Kinetics and Products of Alkene Ozonolysis in the HIRAC Chamber

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1. Why study alkene ozonolysis?

• O_3 plays a large role in air pollution and has significant properties as a greenhouse gas. Understanding its chemistry is vital to our understanding of the atmosphere.

• Alkene + O_3 reactions are an important non-photolytic source of HO_x radicals, the principal oxidising agents of the troposphere.

• Alkene ozonolysis reactions are a major source of organic acids and hydroperoxides and form particulate products.

• Isoprene is the largest emission rate biogenic VOCs (volatile organic compounds) in the troposphere.[1]

• Previous studies of isoprene ozonolysis in HIRAC have revealed uncertainties in the mechanism included in the Master Chemical Mechanism (MCM v3.1) (Fig. 1).[2]

• The MCM is a near explicit mechanism for describing degradation of atmospheric VOCs.[3]

• This projects aims to investigate the isoprene ozonolysis mechanism by studying product yields e.g. propene, MVK and MACR as a function of pressure and temperature.
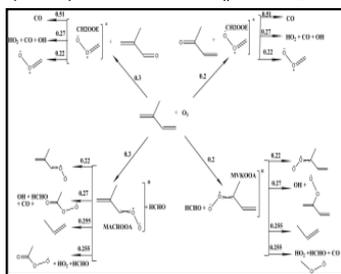

Fig. 1: *MCM isoprene ozonolysis mechanism.[1]*

2. Highly Instrumented Reactor for Atmospheric Chemistry

Atmospheric simulation chambers, such as HIRAC, bridge the gap between field measurements and laboratory studies:

➢ Give a highly instrumented test bed.

➢ Allow performance of longer time scale kinetics experiments.

➢ Simulate and allow control of atmospheric conditions.

➢ Less complicated than the real atmosphere.

HIRAC Design

• 2.25 m^3 stainless steel drum (Fig. 2).

• 4 mixing fans give mixing times of ≤70 s.

• 8 rows of photolysis lamps (Fig. 3).

• Equipped with FAGE (OH and HO_2), CRDS (NO_3), FTIR, GC-FID (VOCs) and commercial analysers (O_3, NO_x, H_2O).

• Pressure variable (0.1 - 1200 mbar).

• Temperature variable (220 - 330 K).

Fig. 2: *The HIRAC laboratory.*

Fig. 3: *Photolysis lamps.*

3. O_3 wall losses

• There are concerns regarding possible reactions at the walls of metal chambers.

• For O_3 + alkene reactions, there is particular uncertainty about O_3 wall-losses.

• 'Dark' experiments carried out at different temperatures and pressures, monitoring O_3 concentrations as a function of time (Table 1).

• Average wall-loss rate at room temperature and 1000 mbar (1.74±0.55) x 10^{-5} s^{-1}.

• This increases with temperature, to (2.40±0.36) x 10^{-4} s^{-1} at 323 K, and with decreasing pressure, to (3.69±0.98) x 10^{-5} s^{-1} at 550 mbar.

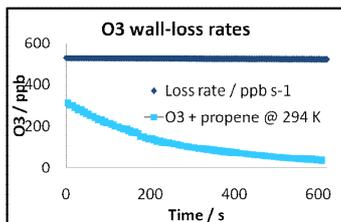• Wall-losses are insignificant relative to O_3 decay for alkene reactions carried out in HIRAC (Fig. 4).

O3 wall-loss rates
- Loss rate / ppb s-1
- O3 + propene @ 294 K

Fig. 4: *Comparison of O_3 + propene decay and 'dark' O_3 decay at 294 K and 1000 mbar.*

Source	Wall loss / s^{-1}	1σ	Chamber	Chamber properties
This work, 1000 mbar, 291 K	1.77×10^{-5}	5.32×10^{-6}	HIRAC	2250 L stainless steel
This work, 1000 mbar, 291 K	1.71×10^{-5}	5.62×10^{-6}	HIRAC	2250 L stainless steel
This work, 550 mbar, 291 K	3.69×10^{-5}	9.83×10^{-6}	HIRAC	2250 L stainless steel
This work, 1000 mbar, 323 K	2.40×10^{-4}	3.59×10^{-5}	HIRAC	2250 L stainless steel
T. L. Malkin, 2010	3.2×10^{-5}	Not disclosed	HIRAC	2250 L stainless steel
Doussin *et al.*, 2011	3.00×10^{-4}	Not disclosed	CESAM	4200 L stainless steel
Hynes et al., 2005	1×10^{-6} after first month	Not disclosed	CSIRO	18100 L aluminium coated with Teflon film
	2×10^{-7} after 3 yrs	Not disclosed		
Akimoto et al., 1979	3.11×10^{-4} after baking	4.11×10^{-4}	NIES	6065 L stainless steel coated with PFA
	1.94×10^{-4} after O_3 treatment	2.78×10^{-4}		

Table 1: *Comparison of O_3 wall-loss rates for several different atmospheric simulation chambers.*

4. Isoprene ozonolysis product studies

• Previous studies in HIRAC of isoprene ozonolysis found a positive pressure dependence of OH yields (Y_{OH} = 0.17 − 0.26 for pressures from 100 to 1000 mbar) and no pressure dependence of HO_2 yields (Y_{HO2} = 0.26).[2]

• MCM v3.1 does not include any pressure dependence to Y_{OH}. Product studies at varying temperatures and pressures will help to elucidate the mechanism.

• Initial isoprene ozonolysis product studies were carried out in 1012 mbar air at 291 K.

• The products methacrolein (MACR), methyl vinyl ketone (MVK) and propene were monitored as a function of time by a GC-FID previously calibrated with known standards.

• Experiments were modelled using the isoprene ozonolysis mechanism extracted from the MCM v3.1 with AtChem and compared to measurements (Fig. 5).

• [MACR] and [propene] were under predicted (by up to 50% and 32% respectively) whilst [MVK] was over predicted (by up to 36%).

• This indicates errors in the current understanding of the gas-phase oxidation mechanism for isoprene.

• Many recent studies have shown we have a lack of understanding of OH-initiated isoprene oxidation which may account for the model / measurement discrepancy.[4]
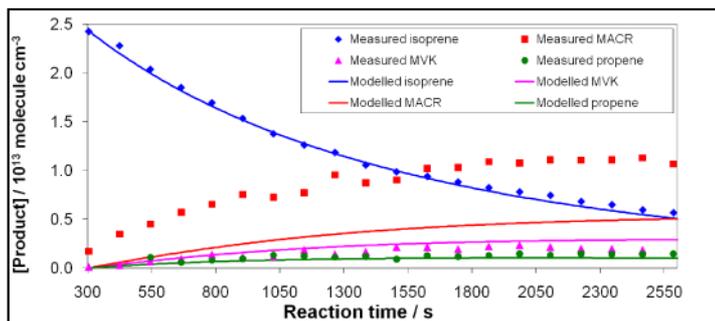
Fig. 5: *Measured and modelled concentrations of isoprene and several reaction products from the ozonolysis of isoprene in 1012 mbar of air.*

5. Propene ozonolysis kinetics

• Recent modifications to HIRAC permit temperature variation between 220 - 330 K.

• O_3 + propene kinetics are well-documented and facilitate a useful test bed for assessing HIRAC temperature control.

• Pseudo-first order experiments were carried out in air in an excess of propene (2.5 – 34.7 ppmv) with O_3 (0.3 ppmv) at temperatures from 233 - 326 K and 1000 mbar, monitored with a commercial O_3 analyser.

• Bimolecular rate constants (k_{bim}) were determined   using plots of first-order rate constants against [propene].

• An Arrhenius plot of bimolecular rate constants gave E_a = 19.84±0.46 kJ mol^{-1} (Fig. 6).

• This value is within error of literature data including IUPAC recommendations (Fig. 6).[5]

• Results indicate excellent temperature control and reveal HIRAC to be an effective, accurate vessel for the investigation of temperature controlled kinetics.
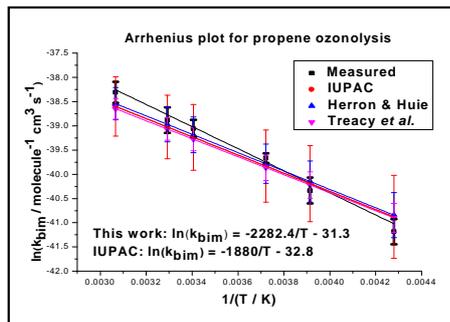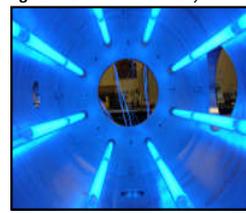

Arrhenius plot for propene ozonolysis
- Measured
- IUPAC
- Herron & Huie
- Treacy *et al.*

This work: $\ln(k_{bim})$ = -2282.4/T - 31.3
IUPAC: $\ln(k_{bim})$ = -1880/T - 32.8

Fig. 6: *Measured and literature Arrhenius plots from propene ozonolysis at 1000 mbar. Error bars represent ±1σ uncertainty.*

6. Conclusions and future work

• Previous work by Malkin *et al.* (2010) showed uncertainties in the isoprene ozonolysis mechanism included in the MCM v3.1.[2]

• Product studies showed inconsistencies between modelled and measured product concentrations.

• These indicate uncertainties in our current understanding of the gas-phase isoprene degradation mechanism.

• Recent studies have shown we have a lack of understanding of isoprene oxidation.[4]

• OH scavenger studies would clarify any disagreement between models and measurements of products from isoprene ozonolysis due to OH chemistry.

References

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2) T. L. Malkin, Detection of free-radicals and other species to investigate atmospheric chemistry in the HIRAC chamber, Thesis, 2010.
3) S. M. Saunders *et al.*, Protocol for the development of the Master Chemical Mechanism, MCM v3 (Part A: tropospheric degradation of non-aromatic volatile organic compounds, *Atmos. Chem. Phys.*, 3, pp. 161-180, 2003.
4) J. Lelieveld *et al.*, Atmospheric oxidation capacity sustained by a tropical forest, *Nature* , 452, 737-740, 2008.
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