Computational and Experimental Study of the Kinetics and Thermodynamics of New Particle Formation

The measured concentration of particles in the atmosphere is often higher than predicted by atmospheric models. In order to reconcile the difference between measured and modeled particle concentrations new mechanisms for particle formation need to be determined. Formation of particles has frequently been modeled using classical nucleation theory (CNT). The first step in CNT is the nucleation step where molecular clusters form. In a second step, these clusters grow into particles through coagulation or condensation. Previous research has shown that for prototypical clusters such as the sulfuric acid-water (H2SO4-H2O) and methane sulfonic acid-water (MSA-H2O) systems that the rate of particle formation is enhanced by the inclusion of ppt concentrations of amines to the reaction mixture. We have investigated computationally and experimentally the ability of the formic acid-water (HCOOH-H2O) and hydroperoxy radical-water (HO2-H2O) complexes to serve as nucleating clusters for new particle formation in the absence and presence of trace amounts of amines. Our results show that the inclusion of amines into a reaction mixture containing formic acid and water vapor serves to stabilize the HCOOH-H2O and HO2-H2O complexes. These results suggest that the addition of amines to formic acid or HO2 with water vapor may serve as a viable mechanism for new particle formation in the atmosphere.