KINETICS MEASUREMENTS OF HO₂ AND RO₂ SELF AND CROSS REACTIONS USING INFRARED KINETIC SPECTROSCOPY (IRKS)

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Reactions between RO₂ and HO₂ are important in the gas phase oxidation of volatile organics in the atmosphere. The rate constants for the reactions of HO₂ + C₂H₅O₂, and C₂H₅O₂ + C₂H₅O₂ were measured using a novel approach to radical radical reactions that employs two independent spectroscopic probes. HO₂ was monitored at 6638.2 cm⁻¹ using near-IR diode laser WM spectroscopy, and C₂H₅O₂ was monitored at 250 nm using UV absorption. Experiments were run under conditions relevant to the upper troposphere (221-298 K and 50-400 Torr). Measurements of the rate constants for both reactions as well as a measurement of the branching fraction leading to the alkoxy channel of the C₂H₅O₂ self reaction will be discussed. Preliminary results are: $k_{HC} = (6.4 \pm 1.4) \times 10^{-13}$ cm³ molec⁻¹ s⁻¹ Exp((601 ± 120)/ T), $k_{CC} = (1.10 \pm 0.20) \times 10^{-13}$ cm³ molec⁻¹ s⁻¹ independent of temperature, and a branching fraction of 0.32 ± 0.13.