Atmospheric significance of the aqueous-phase reactions of Green Leaf Volatiles: 1-penten-3-ol, (Z)-2-hexen-1-ol, and (E)-2-hexen-1-al with atmospheric radicals

Kumar Sarang [†][*], Tobias Otto[§], Krzysztof Rudzinski [†], Irena Grgić[‡], Klara Nestorowicz [†], Hartmut Herrmann[§] and Rafal Szmigielski [†][*]

[†]Environmental Chemistry Group, Institute of Physical Chemistry Polish Academy of Sciences, 01-224 Warsaw, Poland;

[‡]Department of Analytical Chemistry, National Institute of Chemistry, SI-1000, Ljubljana, Slovenia;

[§]Atmospheric Chemistry Department, Leibniz Institute for Tropospheric Research, 04318, Leipzig, Germany.

[*]To whom correspondence should be addressed. Email: ksarang@ichf.edu.pl, ralf@ichf.edu.pl, phone: (+48-22343-3402)

Abstract

The most dominant particulate matter masses in the atmosphere are composed of organic aerosols (OA), of which up to 90% exists as secondary organic aerosol (SOA), the incomplete knowledge of SOA precursors has led to the discrepancies between field measurements, and computer-modeled SOA budget. One such potentially important and missing source of SOA is a class of compounds known as green leaf volatiles (GLVs). GLVs are C6-C5 unsaturated alcohols, aldehydes, or esters, which are released when a plant undergoes stress or mechanical wounding such as cutting, freezing, or drying. The estimated annual global emission of C6 GLVs can alone give rise to 1-5 Tg C/yr SOA, i.e., at least one-third of that isoprene. We investigated the temperature-dependent aqueous-phase kinetics of three GLVs: 1-penten-3-ol, (Z)-2-hexen-1-ol and (E)-2-hexen-1-al with $SO_4^{\bullet-}$ and $^{\bullet}OH$ radicals. The second-order rate constants determined, range from 10^8-10^9 L mol^{-1}s^{-1} for GLV+$SO_4^{\bullet-}$ kinetics and from 10^9 to 10^{10} L mol^{-1}s^{-1} for GLV+$^{\bullet}OH$ kinetics. Various thermodynamic parameters such as activation energy (E_A), molar enthalpy of activation ($\Delta H^{\ddagger}$), molar entropy of activation ($\Delta S^{\ddagger}$), and Gibb's free energy of activation ($\Delta G^{\ddagger}$) were calculated. The activation energies of less than 20 kJ mol^{-1} indicated the weak temperature dependence of the reactions. The second-order rate constants, especially of the order 10^9 L mol^{-1}s^{-1}, are diffusion-controlled, and therefore, we investigated them for the diffusion limitation, and diffusion-corrected rate constants were obtained. To explain the atmospheric significance of these aqueous-phase reactions, we calculated the aqueous-phase lifetime and the relative removal rate of GLVs by the overall gas- and aqueous-phase to the aqueous-phase reactions. The calculations demonstrated the dominance of aqueous-phase reactions of GLVs in cloud and rains waters under certain specific conditions for available radical concentrations.