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Tropospheric Aqueous-phase Oxidation of Green Leaf Volatiles with Hydroxyl, Sulfate and Nitrate Radicals

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Introduction

Numerous green leaf volatiles (GLVs) are released into the atmosphere due to the stress, cell damage or wounding. Fog forming over vegetation takes up these compounds, promoting their aqueous-phase oxidation to less volatile compounds. The droplets eventually dry out, leaving behind the secondary organic aerosol (SOA). These pathways are still poorly recognized as potentially novel routes for the formation of atmospheric SOA. Kinetic investigations of GLVs in the gas phase have already been reported by Shalamzari et. al. 2014, Davis et. al. 2011 and many others, while there is no kinetic data on the aqueous phase reactions of selected C6 and C5 GLVs. In the present study, we focussed on the kinetic studies of GLVs with the hydroxyl, sulfate and nitrate radicals as a possible source of aqueous SOA.

Experimental method

The rate constants of reactions of GLVs with atmospherically relevant radicals were studied using a laser flash photolysis-laser long path absorption (LFP-LLPA). Kinetic investigations of GLVs with hydroxyl radicals were performed using competition kinetics, where H₂O₂ (2 × 10⁻⁴ mol L⁻¹) was used as a radical precursor and KSCN (2 × 10⁻⁵ mol L⁻¹) as a reference compound. The method is similar to that introduced by Behar, et al. 1972. Kinetic measurements of sulfate and nitrate radicals with GLVs, were done using a direct flash photolysis method, where sodium persulfate (5 × 10⁻⁴ mol L⁻¹) was the precursor in the generation of SO₄^{•-} and sodium nitrate (1 × 10⁻¹ mol L⁻¹) and sodium sulfate (3 × 10⁻² mol L⁻¹) were the precursor for the generation of nitrate radicals.

Conclusions

In the present study, we explored the kinetics of aqueous-phase reactions of three GLVs- 1-penten-3-ol, cis-2-hexen-1-ol and 2-E-hexenal - with atmospheric radicals SO₄^{•-}, [•]OH and NO₃[•]. The second-order rate constants were determined for a temperature range of 278 K to 318 K. A weak temperature dependence was observed for the aqueous-phase kinetics of all three GLVs with selected atmospherically relevant radicals. To explain the weak temperature dependence of aqueous-phase reaction of GLVs with atmospheric radicals, rate constants were investigated for the diffusion limitation. The atmospheric significance of the aqueous-phase reaction was

evaluated, by calculating aqueous-phase lifetime and their relative rate to the gas phase reactions with respective radicals, which clearly demonstrated their importance above the gas-phase reactions in tropospheric aqueous-phase. The present work is a part of the bigger research project on the aqueous-phase reactions of a series of atmospherically relevant GLVs whereas a next step oxidation products in the aqueous-phase are being investigated at a present stage.

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