

L. N. Farrugia, M. A. Blitz, S. C. Smith, S. C. Orr, D. E. Heard and P. W. Seakins

School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK e-mail: cmlnf@leeds.ac.uk

1. Importance of studying alkene ozonolysis reactions

- Alkene ozonolysis is an important tropospheric process that impacts on climate change and human health.
- Reactions of O_3 with alkenes produce HO_x radicals (Fig. 1), the major daytime oxidising agents in the troposphere, as well as organic acids and peroxides that lead to formation of particulate matter.
- These reactions take place via a Criegee intermediate (Fig. 1) and products formed depend on the reacting alkene and intermediate formed.

These reactions have also been suggested to be a significant night time source of OH [1].

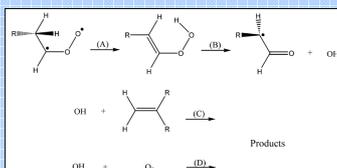


Fig. 1 OH radical formation from a 1,4-sigmatropic shift of the Criegee intermediate (A) followed by bond fission (B) and possible secondary chemical pathways during alkene ozonolysis (C and D).

- Numerous alkene ozonolysis rate constants have been reported in the literature, however few studies reporting the temperature-dependence of these reactions are available [2].
- Ethene, propene and trans-2-butene reactions with O_3 are reported here, with studies being carried out in a flow tube, using CRDS (Cavity ring down spectroscopy) and in an atmospheric chamber using GC-FID (Gas Chromatography-Flame Ionisation Detection) and a commercial ozone analyser.
- The results obtained from these studies aim at enhancing the Master Chemical Mechanism (MCM), a database set up at the University of Leeds that describes tropospheric degradation mechanisms of more than 142 non-methane volatile organic compounds (VOCs).
- A particular focus of this study of alkene ozonolysis will be the pressure and temperature dependence of these reactions, along with product studies under these varying conditions which will be important in enhancing the MCM.

2. CRDS flow tube setup

- Cavity ring-down spectroscopy (CRDS) is a laser based direct absorption method that is finding wide use in the detection of trace atmospheric species.
- The setup used (Fig. 2 and 3) consists of a laser system, two high reflectivity mirrors (>99.9%) and a photosensitive detector. A pulsed Nd:YAG pumped dye laser is used to produce red light at 623 nm matched to an absorption band of O_3 .

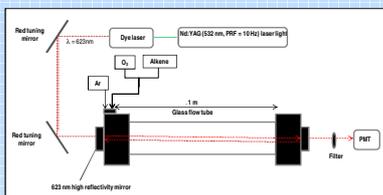


Fig. 2: Schematic of the CRDS flow tube setup.

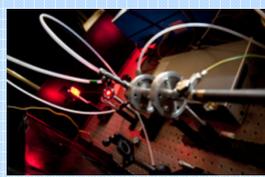


Fig. 3: Laser light transmitted into the CRDS flow tube system.

- Most of the laser light is reflected straight back, but a small fraction (<0.1%) is transmitted through the back of the first high reflectivity mirror. This light is trapped in the cavity and traverses it many times giving large effective path lengths.
- A small portion of the light trapped in the cavity leaks out through the second high reflectivity mirror and the intensity of this light is measured using a photosensitive detector (PMT).
- The ring-down time (RDT) is defined as the time taken for the laser light exiting the cavity to decay to $1/e$ of its original intensity, and this RDT reduces in the presence of an absorbing species.

Large effective path lengths are achieved that contribute to a high sensitivity of this method. This setup enables the study of kinetics over reaction times between 10 seconds and a few minutes.

3. O_3 +alkene CRDS Results

- A series of alkenes (C2 – C4) were used to test the flow tube CRDS system. These experiments were carried out at <100 mbar in a N_2/Ar bath gas. O_3 was prepared by a commercial O_3 generator (0.1% O_3/O_2). All gas flows were controlled by calibrated mass flow controllers.
- The decay in $[O_3]$ was observed in the presence of each alkene (Fig. 4) under pseudo first order conditions, with the alkene being ≤ 3 times in excess of O_3 .
- A plot of the natural log of the decay of $[O_3]$ as a function of the [alkene] multiplied by the contact time gives $k_{O_3+alkene}$ as the gradient.

$$\ln [O_3]_t = k ([alkene] t) + \ln [O_3]_0$$

Compound	This work	IUPAC (Atkinson et al., 2004)
Ethene	0.87 (± 0.45)	1.32 (± 0.46)
Propene	9.82 (± 3.82)	8.79 (± 0.46)
Trans-2-butene	109 (± 56.9)	175 (± 37.1)

Table 1: A comparison of experimentally determined pseudo-first order rate constants (10^{-18} molecule $cm^{-3} s^{-1}$) with the literature (IUPAC) for the reaction of O_3 with ethene, propene and trans-2-butene at 292 K.

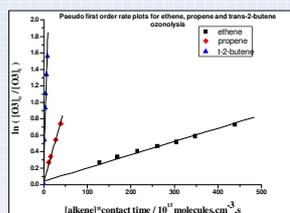


Fig. 4: Pseudo first order rate plots for the reaction of O_3 with ethene, propene and trans-2-butene with O_3 at 292 K and 100 mbar.

All of the experimentally determined O_3 +alkene rate constants were found to be within error of literature values (Table 1).

The main uncertainty associated with our setup comes from the estimation of our contact time which is very important in determining the absolute rate constants in our setup. Relative-rate type experiments are planned in order to deal with this issue.

4. HIRAC Chamber (Highly Instrumented Reactor for Atmospheric Chemistry)

- The HIRAC chamber (Fig. 5) is a NERC funded atmospheric simulation chamber designed at the University of Leeds [2]. It is a 2.25 m³ stainless steel chamber consisting of 4 circulating fans and 8 rows of photolysis lamps.
- It is equipped with a range of instruments, including GC-FID (VOCs) and FTIR, Fluorescence Assay by Gas Expansion - FAGE (HO_x), CRDS (NO_3) and various commercial analysers (O_3 , NO_x , H_2O).
- Recent installation of a temperature control system enables studies at temperatures between 223 – 323 K.
- Contrary to the CRDS flow tube system, HIRAC allows the study of reaction times in the order of tens of minutes, and thus has the benefit of being used in monitoring primary and secondary products.



Fig. 5: The HIRAC chamber equipped with recently installed temperature control system.

Alkene Ozonolysis - HIRAC Results

- Relative-rate constants (Fig. 6) were obtained using GC-FID measurements. The studies involved reaction of a set of two alkenes with O_3 .
- Experimentally determined relative-rate constants were obtained for $k_{O_3+ethene} = 1.68 (\pm 0.26) \times 10^{-18}$ and $k_{O_3+propene} = 9.27 (\pm 0.38) \times 10^{-18}$ in molecule $cm^{-3} s^{-1}$, with isoprene being used as a reference, methane as an internal standard and cyclohexane as an OH scavenger.
- Results obtained are within error of IUPAC recommendations.

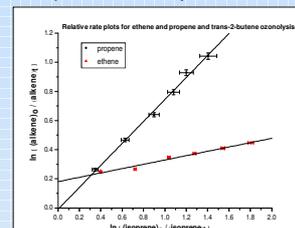


Fig. 6: Relative-rate plots for ethene and propene at 1000 mbar and 292 K, using isoprene as a reference and cyclohexane as an OH scavenger.

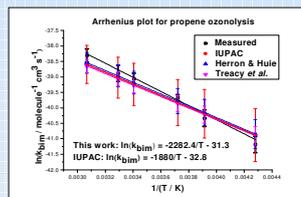


Fig. 7: Arrhenius plot for propene at 1000 mbar and over a temperature range of 233 – 323 K [4].

Experimentally determined relative-rate constants are in better agreement with the IUPAC than the flow tube setup. Temperature-dependent study demonstrates the suitability of HIRAC for further temperature-dependent.

- A temperature-dependent study under pseudo-first order conditions with excess propene (2.5 – 34.7 ppmv) over O_3 (0.3 ppmv) was performed using a commercial O_3 analyser at 233 – 323 K.
- An Arrhenius plot of the bimolecular rate constant for propene gave $E_a = 19.84 \pm 0.46$ kJ mol^{-1} (Fig. 7). This value is within error of IUPAC and literature data.

5. Conclusions and Future work

- Both initial results of flow tube experiments and HIRAC were within error of IUPAC.
- Further flow tube experiments yielding absolute rate constants are dependent on a better estimation of the contact time, to be estimated better using relative-rate type experiments.
- Both HIRAC and the CRDS flow tube setup possess the benefit of being used to study reactions over varying temperatures, and can thus result obtained for temperature-dependent studies can be intercompared.
- Flow tube has potential of generating data quicker than HIRAC, and could be useful in order to build structural activity relationships (SARs) for incorporation in the MCM.
- HIRAC has been used to carry out product studies of these reactions, and further studies will be carried out to test the temperature and pressure dependence of these systems and the products formed.
- NO_3 chemistry studies will be carried out using CRDS in both HIRAC and the flow tube setup, and initial tests have already been carried out for this.

6. References

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