



Investigation of the α -pinene & pinonaldehyde photooxidation by OH in the atmospheric simulation chamber SAPHIR

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Recent field studies in forested environments showed large discrepancies between measured and modelled hydroxyl (OH) and hydroperoxyl (HO_2) radical concentrations. These environments are characterized by large concentrations of biogenic volatile organic compounds (BVOC). Isoprene and monoterpenes represent the majority of these BVOCs and, although new efficient OH radical regeneration pathways in the isoprene oxidation mechanism improved the agreement between measurements and existing models, less is known regarding monoterpenes and their oxidation products. In this study, the photooxidation of α -pinene and pinonaldehyde by OH was investigated in the atmospheric simulation chamber SAPHIR focusing on the budget of HO_x (OH + HO_2) radicals. Experiments were done at low NO conditions (≤ 150 ppt) and atmospheric α -pinene concentrations (≤ 4.5 ppb). Measurements of OH and HO_2 radicals, α -pinene, OH precursors and organic products (pinonaldehyde, acetone and formaldehyde) allow to test our current understanding of the OH-oxidation mechanism for α -pinene by comparing the measurements with model calculations using the Master Chemical mechanism (MCM 3.3.1). This study shows that OH and HO_2 are underestimated by the MCM model for both α -pinene and pinonaldehyde experiments. In addition, the MCM produces significantly more pinonaldehyde compared to the measured values. Implementation of recent suggestions by Vereecken et al. (2007) improves the model-measurement agreement including radicals, but pinonaldehyde is still overestimated by the model in this case. In the pinonaldehyde experiments, product yields of acetone and formaldehyde need to be adjusted in the MCM to match observations. In addition, a HO_2 source needs to be added, to bring measured and modelled HO_2 and therefore OH into agreement.