Contribution ID: **24** Type: **Talk**

Multiplexed Photo-Ionization Mass Spectrometry Studies of Atmospheric Peroxy Radical Reactions

Tuesday, 30 September 2014 14:25 (25 minutes)

Peroxy radicals are important intermediates in the oxidation of Volatile Organic Compounds(VOCs) in the troposphere, and play a crucial role in air pollution, the formation of photochemical smog and organic aerosols. The reactions of peroxy radicals with the hydroperoxyl radical are important loss processes in atmospheres with low nitrogen oxide concentrations. Laboratory studies of the kinetics of peroxy radical reactions are complicated by the many competing self- and cross-reactions that typically occur. The large number of possible products, especially chain-propagating radical channels, further complicates the chemistry.
Time-resolved photoionization mass spectrometry (PIMS) using VUV synchrotron radiation provides a powerful approach for studying the product branching ratios and reaction rates, by selective time-resolved detection of most of the reactants, intermediates, and primary products. We report our studies of this reaction in a laser-photolysis low-pressure flow cell experiment which utilizes tunable VUV radiation generated at the Advanced Light Source synchrotron at the Lawrence Berkeley Laboratory, coupled to the Sandia multiplexed PIMS apparatus. Here we describe experiments on the self-reaction of the ethyl peroxy radical, as well as the reaction of the acetyl peroxy radical with the hydroperoxyl radical. We are able to determine relative product yields based on measurements of absolute radical concentrations, coupled with kinetic modeling of the time-dependence of the observed species.

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Session Classification: Session 4 Coincidence Spectrometry (Gerber)