Geophysical Research Abstracts Vol. 12, EGU2010-9863, 2010 EGU General Assembly 2010 © Author(s) 2010



Illuminating the Atmospheric Oxidation Mechanisms, SOA Formation Pathways and Radical Yields of the Monoterpene Myrcene

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Biogenic Volatile Organic Compounds (BVOCs) are ubiquitous in the global troposphere, being emitted primarily from terrestrial plant life in significant quantities. Indeed, it is estimated that the total annual emission rate of all (non-methane) BVOCs is roughly ten times that of all anthropogenic volatile organic compounds (Guenther et al., 1995). With the exception of methane, the most dominant species of BVOC, in terms of emission strength, reactivity and their impact upon the atmosphere, are terpenes. Terpenes are a subdivision of BVOCs, composed primarily of hemiterpenes (C5), monoterpenes (C10), sesquiterpenes (C15) and diterpenes (C20). Under troposheric conditions terpenes react via complex and extensive gas phase oxidation pathways, have strong photochemical ozone creation potentials, constitute a significant radical source and are known to generate secondary organic aerosol (SOA) in high yields.

At present there exists a certain lack of understanding regarding the oxidation mechanisms of certain terpenes and their role in SOA and radical formation. Consequently, as part of the NERC funded Aerosol Coupling in the Earth's System (ACES) and Total RAdical Production from the OZonolysis of alkenes (TRAPOZ) projects, a comprehensive series of simulation chamber experiments were conducted at the University of Manchester aerosol chamber facility, and at the EUropean PHOto REactor (EUPHORE) in order to investigate the gas phase degradation mechanisms, and SOA and radical formation potentials of a number of atmospherically significant terpenes. Both simulation chambers were highly instrumented during all experiments such that detailed and concomitant gas and aerosol phase measurements were made across a range of conditions.

The work presented here describes the findings obtained from both photooxidation and ozonolysis experiments involving the common, but less well studied, aliphatic monoterpene, myrcene. The data presented include NOx and ozone measurements and high temporal and spectral resolution Chemical Ionisation Reaction Time-of-Flight Mass Spectrometric (CIR-TOF-MS) VOC measurements, which help to illuminate the gas phase oxidation mechanisms of myrcene. Findings from the gas phase instrumentation are combined with data from Differential Mobility Particle Sizers (DMPS), Scanning Mobility Particle Sizers (SMPS), Aerosol Mass Spectrometry (AMS) and aerosol composition measurements (made using Two Dimensional Gas Chromatography coupled to Time-of-Flight Mass Spectrometry- 2D-GC-TOF-MS), to provide identification of species that comprise myrcene SOA. Important findings regarding the aging of myrcene SOA and radical measurements made by Laser Induced Flouresence (LIF) and Peroxy Radical Chemical Amplification (PERCA) will also be presented and discussed.