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).

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Abstract:

The hydroperoxy radical, HO2, and methylperoxy radicals, CH3O2, 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 HO2 in the atmosphere by conversion of HO2 to OH by reaction with added NO followed by OH on-resonance LIF at 308 nm. A new method has been developed for the sensitive and selective detection of CH3O2. The method is similar to the FAGE method for HO2 detection and consists in the titration of CH3O2 to CH3O by reaction with NO followed by the detection of the resultant CH3O by off-resonant LIF. Recently, the first near infrared CRDS measurements of HO2 and CH3O2 in an atmospheric simulation chamber (HIRAC) were inter-compared against FAGE. The good agreement between HO2 and CH3O2, respectively concentrations measured using the two techniques at 1000 mbar of air provides a validation for the FAGE method for both HO2 and CH3O2 detection.

The HO2 + CH3O2 cross-reaction is important under clean, low NOx levels, yet there are large uncertainties associated with its kinetics. The FAGE technique has been used to measure kinetic decays of HO2 and CH3O2 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 1σ level with the IUPAC preferred values at all three
temperatures.\textsuperscript{5}

4. L. Onel et al., MS in preparation.