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Ozonolysis of unsaturated BVOCs in the presence of SO_2: formation of Stabilised Criegee Intermediates, their reactivity and role in the particle formation

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Biogenic volatile organic compounds (BVOCs), including monoterpenes, are one of the most abundant chemical group in the troposphere having major influences on air quality, climate and human health through chemical oxidation processes and secondary organic aerosol (SOA) formation.

It is now established that gas-phase ozonolysis of monoterpenes leads to the formation of Stabilized Criegee Intermediates (SCIs) which can act as atmospheric oxidant for trace gases and lead to the formation of sulfate aerosols. However, the fate of these biradical species remains uncertain and need further investigation.

Here we present the results of the first set of experiments which are a part of the COGNAC project (Chemistry of Organic biradicals: GeNesis of AtmospheriC aerosols). We have investigated the gas-phase ozonolysis of several BVOCs, including isoprene, a-pinene and limonene, in the presence or absence of SO_2, in order to explore the fate of different SCIs. Experiments were performed in HELIOS simulation chamber, a large 90m3 Teflon chamber (S/V = 1.2 m-1), using different analytical instruments for the chemical and physical characterization of the gaseous and particulate species: an in-situ FTIR for monitoring organic and inorganic infra-red absorbing species (optical length = 302.6 m) including SF6 for the calculation of the dilution rate, a PTR-ToF-MS 8000 (Ionicon Analytik Gmbh) for the gas-phase detection of the reacting monoterpenes and products, a Figaero-ToF-CIMS (Aerodyne Research) in H3O+ and acetate mode, allowing the detection of both gas and particulate phases, a chemical ionisation mass spectrometer (CIMS) for the detection of hydroxyl and peroxy radical species and sulfuric acid, and a ATD-GC-MS (Thermo Fisher Scientific). Measurements of ancillary data (particle size distribution and mass concentration, O_3, CO, SO_2 and HCHO concentrations) were also conducted using a set of online monitors.

Kinetic rate constants of a-pinene, limonene and isoprene ozonolysis have been determined using an absolute method ((1.28±0.04) × 10˘16, 2.02× 10˘17, 2.25 × 10ˆ-16 cm3.molecule-1.s-1, respectively). Since H2SO4 can be formed by the reaction between SCIs and SO_2 (and by the reaction between SO_2 and OH, if present), its concentration given by CIMS can therefore be used as a proxy for SCIs detection in this study. The Figaero-ToF-CIMS shows a significant response up to m/z 417 in the particulate phase. Analysis of the observed high-resolution mass spectra have been used for mass assignment. This set of experiments is a preliminary study for a better understanding of SCIs formation, reactivity and fate, and the reaction mechanism of monoterpene ozonolysis in the presence of SO_2.