

Ozone uptake and formation of reactive oxygen intermediates on glassy, semi-solid and liquid organic matter

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Heterogeneous and multiphase reactions of ozone are important pathways for chemical ageing of atmospheric organic aerosols (Abbatt, Lee and Thornton, 2012). The effects of particle phase state on the reaction kinetics are still not fully elucidated and cannot be described by classical models assuming a homogeneous condensed phase (Berkemeier *et al.*, 2013). We apply a kinetic multi-layer model, explicitly resolving gas adsorption, condensed phase diffusion and condensed phase chemistry (Shiraiwa *et al.*, 2010), to systematic measurements of ozone uptake onto proxies for secondary organic aerosols (SOA). Our findings show how moisture-induced phase changes affect the gas uptake and chemical transformation of organic matter through change in the physicochemical properties of the substrate: the diffusion coefficients are found to be low under dry conditions, but increase by several orders of magnitude toward higher relative humidity (RH). The solubility of ozone in the dry organic matrix is found to be one order of magnitude higher than in the dilute aqueous solution.

The model simulations reveal that at high RH, ozone uptake is mainly controlled by reaction throughout the particle bulk, whereas at low RH, bulk diffusion is retarded severely and reaction at the surface becomes the dominant pathway, with ozone uptake being limited by replenishment of unreacted organic molecules from the bulk phase. The experimental results can only be reconciled including a pathway for ozone self-reaction, which becomes especially important under dry and polluted conditions. Ozone self-reaction can be interpreted as formation and recombination of long-lived reactive oxygen intermediates at the aerosol surface, which could also explain several kinetic parameters and has implications for the health effects of organic aerosol particles.

This study hence outlines how kinetic modelling can be used to gain mechanistic insight into the coupling of mass transport, phase changes, and chemical reactions in complex multiphase reaction systems.

References

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