Free energy barrier in the growth of sulfuric acid clusters

T. Olenius[1], O. Kupiainen[1], I.K. Ortega[1] and H. Vehkamäki[1]

[1]Department of Physics, University of Helsinki, Helsinki, FI-00014, Finland
Keywords: sulfuric acid, molecular clusters, modeling, new particle formation
Presenting author email: tinja.olenius@helsinki.fi

Formation of secondary atmospheric particles begins with the clustering of gas phase molecules into small molecular clusters, which can grow by colliding with gas molecules and each other. As experimental observation of the smallest clusters is extremely difficult, theoretical methods provide necessary tools to study the properties of these clusters.

We have used first principles quantum chemistry combined with a dynamic model to study the kinetics of sets of small clusters containing either sulfuric acid (H_2SO_4) and ammonia (NH_3) or sulfuric acid and dimethylamine (DMA, $(CH_3)_2NH$) molecules. The model (Atmospheric Cluster Dynamics Code; McGrath *et al*, 2012) solves the steady-state of the system considering all possible collision and evaporation processes. Collision rates are calculated as in the kinetic gas theory, and evaporation rates are derived from quantum chemical Gibbs free energy of formation of the clusters (Ortega *et al*, 2012). We included in the simulations clusters containing in principle up to four acid and four base molecules for DMA; for ammonia, the behavior of the system was not as straightforward as for DMA and therefore the set was extended to include clusters with up to five acids and five bases in order to better understand the system. Both sets were studied with and without electrically charged clusters.

We performed the simulations in atmospherically relevant conditions. The base concentration was fixed by setting a constant base monomer concentration, whereas the acid concentration was set by fixing the sum of all neutral clusters containing one acid and any number of base molecules, as the instrument for measuring the acid concentration (CIMS; Chemical Ionization Mass Spectrometer) is likely to detect also these clusters as acid monomers. We tracked the main clustering pathways in each system and converted the quantum chemical Gibbs free energies of formation of the growing clusters to the acid and base concentrations used in the simulations.

Figure 1 shows the Gibbs free energy of formation of the growing clusters as a function of growth step in the studied systems. In the system with sulfuric acid and ammonia, there are energy barriers in the main growth pathways both in the electrically neutral and ionic systems. Charged clusters dominate the clustering routes in the ionic system by growing out as negative or positive cluster ions and forming neutral clusters by recombination. In the acid-DMA system the growth along the most significant pathways is barrierless and occurs via electrically neutral clusters also when ions are present.

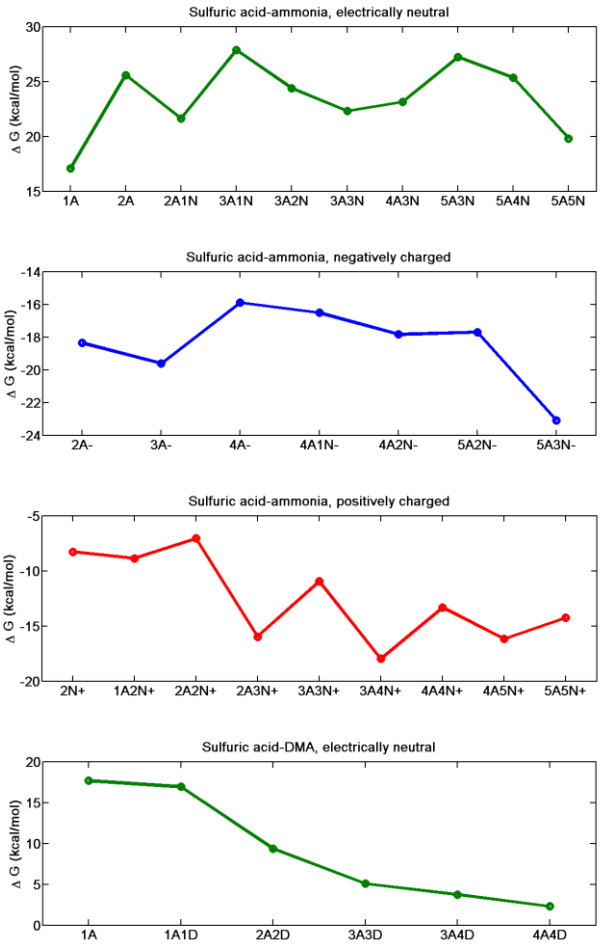

Figure 1. Gibbs free energy of formation as a function of growth step along the most significant growth routes in the sulfuric acid-ammonia and sulfuric acid-DMA systems at T=5 °C, $[H_2SO_4]=10^6$ cm^{-3} and $[NH_3]$=100 ppt or [DMA]=1 ppt. For ammonia, both electrically neutral and charged growth routes are shown; for DMA, only the neutral route is shown as the contribution of ions is insignificant. Acid, ammonia and DMA molecules are denoted with A, N, and D, respectively.

This work was supported by FP7-MOCAPAF project No 257360, FP7-ATMNUCLE project No 227463, Väisälä Foundation and Academy of Finland. The authors thank CSC- IT Center for Science in Espoo, Finland for the computing time.

McGrath, M.J. *et al* (2012) *Atmos. Chem. Phys.* **12**, 2345-2355.

Ortega, I.K. *et al* (2012) *Atmos. Chem. Phys.* **12**, 225-235.