

Abstract in English of the doctoral dissertation entitled

Kinetics and product's yield of mono and sesquiterpenes secondary organic aerosol (SOA) components in the aqueous phase reactions with ozone and OH radicals

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Abstract

The first step of this work was the construction of the flow reactor which used to generate SOA by the gas-phase ozonolysis of limonene (lim_{SOA}). The generation of lim_{SOA} was performed under precisely controlled conditions (RH, temperature, pressure as well as concentrations of the ozone and the precursor). Precursor concentration of limonene inside the flow reactor was monitored off-line with GC/FID. In the flow reactor, it was possible to generate 20 limonene oxidation products since a separate synthesis and purification of each of these compounds would be very complicated and time-consuming.

Afterward, the lim_{SOA} produced in the flow reactor were extracted into a buffered water solution and oxidized by OH and O_3 under different pH conditions. Since the atmosphere contains a large amount of liquid water, this work allows to provide detailed insights into the kinetics of lim_{SOA} aging in clouds, fogs, and wet aerosols. Lim_{SOA} oxidation by OH and O_3 were investigated using LC-ESI/MS/MS.

The second step of this work was the investigation of kinetics, mechanisms and the yield of the products resulting from the ozonolysis of LA and BCA in the aqueous phase. Initially, LA and BCA were synthesized and purified by semi-preparative liquid chromatography since these acids are not commercially available. Obtained results indicate that k_{ozone} for the reaction of ozone with BCA was higher than those for the reaction of ozone with LA under both acidic and basic conditions most likely due to the cyclobutyl ring strain in the BCA molecule.

Subsequently, the molar yields of BCA and LA ozonolysis products were quantified. LC/MS as well as UV-Vis spectroscopy for analyzing formaldehyde and hydroperoxides were used. The data acquired with LC coupled to the ultrahigh-resolution MS indicated that the terminal C=C bond in LA and BCA was converted into C=O moiety forming a keto-LA and keto-BCA as products. As inferred from the data acquired, products of LA and BCA have similar molar yields which indicated that these acids react with ozone in a similar way. It was proposed that H_2O_2 and formaldehyde are formed by the

decomposition of stabilized Criegee intermediate (SCI) as a result of its reaction with water. Moreover, the molar yields of peroxides, formaldehyde, and keto-acids, along with the experimental data acquired are strongly indicated that the branching ratios of the primary ozonides (POZs) or both acids (LA and BCA) were nearly identical.

The third step was the investigation of kinetics and mechanism of the aqueous-phase oxidation of BCA by hydroxyl radicals. The obtained results indicate that k_{OH} of BCA exceeds the diffusion limit for the aqueous-phase oxidation of organic compounds by OH.

Since OH reacts unselectively with organic compounds, a number of products were identified by ultrahigh-resolution MS resulting from OH reaction with BCA. Three generation of products were found. First-generation products that were identified are keto-BCA and hydroxyl-hydroperoxy BCA. These two molecules were following OH addition to the terminal C=C bond of the precursor. The rest of the products were identified as second and third-generation products which are oxygenated BCA derivatives with O:C ratios higher than the precursor although some fragmentation of the original carbon backbone was also observed. The first-generation products are mainly generated via the decomposition of tetroxides forming for pathways which in turn produced the first-generation products. The second-generation products are produced by the cyclobutene ring-opening or via the further oxidation of the first-generation products. The third-generation product was identified as highly oxidized products with two carboxylic moieties resulting from the conversion of second-generation product. Thus, the data acquired provided detailed insights into the mechanism of BCA + OH reaction.