2.006 An inter-comparison of methods for HO2 and CH3O2 detection and kinetic study of the HO2 + CH3O2 cross-reaction in the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC).

Presenting Author:
Lavinia ONEL, School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK, chmlo@leeds.ac.uk

Co-Authors:
Alexander Brennan, School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK
Freja F. Oesterstroem, School of Chemistry, University of Leeds, Leeds, LS2 9JT, UK
Michele Gianella, Department of Chemistry, Physical and Theoretical Chemistry Laboratory, University of Oxford, Oxford, OX1 3QZ, UK
Gus Hancock, Department of Chemistry, Physical and Theoretical Chemistry Laboratory, University of Oxford, Oxford, OX1 3QZ, UK
Lisa Whalley, School of Chemistry and National Centre for Atmospheric Science, University of Leeds, Leeds, LS2 9JT, UK
Paul Seakins, School of Chemistry and National Centre for Atmospheric Science, University of Leeds, Leeds, LS2 9JT, UK
Dwayne Heard, School of Chemistry and National Centre for Atmospheric Science, University of Leeds, Leeds, LS2 9JT, UK

Abstract:

The hydroperoxy radical, HO_2, and methylperoxy radicals, CH_3O_2, participate in rapid chemical cycling at the heart of tropospheric oxidation. Laser-induced fluorescence (LIF) spectroscopy at low-pressure, known as the Fluorescence Assay by Gas Expansion (FAGE) technique, is most commonly used for the measurements of HO_2 in the atmosphere by conversion of HO_2 to OH by reaction with added NO followed by OH on-resonance LIF at 308 nm.[1] A new method has been developed for the sensitive and selective detection of CH_3O_2.[2] The method is similar to the FAGE method for HO_2 detection and consists in the titration of CH_3O_2 to CH_3O by reaction with NO followed by the detection of the resultant CH_3O by off-resonant LIF. Recently, the first near infrared CRDS measurements of HO_2 and CH_3O_2 in an atmospheric simulation chamber (HIRAC) were inter-compared against FAGE.[3, 4] The good agreement between HO_2 and CH_3O_2, respectively concentrations measured using the two techniques at 1000 mbar of air provides a validation for the FAGE method for both HO_2 and CH_3O_2 detection.
The HO_2 + CH_3O_2 cross-reaction is important under clean, low NO_x levels, yet there are large uncertainties associated with its kinetics.[5] The FAGE technique has been used to measure kinetic decays of HO_2 and CH_3O_2 radicals by the cross-reaction at 268, 295 and 323 K and 1000 mbar of air in the HIRAC chamber. The preliminary results have overlapping error limits at 1sigma level with the IUPAC preferred values at all three

temperatures.[5]

1. D. E. Heard and M. J. Pilling, *Chem. Rev.*, 2003, **103**, 5163-5198.
2. L. Onel et al. , *Atmos. Meas. Tech.*, 2017, **10**, 3985-4000.
3. L. Onel et al., *Atmos. Meas. Tech.*, 2017, **10**, 4877-4894.
4. L. Onel et al., MS in preparation.
5. R. Atkinson et al., *Atmos. Chem. Phys.*, 2006, **6**, 3625-4055.