

Oxidation Kinetics of Terpene-Derived Acids in the Aqueous Phase

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The tropospheric aqueous phase is increasingly getting into focus over the last years to be important for the formation of a relevant fraction of secondary organic aerosol (SOA), addressed as aqueous secondary aerosol (aqSOA). A principal fraction of SOA originated from the oxidation of emitted biogenic volatile organic compounds, such as terpenes, is formed in the gas phase. Nevertheless, the majority of aqueous-phase processes of water-soluble terpene-derived oxidation are still insufficiently studied.

In the present laboratory study, the aqueous-phase kinetics of the radical-driven oxidation reactions of *cis*-pinonic acid (CPA) and (+)-camphoric acid (+CA) by hydroxyl (OH), nitrate (NO₃) and sulfate (SO₄⁻) radicals were investigated. CPA is major products of the gas-phase oxidation of α-pinene while +CA can be seen as a surrogate for terpene-derived diprotic carboxylic acids. Both acids are well water soluble due to their functionalization ($H^{CP}_{estimated}(CPA) = 7.63 \times 10^7 \text{ mol L}^{-1} \text{ atm}^{-1}$ and $H^{CP}_{estimated}(+CA) = 1.12 \times 10^6 \text{ mol L}^{-1} \text{ atm}^{-1}$).

The kinetic measurements were performed applying a laser flash photolysis – laser long path absorption setup (LFP-LLPA) to determine temperature and pH dependent reaction rate constants for the reactions of *cis*-pinonic acid and (+)-camphoric acid with OH, NO₃ and SO₄⁻ radicals. The determined OH second order rate constants are in the range of $10^9 \text{ mol L}^{-1} \text{ s}^{-1}$ and the SO₄⁻ second order rate constants in the range of $10^7 \text{ mol L}^{-1} \text{ s}^{-1}$.

Aqueous-Phase lifetimes were derived from the obtained results to examine their relevance for tropospheric conditions. In addition, the results can be used to determine the contribution to aqueous sink and source processes of terpene-derived SOA, which is not yet accounted in literature.