

Ph.D. Defense Announcement

Jared Brewer

January 10, 2020 at Noon

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Ph.D. Defense

Friday, January 10, 2020
12:00 p.m.

Defense
ATS Large Classroom (101 ATS)

Post Defense Meeting
Riehl Room (211 ACRC)

Committee:
Emily Fischer (Advisor)
A.R. Ravishankara (Co-advisor)
Elizabeth Barnes
Shantanu Jathar (Mechanical Engineering)

A Year in the Life of an Atmospheric Ketone

Ketones play an important role in atmospheric chemistry of the troposphere because they are oxidized volatile organic compounds (VOCs) that are both relatively abundant and have sufficiently long-lifetimes to be distributed regionally. Ketone photolysis is a potentially important source of HOx (HOx = OH + HO₂) radicals in the upper troposphere; it can also serve as a source of peroxy radicals which contribute to the formation of peroxy acyl nitrate-type (PAN-type) compounds. My thesis focuses on the atmospheric processes and budgets of smaller ketones. We discuss a series of four studies aimed at understanding the importance of atmospheric ketones to production of oxidants and PAN-type compounds. The four studies covered here involve laboratory measurements, interpretation of atmospheric observations, and modeling calculations.

Chapter 2 of this thesis discusses an update to and global sensitivity analysis of the global budget of acetone. We test how sensitive a global simulation of acetone is to literature-derived ranges of input factors used to represent 1) direct emissions and secondary natural sources of acetone from the biosphere, 2) loss via photolysis, and 3) dry deposition. We use the Morris method (one-at-a-time variations) to identify and prioritize potential reasons for model-measurement differences for acetone. This study helps identify what specific processes and/or geographic regions deserve further attention via modeling and/or measurements to constrain the global budget of this species. Of the sources tested, acetone is globally most sensitive to the direct emissions from the biosphere, with other sources and sinks being important on a seasonal and regional basis.

Chapter 3 presents the results of laboratory measurements of absorption cross sections of MEK and DEK (along with their uncertainties) measured in the laboratory between 200-335 nm at temperatures ranging from 242-320 K, with a spectral resolution of 1 nm. We also report absorption cross sections for PEK at the same resolution and wavelengths at 296 K. We present a simple "two-state" physically based model to understand the temperature variation of the cross sections and to extrapolate cross sections beyond the temperatures of the measurements. The implementation of these temperature-dependent cross-sections is most important in the colder upper troposphere, where this work suggests a ~20% decrease in MEK photolysis rate relative to the previous understanding.

In Chapter 4, we present an analysis of aircraft observations of MEK in the remote marine troposphere from the Atmospheric Tomography (ATom) project. We show that the observed vertical profiles over clean oceans suggests an oceanic source of MEK. We show that the ocean serves as a source of MEK to the atmosphere during both meteorological winter and summer. MEK in clean marine air over the remote oceans correlates with both acetone and acetaldehyde, whose primary sources in the ocean water are the photooxidation of organic material.

Finally, in Chapter 5, we bring together the information gathered from Chapters 2 and 3 to improve our ability to simulate MEK throughout the troposphere, with these and other model improvements, present the first global budget of MEK. We discuss the magnitudes, distribution, and seasonality of the sinks, sources, and atmospheric mixing ratios of MEK as well. We also present a comparison of simulated MEK abundances using a suite of available aircraft observations of MEK from around the globe. Our results suggest that MEK is much less abundant in the atmosphere than acetone, but the total global flux of MEK into the atmosphere is about a tenth of that of acetone. The most important sources of MEK to the atmosphere are from the ocean and the oxidation of primarily anthropogenic alkanes, while the most important sinks of MEK are photolysis and oxidation by OH.

We pull the information from all these four studies to show that our knowledge of the atmospheric role of acetone and MEK has improved. We also identify gaps in our knowledge that should be pursued to better quantify the roles of ketones in the troposphere.