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Accelerated Free Radical Chemistry in the Heterogeneous Oxidation of Semisolid Organic Aerosol

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In regional climate and air quality models, organic aerosol is treated as a well-mixed liquid in thermodynamic equilibrium with the surrounding gas, but several recent studies have shown that organic aerosol often exists in soft semi-solid or glassy states as well. However, how these phase states influence the heterogeneous oxidation of these organic aerosols is not well understood. To investigate the effect of phase state on the free radical chemistry, a stochastic kinetics model is developed that provides spatial information about the particle as a function of time and self-diffusion coefficient. This model is then compared to experiments investigating the semi-solid OH + Triacontane and OH + citric acid organic aerosol systems, which are reasonable proxies of primary and secondary organic aerosols, respectively.

In diffusion limited cases, chemical pathways that are normally too slow in well-mixed, liquid or aqueous particles as well as evaporation of fragmentation products from the particle are enhanced due to the confinement of the free radical intermediates near the surface of the semisolid particle. Intriguingly, the model also shows that these semisolid aerosols have steep surface-bulk gradients in chemical composition (e.g. O/C ratio) that are not reflected by the measured bulk average. These chemical gradients could lead to different optical properties and enhanced hygroscopicity in ways not accurately captured by average chemical composition.

These two aerosol systems that approximate primary and secondary organic aerosols are then compared to investigate the similarities and differences in their physical and chemical properties after oxidation. Notably, in the case of citric acid and thus secondary organic aerosol, water, in addition to acting as a plasticizing agent, also unlocks new chemical pathways such as the formation of geminal diols from aldehyde hydration reactions that are not possible under dry or hydrophobic conditions. The presence of water thus alters the balance between functionalization and fragmentation reactions in addition to influencing the diffusion coefficient of the organic materials.