Geophysical Research Abstracts
Vol. 14, EGU2012-9491, 2012
EGU General Assembly 2012

Assessment of the role of stabilized Criegee Intermediates in OH radical measurements by LIF.

A. Novelli (1), H. Harder (1), and the HUMPPA-COPEC 2010 (1,2,4) and IPI (1,3,4) Team

(1) Max Planck Institute for Chemistry, 55128 Mainz, Germany (anna.novelli@mpic.de), (2) Dept Phys, 00014 University of Helsinki, Finland, (3) Atmospheric Research and Instrumentation Branch, Atmospheric Sounding Station 'El Arenosillo' National Institute for Aerospace Technology, INTA, Huelva, Spain., (4) University of Wollongong, School of Chemistry, Wollonong, NSW, Australia

OH radicals are the primary oxidant in the atmosphere, to a large extent controlling the oxidative capacity in the troposphere. Due to its high reactivity and low concentrations, it is difficult to measure. LIF (Laser Induced Fluorescence) is one of the very few techniques available, measuring the fluorescence of the OH radical following excitation at 308 nm in a low pressure detection cell. In order to test for possible interferences from OH generated within the instrument, a new method has been developed and deployed. Intermittently within regular measurements, OH generated within the instrument is quantified by addition of an OH scavenger in front of the instrument nozzle, effectively removing the ambient OH. Due to the low pressure and short residence time of the air sample within the instrument, internally generated OH is not or only partially affected by the scavenger. Results using this novel technique at several measurement sites, including Finland, Spain, and Germany, revealed that the OH generated within the measurement apparatus was a non-negligible fraction of the total OH measured. Contrary to prior interferences in the history of LIF, the internally produced OH can be shown not to be generated by the laser light. Beyond the importance of understanding and quantifying this interference in the measurement of ambient OH, the process by which OH can be produced within the instrument is intriguing.

In this work, we will present evidence that the measured signal after OH removal in front of the nozzle is indeed caused by OH radicals, and examine some potential sources of OH within the apparatus. A promising mechanism is the decomposition of stabilized Criegee Intermediates (SCI) in the low pressure environment within the instrument, generating OH through the so-called vinyl-hydroperoxide channel. This channel has been proposed to be a significant source of OH in the troposphere. Detailed analysis of the formation and destruction pathways of SCI in the atmosphere based on the available literature furthermore reveals that reactions of these SCI can also be a source of other compounds observed during our field campaigns, such as sulphuric acid whose measured concentration often cannot be readily explained by traditional chemistry. Critical in this analysis are the large differences in reactivity of SCI with respect to water, water dimer, and other co-reactants, where the rate coefficients can vary by over five orders of magnitude depending on the specific SCI.