

Abstract (in English)

The goal of my Ph.D. research was to assess the role of aqueous-phase reactions of selected green leaf volatiles (GLVs) with atmospheric oxidants leading to the formation of secondary organic aerosol (SOA). The research included: (i) detailed kinetic analysis of 1-penten-3-ol, (*Z*)-2-hexen-1-ol, and (*E*)-2-hexen-1-al reactions with hydroxyl ($\cdot\text{OH}$), sulfate ($\text{SO}_4^{\cdot-}$) and nitrate (NO_3^{\cdot}) radicals in dilute aqueous solutions; (ii) chemical characterization of novel SOA products at the molecular level using high-resolution tandem mass spectrometry in combination with theoretical calculations using quantum-based density functional theory (DFT).

Atmospheric aerosol is a suspension of liquid or solid particles (organic and inorganic) in the air with complex chemical composition and sizes far below 100 μm . It includes primary organic aerosol (POA) emitted directly from various sources (e.g., volcano eruptions) and secondary organic aerosol (SOA), which forms through chemical reactions of organic trace gases combined with physical processes, such as nucleation and condensation. With increasing emissions of anthropogenic pollutants, frequently changing weather patterns, and climate change, the Earth's natural vegetation, such as forests, is permanently exposed to extreme stress conditions. The stress profoundly alters the emission patterns of volatile organic compounds (VOCs), which affect the formation of SOA in the Earth's atmosphere. In the presence of various oxidants, such as ozone (O_3), $\cdot\text{OH}$, and NO_3^{\cdot} radicals, VOCs undergo gas-, aqueous-, and multiphase oxidation, which leads to SOA formation and aging. The limited knowledge of the SOA formation processes leads to a significant underestimation of the global SOA budget and its impact on climate change and health.

To reduce discrepancies between hitherto modeling results and field measurement data, I decided to provide experimental evidence on the potential role of actual plant emissions, known as green leaf volatiles (GLVs), in increasing the SOA burden. GLVs actively participate in the gas- and aqueous-phase atmospheric chemistry, like the key plant volatiles isoprene and monoterpenes. In the last decade, the characterization of the aqueous transformation of GLVs has posed a challenge to atmospheric scientists, as it is a potentially relevant source of SOA loads in the atmosphere.

This Ph.D. thesis unveils the potential of GLVs as the missing source of SOA particles in the atmosphere *via* in-cloud reactions with atmospherically relevant radicals. The first part resolves the kinetics of aqueous-phase reactions of three selected GLVs, i.e., 1-penten-3-ol, (*Z*)-2-hexen-1-ol, and (*E*)-2-hexen-1-al reactions with $\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$ and NO_3^{\cdot} radicals using the technique of laser flash photolysis-laser long path absorption (LFP-LLPA). The rate constants determined for the aqueous-phase reactions of selected GLVs with $\cdot\text{OH}$, $\text{SO}_4^{\cdot-}$, and NO_3^{\cdot} are of the order of 10^9 , 10^8 , and $10^7 \text{ L mol}^{-1} \text{ s}^{-1}$, respectively. The $\cdot\text{OH}$ -driven reactions are partially controlled by diffusion of reactants, while those with $\text{SO}_4^{\cdot-}$, and NO_3^{\cdot} radicals are rather chemically-controlled. The activation energies determined from the temperature variation of the second-order rate constants (278 K to 318 K) reveal GLV differ in rate of reactivity towards various radicals. The expected atmospheric lifetimes of GLV vary from a few seconds to a few days. Generally, GLV may effectively contribute to the formation of SOA.

The rate constants for GLV reactions with NO_3^{\cdot} were determined without accounting for a few reactions that could consume the radical. They included the reactions with $\cdot\text{OH}$, HO_2^{\cdot} , H_2O , and $\text{S}_2\text{O}_8^{2-}$, and the autoxidation of alkyl compounds to ROO^{\cdot} radicals. I developed a complete kinetic model of GLV – NO_3^{\cdot} reactions and analyzed it using the COPASI software package to evaluate the bias in the rate constants determined. The analysis showed that the intrinsic experimental uncertainty for the rate constants determined using the LFP-LLPA procedure was significantly higher than the bias due to the “neglected” reactions. Thus the LFP-LLPA experimental method appeared applicable and robust to determine GLV – NO_3^{\cdot} reaction kinetics.

The second part of my Ph.D. research aimed to explain the chemical mechanisms of aqueous-phase reactions of GLV with $\cdot\text{OH}$ radicals. The oxidation of 1-penten-3-ol, (*Z*)-2-hexen-1-ol, and (*E*)-2-hexen-1-al with $\cdot\text{OH}$ radicals was pursued using the aqueous-phase photoreactor under simulated sunlight conditions. The product analysis targeted carbonyls, alcohols, and carboxylic acids as likely abundant oxidation products. It included the advanced hyphenated mass spectrometry (capillary GC-MS, reversed-phase LC with high resolution MS detection, and MS/MS analyses). The analyses confirmed the presence of various carbonyl products, including propanal, butanal, 1-penten-3-one, (*E/Z*)-2-hexen-1-al, and an unknown product of the formula $\text{C}_6\text{H}_{10}\text{O}_2$. The identified carbonyls, chiefly propanal and butanal are highly important because of their high reactivity with OH , O_3 , and other radicals, leading to peroxy acyl nitrates or carboxylic

acids. The observed highly reactive primary oxidation products can possibly hydrate and further react with other aldehydes and parent GLVs to produce higher molecular weight oligomers. The latter end products may adversely affect air quality and human health in regions where an increased GLVs mixing ratio occurs. The other carbonyl products detected, including $C_6H_{10}O_2$ (possibly hydroxy-hexenal or hydroxy-hexenone), and 1-penten-3-one, may indicate SOA aging in the ambient atmosphere via various pathways; e.g., organosulfates formation.

Using the density functional theory (DFT)-based quantum calculations, I provided more insights into mechanistic pathways of the above investigated reactions of GLVs with $\cdot OH$. An emphasis was given to resolving the addition and hydrogen-abstraction reaction routes and their relative importance. Simple CPCM based continuum solvation model within DFT helped to explain the mechanistic pathways of the formation of experimentally observed reaction products, and identification of all possible mechanistic pathway of unknown product $C_6H_{10}O_2$ formation. Along with suggested activation barrier less fast addition reactions, the results also highlight importance of hydrogen-abstraction route to the formation of experimentally observed products.

The studied aqueous-phase reactions were evaluated for their atmospheric relevance or significance. For this purpose, GLVs atmospheric lifetimes and removal rates were calculated. The results showed that the role of selected GLVs appeared negligible in deliquescent aerosol and haze water. However, it became significant in atmospheric systems of high liquid water contents, such as clouds, rains, and storms. Under such conditions, the atmospheric GLV lifetimes decreased from years or hundred days to a few minutes. The aqueous-phase GLV reactions with $SO_4^{\cdot -}$ radicals dominated over combined gas- and aqueous-phase reactions with $\cdot OH$ or NO_3^{\cdot} in a few given conditions. The reaction of GLVs with $\cdot OH$ radicals dominated over all other oxidants in atmospheric waters, however represents less than 0.1% of the total flux removal by combined gas- and aqueous-phase reactions, indicating required future evaluation of their reaction at the air-water interface than in bulk aqueous phase. In addition, the experimental determination of Henry's constant may further help to improve these results.

A part of my research was an evaluation of the selected physical properties of GLVs. I experimentally obtained the UV spectra of GLV in the aqueous solutions and estimated vapor pressure, solubility, and Henry's constants using the EPI Suite software available from EPA to

evaluate their reactivity in the atmospheric waters. The estimated values indicate GLVs as a compound with moderate solubility and fair partitioning into the aqueous phase.

The work of the thesis presented herein, provides a unique inclusive study of the potential of GLVs as a missing SOA source in the atmosphere via complete understanding of their aqueous chemistry involving physical properties, kinetics, and mechanisms.