



Reaction of OH radicals with secondary organic aerosol from the ozonolysis of alpha-pinene

Harald Saathoff (1), Karl-Heinz Naumann (1), Ottmar Möhler (1), Ralf Tillmann (2), Thomas F. Mentel (2), Neil Donahue (3), and Thomas Leisner (1)

(1) Karlsruhe Institute of Technology, Institute for Meteorology and Climate Research (IMK-AAF), Eggenstein-Leopoldshafen, Germany (harald.saathoff@kit.edu), (2) Institute of Chemistry and Dynamic of the Geosphere, Forschungszentrum Jülich, Germany, (3) Carnegie Mellon University, Centre for Atmospheric Particle Studies, Pittsburgh, PA, USA

OH radicals are the most important agents for oxidation of atmospheric constituents and they play an important role in formation and aging of atmospheric aerosols e.g. secondary organic aerosols (SOA). Since the influence of temperature on aerosol formation and aging is one of the major uncertainties for understanding aerosol transformations (Tsigaridis et al., 2005) we investigated SOA aging by OH radicals in the large temperature controlled but dark AIDA aerosol chamber (Saathoff et al., 2009).

As a dark source of OH radicals we employed controlled ozonolysis of 2,3-dimethyl-2-butene (TME) in a similar way as described by Lambe et al., (2007). Since no direct measurement of OH radicals was available the OH radical concentrations generated in the AIDA simulation chamber were calculated by comparing the results of MCM 3.1 simulations with the measured depletion of hydrocarbons like the tracer 3-pentanol or the product of the alpha-pinene ozonolysis, pinonaldehyde. Once characterised the dark OH source was used in aging experiments on SOA material formed by ozonolysis of alpha-pinene under simulated tropospheric conditions in the large aerosol & cloud chamber AIDA on time scales of up to 30 hours and at temperatures between 253 and 313 K. The organic aerosol was generated by controlled oxidation with an excess of ozone and the aerosol mass concentrations were calculated from size distributions measured with differential mobility analysers (SMPS, TSI, 3071). Various instruments were used to measure the time evolutions of hydrocarbons (PTR-MS, FTIR), ozone (UV-Absorption), aerosol particle mass & size (TOF-AMS, SMPS) and number concentrations (CPC). The experimentally determined values were analysed using the aerosol behaviour code COSIMA (Naumann, 2003), supplemented by a SOA module.

The model calculations can reproduce the observations based on known rate coefficients and the measured trace gas concentrations. According to the analysis the OH radical levels in the AIDA chamber from ozonolysis of TME ranged from 106 to 107 molecules cm⁻³ depending on the experimental conditions. Generating the OH radicals this way in the presence of SOA from ozonolysis of alpha-pinene resulted in additional formation of SOA mass in the order of 10-35% within two hours or less. The additional mass formed is smaller for lower temperatures. The model analysis takes into account the wall losses of semi volatile SOA compounds and also the impact of the OH radicals formed already during the terpene ozonolysis.

This paper will present quantitative results on the OH radical induced aging of alpha-pinene SOA for simulated tropospheric conditions with low NO_x.

Lambe, A.T., Zhang, J.Y., Sage, A.M., Donahue, N.M. (2007) Environ. Sci., & Technol., 41, 2357.

Naumann, K. – H. (2003) J. Aerosol Science, 34, 1371.

Saathoff, H., Naumann, K. – H., Moehler, O., Jonsson, M., Hallquist, M., Kiendler – Scharr, A., Mentel, Th.F., Tillmann, R., Schurath, U. (2009) Atmos. Chem. Phys. 9(5), 1551.

Tsigaridis, K., Lathiere, J., Kanakidou, M., Hauglustaine, D.A. (2005) Atmos. Chem. Phys. 5, 1891.