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OH Yields from Gas-Phase Ozonolysis of Isoprene

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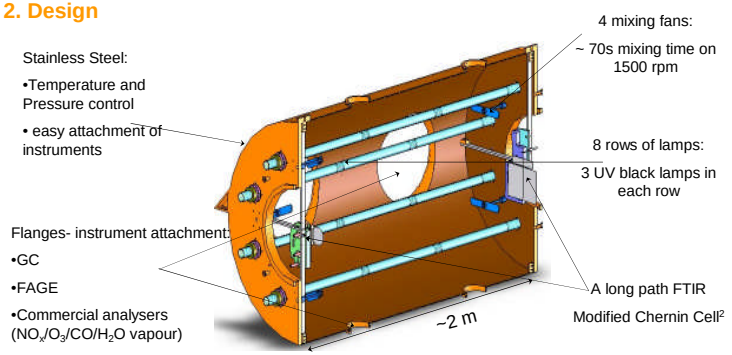
1. Introduction

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[1] 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.

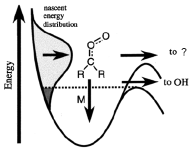
2. Design



3. Reaction of O_3 with Isoprene

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 (especially forested) air.

Isoprene account for ~31% of global hydrocarbon emissions and is sufficiently reactive to influence oxidant levels over large portions of the continental troposphere. Isoprene is also frequently found to be the dominant non-methane hydrocarbon in rural air. Although ozonolysis of isoprene represents an important night-time source of tropospheric hydroxyl radicals, its chemical mechanism and OH yield remains highly uncertain.



Aim:

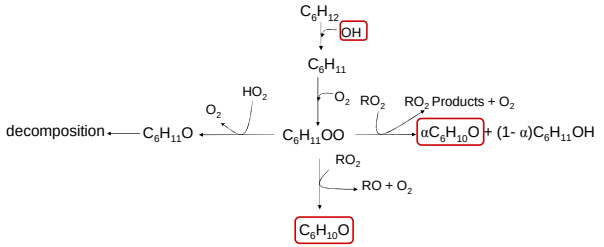
Determine the OH yield of the reaction of ozone and isoprene and whether this yield is pressure dependant.

4. Scavenger Technique

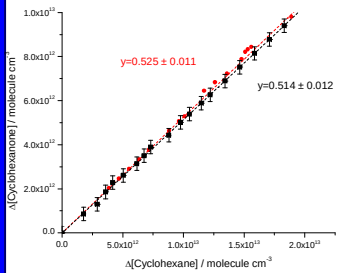
For this work OH radicals are not detected directly but via a scavenger.

How Scavengers Work?

The reaction of isoprene with ozone was performed in the presence of excess cyclohexane in air. The concentration of cyclohexane was enough to scavenge >95% of the OH produced. The product (cyclohexanone) of the OH radical reaction with cyclohexane was monitored by GC-FID and quantified.



5. Cyclohexanone Yield

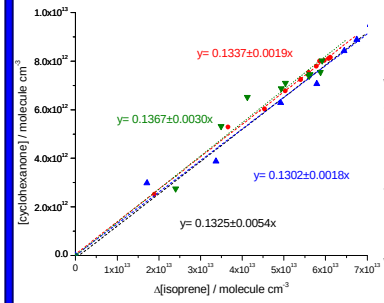


In order to determine the OH yield. The yield of cyclohexanone produced from the reaction of OH with cyclohexane is required at each pressure. This was determined two ways:

1.The production of OH by isoprene ozonolysis- low concentrations of cyclohexane used so the loss of cyclohexane compared to the production of cyclohexanone was determined (red plot).

2. Using methyl nitrite as an OH precursor.- the loss of cyclohexane compared to the production of cyclohexanone was determined (black plot).

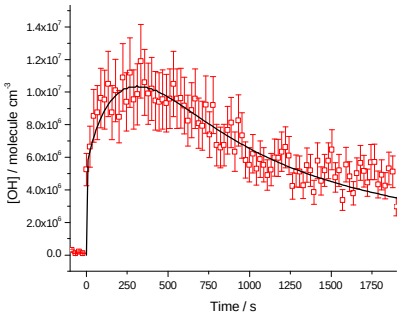
6. OH Yield



At atmospherically relevant pressures (500–1000 mbar) a cyclohexanone yield of 50% was determined at lower pressures (<500 mbar) a cyclohexanone yield of 40% was determined. The cyclohexanone yield at a given pressure is multiplied by the gradient of the loss of isoprene with production of cyclohexanone.

The concentration of cyclohexane is in 20-100 fold excess, hence >95% of the OH produced is scavenged and does not react with the isoprene present. Therefore the loss of isoprene is due to its reaction with ozone.

7. Direct OH Measurement



Direct measurement of OH from the ozonolysis of Isoprene has been achieved by this group [Malkin et al., 2008 and AGU poster A21B-0142]

A model based on the Leeds Master Chemical Mechanism (MCM) (OH yield = 0.27) fits the experimental yield of OH very well. By adapting the model and introducing the OH yield as a variable fitting parameter, to model the OH FAGE data, a yield of 0.255 ± 0.022 was determined.

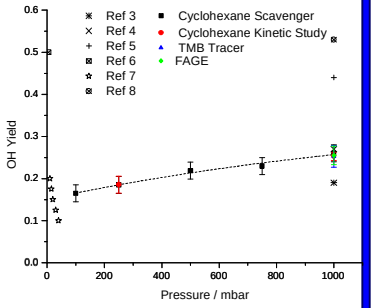
8. Pressure dependent OH Yield

The technique described previously to determine the OH yield was repeated for a range of pressures from 100 – 1000 mbar .

At atmospheric pressure (~1000 mbar) the OH yield was determined by 3 other techniques:

1. By a tracer study- monitoring 1,3,5 trimethylbenzene (TMB) concentration as a function of [ΔO_3].
2. By a kinetic study in the presence and absence of cyclohexane, this was also used at 250 mbar.
3. Direct measurement of the OH by FAGE and subsequent modelling.

The variation in literature OH yields can be seen.



9. Summary of Results

An overview of the average yield for each pressure including those measured using different techniques.

* Determined by cyclohexane scavenger
‡ Determined by TMB tracer
† Determined by cyclohexane kinetic study[9]
# Determined by FAGE

Pressure / mbar	OH yield
1000	0.267 ± 0.012* 0.253 ± 0.026‡ 0.253 ± 0.010† 0.255 ± 0.022#
750	0.230 ± 0.025*
500	0.219 ± 0.023*
250	0.185 ± 0.028* 0.196 ± 0.020†
100	0.162 ± 0.029*

10. Conclusion

The OH yield is pressure dependant. This is relevant for isoprene global chemistry and gives us important mechanistic information.

11. Future work

Calibration of field instruments as a function of pressure, temperature, relative humidity, O_3, NO_x etc.

12. Acknowledgements

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13. References

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