Photolysis of cis-pinonic acid particles at the single-particle scale

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At the global scale, biogenic volatile organic compounds (BVOCs) are predominantly emitted by vegetation (e.g., monoterpenes such as α- and β-pinene) and lead to the formation of biogenic secondary organic aerosols (BSOAs), which are estimated to account for 30–50% of the global organic aerosol budget1. Once formed, BSOAs can undergo further transformations through multiphase aging processes. These reactions modify both the chemical composition and physico-chemical properties of aerosols, such as hygroscopicity, viscosity, and gas–particle partitioning, thereby influencing their atmospheric fate, air quality, and climate impacts. Cis-pinonic acid (CPA) is a key compound in the formation of biogenic secondary organic aerosols originating from the photo-oxidation of α-pinene2,3. Owing to its low vapor pressure (~7 × 10^{-5} Pa) and its Henry's law constant, the CPA, in the atmosphere, can be presence both in the gas phase and in particle. Despite the proven role of CPA in SOA formation and aging, unknowledges gaps remain regarding the photo-oxidative mechanisms involved. The few mechanisms proposed so far are mainly based on studies conducted in bulk aqueous solutions or flow reactors4,5. Investigations at the single-particle scale are still lacking, even though it is known that reactivity in bulk systems can differ from that at the gas–particle interface due to effects related to particle curvature and exchange surface area. At the single-particle level, levitation techniques provide unique advantages for studying aerosol physico-chemical properties and processes, notably by eliminating substrate-induced artifacts and while controlling environmental parameters (e.g. temperature and relative humidity)6. In this context, the present study aims to elucidate the photo-oxidative aging mechanisms of CPA particles, used as a model for BSOAs generated from α-pinene photo-oxidation, in order to improve our understanding of the atmospheric fate and impact of BSOAs.

To achieve these objectives, an original experimental set up coupling acoustic levitation with high-resolution proton-transfer-reaction time-of-flight mass spectrometry (PTR-TOF-MS) was developed. This approach enables real-time observation of volatile compound exchanges between a single particle and the surrounding gas phase during physico-chemical processes. Comparison between bulk and single-particle experiments reveals the emission of methyl vinyl ketone from the particle, produced via a Norrish type II pathway during CPA photolysis. This innovative methodology opens new perspectives for investigating dynamic gas–particle exchanges at the single-particle scale and for a more comprehensive understanding of atmospheric aerosol aging mechanisms.

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