The Role of Highly Oxidized Organics in New Particle Formation

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Atmospheric new particle is an important source of aerosols and cloud condensation nuclei (Merikanto et al. 2009). Is known that sulfuric acid plays a key role in this phenomenon (Sipila et al 2010). On the other hand, typical atmospheric concentrations of sulfuric acid and water can not explain the observed new particle formation rates, thus some additional compound/s able to enhance the formation of particles are needed.

Organic acids produced by oxidation of volatile organic compounds (VOCs) have been proposed as key compounds in new-particle formation as well. However, there is no consensus about the participation of these compounds in new-particle formation; some studies conclude that these oxidized VOC are just involved in particle growth (Laaksonen et al. 2008), while other studies state that they are involved in the very first steps of new-particle formation but not in growth (Zhang et al. 2009).

In the present work we have used quantum chemical methods (Ortega et al 2012) to calculate the formation free energies of clusters formed by sulfuric acid and different organic acids (OxdOrg). We used ACDC (McGrath et al. 2012) model to estimate the effect of organic acids in new particle formation. We have chosen three oxidation products of alpha-pinene with increasing O:C ratio, namely Pinonic acid (PA), 7-Hydroxy-pinonic acid (HPA) and 3-Metyl-1,2,3-butane-tricarboxilyc acid (MBTA).

Results

Figure 1 shows the dependence of simulated formation rates with sulfuric acid concentration for the three different organic acids considered in this study. The simulations include only neutral clusters. We simulated the formation rates at 278K, and assuming a concentration of 1pptv for the OxdOrg.

Formation rates obtained using PA or HPA are 10 – 12 orders of magnitude smaller than the ones observed in Hyytiälä. On the other hand, the same amount of MBTA produced formation rates close to the observed ones. These preliminary results indicate that highly oxidized organic compounds may play a key role in atmospheric new particle formation.

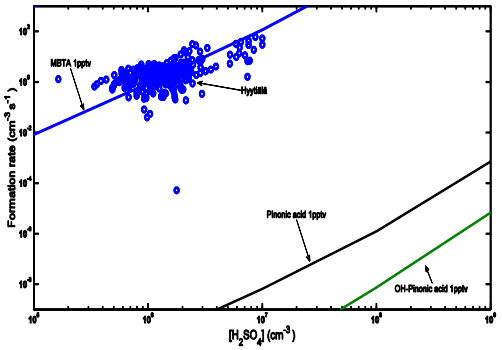

Figure 1. Formation rate versus sulfuric acid concentration. ACDC simulations correspond to 1 pptv of organic acid at 278K and includes only neutral clusters. Blue circles correspond to data measured in Hyytiälä field station, blue line correspond MBTA simulations, black line correspond to PA simulations and Green line correspond to HPA simulations.

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Merikanto, J., Spracklen, D.V., Mann, G.W., Pickering S.J., Carslaw, K.S. (2009) *Atmos.Chem.Phys.* **9**, 8601-8616.

Sipilä, M., et al. (2010) *Science*, **327,** 1243-1246.

Laaksonen, A., et al. (2008) *Atmos. Chem. Phys.* **8**, 2657 - 2665.

Zhang, R., et al. (2009) *Proc. Natl. Acad. Sci*. **106**, 17650- 17654.

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

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