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

SPECIALIZATION IN CHEMISTRY

Atmospheric Oxidation:

Formation and Aging of Biogenic and Traffic-related Secondary Aerosols

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Göteborg, Sweden, 2018

The thesis will be defended in English on Friday, 2th of Feburary 2018,
at 13:00 in the room KB, at Kemigården 4,
Chalmers University of Technology, Göteborg

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ISBN 978-91-629-0386-2 (PRINT)
ISBN 978-91-629-0387-9 (PDF)

DEPARTMENT OF CHEMISTRY AND MOLECULAR BIOLOGY

GÖTEBORGS UNIVERSITET

Abstract

Atmospheric aerosol particles affect the quality of life by influencing climate and by being a significant component of air pollution. Once a particle is released into or formed in the atmosphere, several processes begin to transform its physical and chemical properties. A considerable fraction of the particulate matter is secondary material i.e. formed from gas-to-particle conversion in the atmosphere. This secondary particle formation is an important process in the evolution of atmospheric aerosols. The aim of this thesis is to study the formation and aging of secondary aerosols by experimentally simulating atmospheric oxidation of emissions from biogenic and traffic-related sources. In this work the focus is on particle size, mass and number concentration, as well as on the thermal properties of the particles formed. These measures give insight into properties relevant for understanding the evolution of particles in the ambient atmosphere.

The thermal properties of secondary organic aerosols (SOA) formed from oxidation of monoterpenes in two oxidation flow reactors, G-FROST and PAM, and the atmospheric simulation chamber SAPHIR, was studied using a Volatility Tandem DMA (VTDMA). The detailed laboratory studies show that the formation of monoterpene SOA and its thermal properties depend on chemical structure of the precursor and oxidizing conditions. Furthermore, freshly formed monoterpene SOA comprise of compounds with a wide distribution of volatilities ranging from extremely low volatile to semi volatile compounds. Photochemical aging of SOA was studied in SAPHIR by oxidation induced by natural sun light and in PAM by exposing SOA precursors to high concentration of OH over a short time. The results reveal two opposing processes which drive the evolution of SOA volatility in the two systems.

During the course of this work an oxidation flow reactor, Go:PAM, has been developed. Go:PAM enables studies of secondary particle formation from rapidly changing emission sources, and was used to derive fuel-specific secondary particle emission factors from in-use transit buses under real-world driving conditions. Both primary emissions and the secondary particle formation of 29 buses running on conventional or on more sustainable fuels were investigated. The results emphasize the importance of taking the reduction in OH exposure into consideration when interpreting the secondary particle formation from plumes. However, independent of fuel and technology of the buses, the formation of secondary particulate mass was significantly higher than the primary particle mass. Furthermore, the results indicate there are emissions of non-fuel related compounds that are important for secondary particle formation.

This work provides insight in the formation and aging of secondary particles from biogenic and traffic-related sources. The results highlight the importance of including secondary particle formation when predicting the climate forcing of SOA and designing of air quality strategies.

Keywords: volatility, ozonolysis, hydroxyl radical, OH exposure, α-pinene, β-pinene, limonene, dimer esters, engine exhaust, bus exhaust, air pollution, climate, oxidation flow reactor, atmospheric simulation chamber