Atmospheric Chemistry of CH3OOH and PAN

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Methylhydroperoxide (CH3OOH) and PAN (CH3C(O)OONO2) are ubiquitous gases in the atmosphere. They are formed in the atmospheric oxidation of many organic species including those emitted from vehicles and organic species emitted from trees. These species are important chain termination products formed via the following reactions:

$$CH3OO + HO2 \rightarrow CH3OOH + O2 \quad (1)$$

$$CH3C(O)OO + NO2 \rightarrow CH3C(O)OONO2 \quad (2)$$

My lab has been measuring these compounds using a proton transfer reaction mass spectrometry (PTR-MS). This isntrument is widely used in atmospheric chemistry. It measures organics in "real-time" by chemical ionization using H3O+ as the reagent ion. Data from 2 recent field experiments my group has participated in (SHARP in Houston, TX and CABINEX, rural Michigan) reveal that atmospheric concentrations exhibit a diurnal pattern, presumably due to changes in atmospheric oxidation rates of organics. We would like to better quantify the presence of these compounds in air and examine relationships between these species and photochemical precursors to better understand their atmospheric chemistry. These species are important indicators of the so called VOC and NOx limited regimes that influence photochemical ozone formation in urban areas.

This project will involve synthesizing these compounds in the lab, producing a calibration source and measuring the PTR-MS response to these compounds, and analyzing field data. Since these compounds cannot be purchased they have to be made. The synthesis is reasonably straightforward but will require some experience and skill in using laboratory equipment and working with chemicals. The synthesized compounds will be used in calibration standards to determine the PTR-MS response. The output of the PAN standard will be determined using an NO chemiluminescent analyzer. This analyzer is part of our standard air monitoring equipment package. The student will set-up the analyzer to measure the concentration of PAN emitted from the calibration standard. The output from the standard will then be measured by the PTR-MS instrument. For CH3OOH a Henry's law based calibration standard will be made and the output measured by the PTR-MS in a similar fashion. The student will work with a graduate student in performing the experiments with the NO analyzer and the PTR-MS.

The existing field data will be analyzed to quantify relationships between these compounds and their precursors and other photoproducts. Specifically, CH3OOH and PAN concentrations were measured at 3 heights through a forest canopy as part of last summers CABINEX field experiment in Michigan. I want to establish the daily cycle of formation and loss of these compounds in a forest to better understand the atmospheric chemistry of forests.