



Investigation of Monoterpene Degradation in the Atmospheric Simulation Chamber SAPHIR

Martin Kaminski (1), Ismail-Hakki Acir (1), Birger Bohn (1), Theo Brauers (1), Hans-Peter Dorn (1), Hendrik Fuchs (1), Rolf Haeseler (1), Andreas Hofzumahaus (1), Xin Li (1), Anna Lutz (2), Sascha Nehr (1), Franz Rohrer (1), Ralf Tillmann (1), Robert Wegener (1), and Andreas Wahner (1)

(1) Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich GmbH, Jülich, Germany, (2) Institute for Chemistry and Molecular Biology, Gothenburg University, Gothenburg, Sweden

Monoterpenes are the volatile organic compound (VOC) species with the highest emission rates on a global scale beside isoprene. In the atmosphere these compounds are rapidly oxidized. Due to their high reactivity towards hydroxyl radicals (OH) they determine the radical chemistry under biogenic conditions if monoterpene concentration is higher than isoprene concentration. Recent field campaigns showed large discrepancies between measured and modeled OH concentration at low NO_x conditions together with high reactivity of VOC towards OH (Hofzumahaus et al. 2009) especially in tropical forest areas (Lelieveld et al. 2008). These discrepancies were partly explained by new reaction pathways in the isoprene degradation mechanism (Whalley et al 2011). However, even an additional recycling rate of 2.7 was insufficient to explain the measured OH concentration. So other VOC species could be involved in a nonclassical OH recycling. Since the discrepancies in OH also occurred in the morning hours when the OH chemistry was mainly dominated by monoterpenes, it was assumed that also the degradation of monoterpenes may lead to OH recycling in the absence of NO. (Whalley et al 2011).

The photochemical degradation of four monoterpene species was studied under high VOC reactivity and low NO_x conditions in a dedicated series of experiments in the atmospheric simulation chamber SAPHIR from August to September 2012 to overcome the lack of mechanistic information for monoterpene degradation schemes. α -Pinene, β -pinene and limonene were chosen as most prominent representatives of this substance class. Moreover the degradation of myrcene was investigated due to its structural analogy to isoprene.

The SAPHIR chamber was equipped with instrumentation to measure all important OH precursors (O_3 , HONO, HCHO), the parent VOC and their main oxidation products, radicals (OH, HO_2 , RO_2), the total OH reactivity, and photolysis frequencies to investigate the degradation mechanism of monoterpenes in the SAPHIR chamber. All experiments were carried out under low NO_x conditions ($\leq 2\text{ppb}$) and atmospheric terpene concentrations ($\leq 5\text{ppb}$) with and without addition of ozone into the SAPHIR chamber. The measured temporal profiles of key constituents were compared to model simulations of the experiments using the Master Chemical Mechanism v3.2.