



New insights into the degradation of terpenoids with OH: a study of the OH budget in the atmosphere simulation chamber SAPHIR

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The hydroxyl radical (OH) is the main oxidation agent in the atmosphere during daytime. Recent field campaigns studying the radical chemistry in forested areas showed large discrepancies between measured and modeled OH concentration at low NO_x conditions and when OH reactivity was dominated by VOC. These observations were only partially explained by the evidence for new efficient hydroxyl radical regeneration pathways in the isoprene oxidation mechanism. The question arises if other reactive VOCs with high global emission rates are also capable of additional OH recycling. Beside isoprene, monoterpenes and 2-methyl-3-buten-2-ol (MBO) are the volatile organic compounds (VOC) with the highest global emission rates. Due to their high reactivity towards OH monoterpenes and MBO can dominate the radical chemistry of the atmosphere in forested areas under certain conditions.

In the present study the photochemical degradation mechanism of α -pinene, β -pinene, limonene, myrcene and MBO was investigated in the Jülich atmosphere simulation chamber SAPHIR. The focus of this study was in particular on the investigation of the OH budget in the degradation process.

The photochemical degradation of these terpenoids was studied in a dedicated series of experiments in the years 2012 and 2013. The SAPHIR chamber was equipped with instrumentation to measure radicals (OH, HO_2 , RO_2), the total OH reactivity, all important OH precursors (O_3 , HONO, HCHO), the parent VOC, its main oxidation products and photolysis frequencies to investigate the radical budget in the SAPHIR chamber. All experiments were carried out under low NO_x conditions (≤ 2 ppb) and atmospheric terpene concentrations (≤ 5 ppb) with and without addition of ozone into the SAPHIR chamber.

For the investigation of the OH budget all measured OH production terms were compared to the measured OH destruction. Within the limits of accuracy of the instruments the OH budget was balanced in all cases. Consequently unaccounted OH recycling or primary OH production processes did not play a role for conditions of these experiments.

Despite the OH budget was closed in these experiments simulation results from the Master Chemical Mechanism v3.2 showed that the OH production was underestimated by the model in the α -pinene, β -pinene and limonene experiments. The measured OH destruction was overestimated by the numerical simulation.