



Secondary Organic Aerosol (SOA) Formation from Hydroxyl Radical Oxidation and Ozonolysis of Monoterpenes

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Hydroxyl radical (OH) oxidation and ozonolysis are the two major pathways of daytime biogenic volatile organic compounds (VOCs) oxidation and secondary organic aerosol (SOA) formation. The pure OH oxidation of monoterpenes, an important biogenic VOC class, has seldom been investigated. In order to elucidate the importance of the reaction pathways of the OH oxidation and ozonolysis and their roles in particle formation and growth, we investigated the particle formation of several common monoterpenes (alpha-pinene, beta-pinene, and limonene) in the large atmosphere simulation chamber SAPHIR in Juelich, Germany. The experiments were conducted for both OH dominant and pure ozonolysis case (in the presence of CO as OH scavenger) at ambient relevant conditions (low OA, low VOC and low NO_x concentration). OH and ozone (O₃) concentrations were measured so that the oxidation rates of OH and O₃ with precursors were quantified. The particle formation and growth, aerosol yield, multi-generation reaction process and aerosol composition were analyzed.

Pure ozonolysis generated a large amount of particles indicating ozonolysis plays an important role in particle formation as well as OH oxidation. In individual experiments, particle growth rates did not necessarily correlate with OH or O₃ oxidation rates. However, comparing the growth rates at similar OH or O₃ oxidation rates shows that generally, OH oxidation and ozonolysis have similar efficiency in particle growth.

Multi-generation products are shown to be important in the OH oxidation experiment based on aerosol yield "growth curve" (Ng et al., 2006). The reaction process of OH oxidation experiments was analyzed as a function of OH dose to elucidate the role of functionalization and fragmentation. A novel analysis was developed to link the particle formation with the reaction with OH, which was also used to examine the role of functionalization and fragmentation in the particle formation by OH oxidation. These analyses show that functionalization was dominant in the beginning of the reaction and fragmentation started to be dominant after that.

Moreover, Aerosol Mass Spectrometer data shows that SOA from monoterpene OH oxidation follows a slope of shallower than -1 in the Van Krevelen diagram, indicative of an oxidation process of precursor without significant hydrogen loss. SOA from OH oxidation has a higher H/C than that from O₃ oxidation. In ozonolysis, the process with significant hydrogen loss such as addition of carbonyl seems to play an important role in SOA formation.

Reference:

Ng, N. L. et al. *Sci. & Tech.* 40, 2283-2297, 10.1021/es052269u, 2006.