Secondary organic aerosol formation in the atmospheric aqueous phase: Effects on product and aerosol size distributions

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The major fraction of organic aerosol mass in the atmosphere is formed by chemical processes (secondary organic aerosol, SOA), as opposed to directly emitted organic particles (primary OA). Thus, in order to predict the mass loading and climate-relevant properties of organic aerosol that comprises a significant fraction of atmospheric particulate matter the implementation of detailed chemical mechanisms into models is necessary.

Traditional model approaches assume that SOA formation occurs by absorption of low-volatility or semivolatile oxidation products of gas phase precursors into preexisting aerosol particles. However, many recent laboratory studies have suggested that the oxidation of volatile, water-soluble compounds (e.g., small dialdehydes) in the aqueous phase of cloud droplets or deliquesced aerosol particles can lead to low-volatile products that remain in the particle phase upon water evaporation. Mechanistic studies in relatively dilute aqueous phase, which can be regarded as a proxy of cloud droplets, show the formation of keto- and dicarboxylic acids that are ubiquitous in cloud residual particles. Aqueous solutions that are more highly concentrated in terms of organic and inorganic solutes can be considered as proxies for the aqueous phase associated with aerosol particles. In such aqueous medium the preferred formation of oligomeric compounds has been observed. Such laboratory studies have resulted in the development of detailed chemical mechanisms that can be used in process models.

Results from such model studies will be presented that compare SOA mass formation in cloud droplets and aerosol particles under atmospheric conditions. Similar amounts of SOA are predicted in the two different aqueous phases even though the liquid water content of cloud droplets is about five orders of magnitude greater than that of aerosol particles. The lower solute concentrations in cloud droplets, together with the limited droplet lifetimes, can explain the similar mass production rates in clouds and aqueous aerosol particles.

Finally, differences in SOA formation in the gas and aqueous phases will be addressed. While gas phase reactions often lead to fragmentation, aqueous phase reactions favor functionalization and thus yield more highly oxidized material. Such differences in product distributions affect the SOA hygroscopicity that, in turn, impacts the interactions of aerosol particles with water vapor. Besides such chemical differences, macroscopic properties of aerosol populations are affected differently by the two SOA formation pathways: While absorption of gas phase species leads to mass addition as a function of preexisting (organic) aerosol mass, aqueous phase processes add mass to relatively larger particles that are often more hygroscopic and activated into cloud droplets. Thus, not only chemical composition and hygroscopicity but also aerosol size distributions are impacted in different ways by gas and aqueous phase SOA formation processes.

References

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