Aqueous-Phase Oxidation Kinetics of Terpene-Derived Acids

T. Otto, T. Schaefer, H. Herrmann
Leibniz Institute for Tropospheric Research (TROPOS), Atmospheric Chemistry Department (ACD), Permoserstrasse 15, 04318 Leipzig

Abstract

Over the last years, the tropospheric aqueous phase is increasingly getting into focus to be a relevant source of secondary organic aerosol (SOA), addressed as aqueous secondary organic aerosol (aqSOA). Terpenes are recognized to be the origin of compounds in the gas phase that can further act as SOA precursors, due to gas-phase oxidation processes resulting in oxygenated volatile organic compounds and even semi-volatiles with an enhanced water solubility. However, these formed terpene-derived oxidation products are rarely investigated concerning their possibly ongoing aqueous-phase processes (potential to produce aqSOA).

Aqueous-phase kinetics of the reactions of *cis*-pinonic acid (CPA) and (+)-camphoric acid (+CA) with hydroxyl (OH), nitrate (NO_3) and sulfate (SO_4^-) radicals were investigated in the present laboratory study. CPA is a product of the gas-phase processing of α-pinene while +CA is investigated as a model compound for dibasic carboxylic acids derived from terpene oxidation processes. Kinetic measurements were performed applying a laser flash photolysis – laser long path absorption setup (LFP-LLPA) to determine temperature and pH dependent second order reaction rate constants. For the OH reactions the obtained second order rate constants are in the range of 10^9 mol L^{-1} s^{-1} and for SO_4^- in the range of 10^7 mol L^{-1} s^{-1}. The nitrate second order rate constants are in the range of 10^5 mol L^{-1} s^{-1} to 10^8 mol L^{-1} s^{-1}, depending on the pH.
The derived second order rate constants together with modeled atmospheric steady-state concentrations of the radicals were used to calculate aqueous-phase lifetimes with the aim to assess their relevance under tropospheric conditions.