INSTITUTIONEN FÖR KEMI OCH MOLEKYLÄRBIOLOGI

Thesis for the degree of Doctor of Philosophy in Natural Science,
Specialization in Chemistry

Atmospheric Chemistry of Volatile Organic Compounds: Oxidation Products, Mechanisms and Secondary Organic Aerosol Formation

Julia Hammes
Department of Chemistry and Molecular Biology
University of Gothenburg
412 96 Göteborg, Sweden

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Faculty opponent: Professor William Bloss, PhD
School of Geography, Earth and Environmental Sciences
University of Birmingham, UK

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The results from this work are a piece in understanding the complex puzzle of atmospheric aerosol formation. Secondary organic aerosol (SOA) formed by the oxidation of volatile organic compounds (VOC) in the atmosphere is a key component of air pollution with a strong negative impact on human health and influence on climate, but its formation is poorly understood. Because air pollution and climate change are major challenges facing modern societies, there is a clear need to better understand atmospheric SOA formation. SOA formation can be estimated from distributions of potential oxidation products, but such estimates are only as useful as the underlying chemical mechanisms and physical properties on which they are based.

The work presented in this thesis was conducted to better characterize VOC oxidation products and the chemical mechanisms governing their formation. The SOA precursor compounds α-pinene and limonene (representing biogenic VOC) and 1,3,5-trimethylbenzene (TMB) (an anthropogenic VOC) were studied in the G-FROST and Go:PAM flow reactors to characterize their oxidation and the subsequent SOA-forming processes. Previously unknown compounds including dimer esters, carboxylic acids, nitrates and highly oxygenated molecules were identified using state-of-the-art mass spectrometric methods. These oxidation products were shown to be important SOA contributors and explicit mechanisms for their formation were proposed. Some of the identified compounds were suggested to be of extremely low volatility and thus important for new particle formation. Oxidation of TMB under conditions representative of urban environments reduced particle formation potential; this effect was attributed to the disruption of RO_2 auto-oxidation cycles by NO_x and subsequent nitrate formation at the expense of highly oxygenated molecules. During the course of this work, an automated algorithm was developed to extract compound-specific volatility data from FIGAERO thermograms.

The scientific understanding of SOA formation would be greatly improved by a detailed knowledge of the products of VOC oxidation, the mechanisms by which they are formed, and their vapour pressures, all of which this work aims to contribute to.

Keywords: SOA, VOC, anthropogenic, biogenic, FIGAERO, CIMS, HOMs, ELVOCs, atmospheric oxidation, chemical mechanism, NO_x, limonene, α-pinene, TMB, ozone, nitrate, OH, radical chemistry, RO_2, G-FROST, GO:PAM