Molecular mechanisms behind nocturnal new particle formation

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Keywords: Organic, Nucleation, Modelling, SOA, Quantum Mechanic.

Atmospheric aerosols influence climate directly and indirectly. Unfortunately the role of atmospheric aerosols is still the forcing with the lowest level of scientific understanding, as reported in the newest report by the Intergovernmental Panel on Climate Change (IPCC 2007).

Nucleation events are in most cases observed during daytime but in some locations they can occur also during the night. In Tumbarumba in New South Wales, Australia, these nocturnal events are very intense and frequently observed (Suni et al. 200).

The objective of this study is to evaluate the role of different VOCs in nocturnal nucleation events. The selected VOCs are limonene, alpha-pinene, beta-pinene and 3-carene; these are the most abundant VOCs in Tumbarumba and in Hyytiälä.

We performed a series of chamber experiments with the objective to reproduce the nocturnal events observed in Australia. Additionally we used quantum chemical calculations to study the molecular mechanism behind the nocturnal nucleation events. Finally we have used the quantum chemical results in aerosol formation models to check if the proposed mechanism could explain the observed nucleation events.

Our quantum chemical calculations were performed using a systematic multi-step method recently developed by our group (Ortega et al. 2008).

Table 1. Formation energies calculated for various clusters containing 1 sulphuric acid and different VOCs oxidation products at 298K and 1 atm

Organic Acid	ΔG (kcal/mol)
Caric acid	-10.5
Caronic acid	-14.4
7- hydroxy caronic acid	-19.3
Pinic acid	-7.2
Pinonic acid	-9.4
7- hydroxy pinonic	-11.1
Limonic acid	-4.6
Limononic acid	-10.6
7- hydroxy limononic	-6.9

As we can see in Table 1, the formation energies differences between different compounds are quite important in some cases. If we compare those energies with the formation energy of sulfuric acid dimer, 6.3 kcal/mol, we can see how the most of organic acids studied forms more stable cluster than sulfuric acid on its own, so their presence should enhance nucleation.

During the experiments we were able to produce particles in dark conditions using ozone and different monoterpenes. The results show that the oxidation rate plays a crucial role in the formation of particles, confirming that the oxidation products of monoterpenes rather that the monoterpenes it selves are involved in the formation of new particles.

Model simulations with SOSA show that nucleation rates calculated with the mechanism explained above are in good agreement with nucleation rates based on measured particle size distributions.

Our results show that the oxidation products of VOCs play an important role in nucleation events. Not all these compounds have the same importance, so characterizing the particle formation potential with, for example, the total concentration of VOCs is probably an unsatisfactory approximation. Taking into account the different emission of VOCs in different environments (like Tumbarumba and Hyytiälä) probably can explain the differences in observed nucleation events.

The authors thanks the Scientific Computing Center (CSC) in Espoo, Finland for the computing time, and the Academy of Finland and Emil Aaltonen foundation for financial support

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I.K. Ortega, T. Kurtén, H Vehkamäki and M. Kulmala, (2008) *Atmos. Chem. Phys.* 8, 2859