2.021 The atmosphere of a tropical forest simulated in a chamber: experiments, theory and global significance of OH regeneration in isoprene oxidation.

Early Career Scientist

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Abstract:

New experiments focusing on the OH-initiated oxidation of isoprene over a broad range of NO concentrations were achieved in the atmospheric simulation chamber SAPHIR at Forschungszentrum Jülich, Germany. Measurements of VOCs, NO$_x$, O$_3$, HONO and photolysis frequencies were performed together with measurements of OH radicals (by both LIF-FAGE and DOAS) and OH reactivity. The NO mixing ratio was varied between 0.05 and 2 ppbv allowing the investigation of regeneration paths for OH radicals which originates from the isomerization of the RO$_2$ radicals, and the well-known NO+HO$_2$ mechanism. The observed radicals concentrations were compared with a state-of-the-art model (MCM 3.3.1) which includes isomerization reactions as described in the Leuven-Isoprene-Mechanism 1 (LIM1) [1]. The best agreement (within 10%) between measured and modelled OH radicals and primary oxidation products from isoprene was observed when the yields from the 1,6-hydrogen shift reaction in the MCM 3.3.1 were modified according to findings in recent laboratory studies [2]. The largest contribution to the OH production within the model for experiments with NO < 300 pptv originates from the 1,4-hydrogen shift of the di-HPCARP which is formed after the 1,6-hydrogen shift of Z isomers from the δ-hidroxy peroxy radicals (LIM1). Theoretical calculations confirm that the major degradation path for the di-HPCARP proceed via a 1,4-hydrogen shift with formation of OH radicals with a proposed rate coefficient of ~ 0.1 s$^{-1}$. This reaction path together with the modified yields of the products of the 1,6-hydrogen shift were included in a global chemistry model to assess the impact of the 1,4-hydrogen shift on the OH concentration throughout the troposphere. In light of this enhanced OH regeneration, the sensitivity of OH atmospheric levels to perturbation will be discussed.