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.

1. Peeters J. et al., J. Phys. Chem. A, doi:10.1021/jp5033146, 2014.
2. Teng A.P. et al., J. Am. Chem. Soc., doi:10.1021/jacs.6b12838, 2017.