Implication of Highly Oxidized Organic Compounds in Atmospheric New Particle Formation

J. Elm[1], N. Myllys[2], T. Kurtén[2]

[1]Department of Chemistry, University of Copenhagen, Denmark
[2]Department of Chemistry, University of Helsinki, Finland
Keywords: Nucleation, Quantum Mechanics, ELVOCs, Clusters
Presenting author email: elmjonas@gmail.com

It has recently been inferred by Ehn *et al.*, Nature 2014 and Schobesberger *et al.*, PNAS 2013 that extremely low volatile organic compounds (ELVOCs) participate in the initial steps in nucleation. ELVOCs can be produced through different mechanisms. Either an organic compound can be oxidized by individual OH radical initiated hydrogen abstraction reactions which can lead to an oxidized product with oxygen-to-carbon ratios (O/C) close to one. Alternatively ELVOCs can be formed through a sequence of internal peroxy radical hydrogen shift reactions. This autoxidation scheme leads to highly oxidized compounds with (O/C)-ratio around or even above one. The different mechanism can lead to different functional groups in the compound. The OH-mechanism primarily leads to carboxylic acid moieties, where the autoxidation process yield products with various hydrogen-peroxide groups. Here we present the interaction between the primary nucleation precursor H_2SO_4 and different ELVOC molecules.

Model Systems

The most widely used precursor for studying secondary organic aerosols is α-pinene, a volatile organic compound emitted by pine trees. Several distinct α-pinene oxidation products have previously been identified, such as pinonaldehyde (O/C = 2/10), pinonic acid (O/C = 3/10), pinic acid (O/C = 4/9) and 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA) with O/C = 6/8. Currently there is no specific structural information about ELVOCs produced from α-pinene through an autoxidation scheme, but recently Rissanen *et al.* 2014/2015 reported the ELVOC production from cyclohexene using both experimental and computational methods.
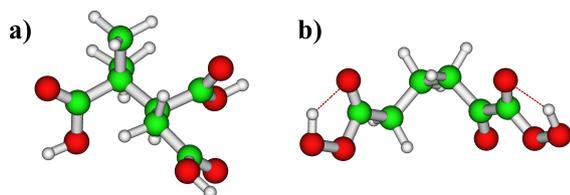

Figure 1: a) MBTCA, b) the $C_6H_8O_7$ ELVOC.

We study the interaction of sulfuric acid with either MBTCA or an $C_6H_8O_7$ cyclohexane oxidation product (Figure 1), to further elucidate the importance of these type of compounds in atmospheric new particle formation.

Methodology

Utilizing density functional theory the molecular structure and vibrational frequencies of the clusters are obtained. To thoroughly sample the configurational space in order to be certain that the best minimum structures are obtained, we use a semi-empirically guided sampling technique. From several thousands of initial guess structures the molecular structure of the clusters are identified. By calculating the formation free energies of the clusters, the most likely growth paths can be analysed. We report the structures of the largest clusters studied using quantum mechanical methods to date, consisting of up to 3 MBTCA and 3 sulfuric acid molecules. An example of the interaction between sulfuric acid and MBTCA can be seen in Figure 2.
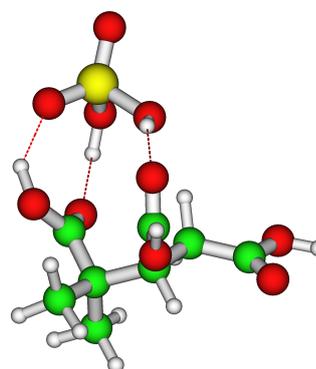

Figure 2: The molecular structure of the complex formation between MBTCA and H_2SO_4.

Conclusions

By studying the Gibbs free energies for the formation of atmospheric molecular clusters consisting of sulfuric acid and oxidized organic compounds, several important trends can be established.

- MBTCA bind strongly to sulfuric acid.

- The peroxy acid groups in the $C_6H_8O_7$ ELVOC compounds bind weakly to sulfuric acid.

We find that more than two strong binding moieties are required for organic compounds to be involved in the initial steps in nucleation.