



INSTITUTIONEN FÖR KEMI OCH MOLEKYLÄRBIOLOGI

THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN NATURAL SCIENCE,
SPECIALIZATION IN CHEMISTRY

NITROGEN-CONTAINING PRODUCTS FROM ATMOSPHERIC OXIDATION OF VOLATILE ORGANIC COMPOUNDS

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Atmospheric oxidation of volatile organic compounds (VOC) produces a wide range of oxygenated organic products that lead to formation of secondary organic aerosol (SOA). SOA represents a significant fraction of the tropospheric aerosol that influence climate and human health. However, the level of understanding of SOA processes is low compared to other aerosol processes and one reason is the complexity of VOC oxidation under various conditions. VOC oxidation under high NO_x conditions or by nitrate radicals (NO_3) leads to formation of various nitrogen-containing compounds. The N-containing products, apart from contributing to SOA formation, can act as NO_x reservoir and/or as permanent sink affecting ozone formation. Also, organic nitrogen can play a role on the atmospheric nitrogen cycle, with ecological impacts. In this work the focus is on the nitrogen-containing oxidation products in the gas phase and their contribution to the particle phase. Laboratory studies on OH-initiated oxidation of 1,3,5-trimethylbenzene (TMB) (an anthropogenic VOC) under different NO_x levels and NO_3 -initiated oxidation of isoprene (the most abundant non-methane biogenic VOC) were conducted utilizing the Go:PAM flow reactor and the atmospheric simulation chamber SAPHIR. The oxidation products from these reactions were detected using chemical ionization mass spectrometry. This method was also applied in the field to measure selected organonitrates related to the laboratory studies.

The TMB oxidation under elevated NO_x conditions favored the formation of organonitrates (ONs) reducing the amount of highly oxygenated organic molecules (HOM) monomers and especially the dimers, leading to suppression of new particle formation. Ambient observations of nitro-aromatic compounds originating from anthropogenic sources demonstrated that nitrophenol and its analogue can be used as direct tracers of primary emissions from biomass burning. NO_3 oxidation of isoprene produced monomers and dimers with 1 to 3 nitrate groups. The specifics of the various time evolutions indicating formation pathways from multi-generation secondary chemistry. Selected products from this secondary chemistry had high propensity to participate to the particle phase. Observations from six locations around the globe showed that the isoprene-derived ONs with chemical formula $\text{C}_4\text{H}_7\text{NO}_5$ observed in the laboratory did dominate the ambient gas phase product distribution both during nighttime and daytime.

To summarize, the objectives of this thesis are to advance our understanding on the nitrogen-containing products from atmospheric oxidation of different VOC, identify their reaction mechanisms and product distributions, and provide insights on their role to SOA formation.

Keywords: VOC, anthropogenic, biogenic, SOA, atmospheric oxidation, organic aerosols, CIMS, FIGAERO, TMB, isoprene, HOM, organonitrates (ONs), NO_x , OH, nitrate (NO_3), Go:PAM, SAPHIR