 10 ppm DCM	20 ppm Cl$_2$	1.02 ± 0.05
30 ppm Propane, 10 ppm i-butane, 10 ppm DCM	20 ppm Cl$_2$	0.973 ±0.039
10 ppm Propane, 30 ppm i-butane, 10 ppm DCM	20 ppm Cl$_2$	0.979 ±0.016
5 ppm Propane, 5 ppm i-butane, 10 ppm DCM	20 ppm Cl$_2$	0.98 ±0.014

Tables 2 and 3 : Rate coefficients experimentally determined by relative rate measurements

Reference	ks/kr
This Work	1.014 ± 0.05
Atkinson et al.,1985	1.02 ± 0.04
Lewis et al., 1980	0.97 ± 0.06

Figure 5: Real time alkane decay (10 ppm each of propane, i-butane and DCM and 20 ppm of Cl$_2$)
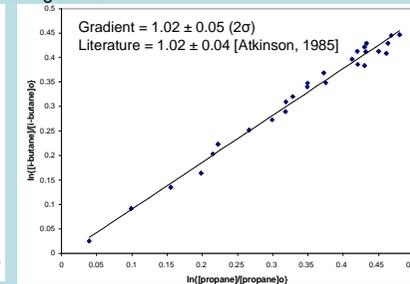

Figure 6: Relative Rate plot for Cl + propane and iso-butane

4. OH yield from O$_3$ + alkene reactions

The OH radical is the major oxidant for volatile organic compounds (VOCs) in the atmosphere. Ozone alkene reactions are a non-photolytic source of HO$_x$ radicals and appear to be a significant source of new HO$_x$ radicals in urban and rural (esp. forested) air [Paulson et al., 2000].

The dark reaction between O$_3$ and *trans*-2-butene has been studied by the detection of reagents and product acetaldehyde (by commercial analysers, GC and FTIR), as well as OH and HO$_2$ concentrations (by FAGE), with excellent agreement. A model based on the Leeds Master Chemical Mechanism (MCM) and previously published OH yields was able to reproduce the temporal profiles of OH, O$_3$ and acetylaldehyde extremely well. (Figs. 7 and 8).
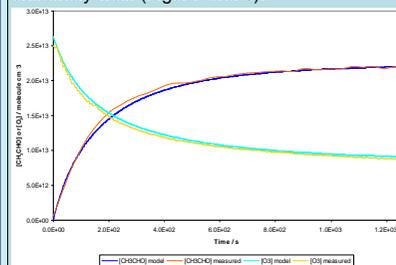
Conditions

HIRAC was evacuated then filled to atmospheric pressure with N$_2$.

1 ppm of both ozone and trans-2-butene were used in these initial investigations.

OH yield

The model which can be seen in figures 7 and 8 assumed an OH yield of 0.57 [Kroll et al., 2001a, b]

Figure 7: Real time O$_3$ decay and Acetylaldehyde Production   Figure 8: OH decay (averaged over 5 seconds).
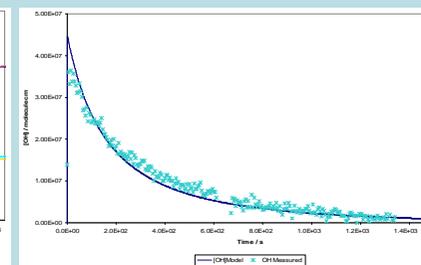
5. Future work

• Calibration of field instruments as a function of pressure, temperature, relative humidity, O$_3$, NO$_x$ etc.

7. References

•Atkinson R., Aschmann SM. (1985)"Kinetics of the gas phase reaction of Cl atoms with a series of organics at 296 ± 2 K and atmospheric pressure". Int. J. Chem. Kinet. 17:1: 33
•Glowacki D.R., A. Goddard and P. Seakins.(2007)"Design and Performance of a Throughput-Matched, Zero-Geometric-Loss, Modified Three Objective Multipass Matrix System for FTIR spectrometry" Applied Optics.Submitted
•Heard D.E, (2006). "Atmospheric field measurements of the hydroxyl radical using laser-induced fluorescence spectroscopy." Annual Review Physical Chemistry. 7:191–216

•Kroll, J.H., T.F. Hanisco, N.M. Donahue, K.L. Demerjian, and J.G Anderson, (2001a). "Accurate, direct measurements of OH yields from gas-phase ozone-alkene reactions using an in situ LIF instrument," Geophys. Res. Lett., 28, 3863,
•Kroll, J.H., S.R. Sahay, J.G. Anderson, K.L. Demerjian, and N.M. Donahue,(2001b). "Mechanism of HOx formation in the gas-phase ozone-alkene reaction.1.Direct, pressure-dependent measurements of prompt OH yields" J.Phys.Chem.A, 105, 4446
•Lewis R.S., S.P. Sander, Wagner, R.T. Watson. (1980) "Temperature-dependent rate constants for the reaction of ground-state chlorine with simple alkanes" J. Phys. Chem. 84: 2009
•Paulson, S.E., A.S. Hasson, M.Y Chung, K.T Kuwata, A.D Converse, and D.J Krohn. Phys. Chem. A (2003), 107, 6176-6182 "OH Formation from Alkene-Ozonolysis in the Presence of Water Vapor."