2.104 ROOOH: the Missing Piece of the Puzzle for OH measurements in low NO Environments.

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Abstract:

Field campaigns have been carried out in remote biogenic environments in the last decade to quantify the in situ concentrations of OH, the main oxidant in the atmosphere. These data have revealed concentrations up to a factor of 10 higher than predicted by models and were interpreted as a major lack in our understanding of the chemistry of biogenic hydrocarbons.

In the following year, and until today, many experimental and theoretical studies have been carried out to improve the knowledge of the oxidation mechanism of biogenic VOCs under low NO conditions in order to bring into agreement model and measurement. Some new reaction paths have been found able to recycle OH radicals under low NO, especially for isoprene, but the strong disagreement between measurements and models still persists until today.

But interferences in the OH concentration measurements of unknown origin have also been discovered for some FAGE instruments, with the intensity increasing with decreasing NO concentration.

We will present here convincing experimental and modeling evidence that the disagreement between model and measurement is due to interference by the unexpected decomposition of a new class of molecule, ROOOH, during expansion within the FAGE instruments. ROOOH is the product of the reaction between peroxy radicals and OH radicals. Including ROOOH reflects the missing piece of the puzzle in our understanding of OH in the remote atmosphere.