UNIVERSITY OF GOTHENBURG

THESIS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY IN NATURAL SCIENCE, SPECIALISING IN CHEMISTRY

Physical Properties and Processes of Secondary Organic Aerosol and its Constituents

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ABSTRACT

Atmospheric aerosol particles are involved in several important processes including the formation of clouds and precipitation. A considerable fraction of the ambient aerosol mass consists of organic compounds of both primary and secondary origin. These organic compounds are often semi-volatile and susceptible to oxidation which makes the organic aerosol a dynamic system, both chemically and physically. Once an aerosol is formed or released into the atmosphere, several processes will begin to alter its chemical and physical properties.

The focus of the work presented in this thesis has been to use experimental methods to characterise single aerosol components and more complex experimental systems, involving the formation and processing of secondary organic aerosol (SOA). The volatility of aerosol particles, e.g. the evaporation rate of the particles upon heating, can provide information of several important properties. From an aerosol consisting only of one pure compound it is possible to derive physical quantities like saturation vapour pressure and enthalpy of evaporation. In more complex systems like a secondary organic aerosol the volatility can give information about changes in composition, state of oxidation and degree of internal or external mixing.

With the use of a volatility tandem differential mobility analyser (VTDMA), the saturation vapour pressures and enthalpies of evaporation have been determined for pure compounds that are known constituents of ambient aerosol samples i.e. nine carboxylic acids. Two of them were cyclic, pinic and pinonic acid and seven of them were straight chain dicarboxylic acids with number of carbons ranging from C_4 to C_{10}. These properties were in addition evaluated for the aminium nitrates of mono-, di-, and trimethylamine, ethyl- and monoethanolamine. The calculated saturation vapour pressures for the carboxylic acids were in the range of 10^{-6} to 10^{-3} Pa and the determined enthalpies of evaporation ranged from 83 to 161 kJ mol^{-1}. The corresponding values for the aminium nitrates were for the calculated saturation vapour pressures approximately 10^{-4} Pa and for the enthalpies of evaporation 54 to 72 kJ mol^{-1}.

The VTDMA system has also been utilised to characterise SOA formed in the AIDA and SAPHIRE smog chambers from the ozonolysis of α-pinene and limonene and the change in the SOA thermal properties during OH radical induced ageing. Further, the effect of elevated ozone concentration and radical chemistry on SOA formed from limonene ozonolysis in the G-FROST laminar flow reactor was investigated. In addition, to compare with vapour pressures of aminium nitrates SOA generated from photooxodation of alkyl amines have been characterised in the EUPHORE smog chamber.

The calculated vapour pressures of all the investigated pure compounds in this work characterise them to be in the semi-volatile organic compound (SVOC) category; hence they will be present both in the gaseous and condensed phase in the atmosphere. This implied that all these compounds will be susceptible for gas phase OH radical oxidation that was demonstrated to be an important process for the complex mixtures investigated in the smog chamber facilities. The OH chemistry was also influencing the volatility of aerosol produced in G-FROST by ozonlysis. Regarding photooxodation of amines the aerosols produced under high NO_x conditions initially mimicked the pure salts but was efficiently transformed by oxidation into an aerosol with similar volatility properties as observed in the terpene oxidation experiments.

Keywords: SOA, ageing, VOC, atmosphere, volatility, VTDMA, monoterpenes

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