

Warsaw, 05.05.2020 r.

Abstract in English of the doctoral dissertation entitled:
„Physicochemical studies of α -pinene oxidation products in aspect of atmospheric secondary organic aerosol”

Author of the dissertation: **Agata Kołodziejczyk**

Supervisor of the dissertation: **prof. Rafał Szmigielski**

Abstract

The Earth's atmosphere is a chemical mixture with complicated and variable composition. Each year about 2,000 Tg (1 Tg = 10⁹ kg) of organic compounds and about 300 Tg of particulates (aerosols) are emitted to the atmosphere. Organic compounds enter the atmosphere directly from natural sources (e.g. volcanic eruptions) and/or anthropogenic (e.g. processes of burning fossil fuels and biomass). On a global scale, the presence of aerosol particles has an impact on the Earth's energy balance and thus contributes to its climate change (global impact), as well as on human's health and life.¹

Secondary organic aerosol (SOA) is a significant fraction of aerosol (20-90%). It forms in the atmosphere through complex chemical reactions in which the substrates are volatile organic compounds (precursors), including isoprene, monoterpenes and sesquiterpenes. For many years, research on the main transformation pathways of these precursors, as well as the chemical composition and physicochemical properties of the resulting SOA have been intensively studied in many laboratories. However, even despite these efforts, it is estimated that only a small portion (approx. <5%) of the aerosol components have been reliably identified.²

Current knowledge does not provide complete data on the characterization of terpene oxidation products, including α -pinene. Therefore, in order to expand the knowledge about an important SOA components, I decided to carry out a series of studies aimed at determining the physical and chemical parameters of the main α -pinene SOA components including *cis*-pinic, *cis*-pinonic, *cis*-norpinic and *cis*-norpinonic, terebic acid, which are products of the early stage of α -pinene oxidation, as well as diaterpenylic acid acetate (DTAA) and 3-methyl-1,2,3-butane-ticarboxylic acid (MBTCA), which are products of further stage of α -pinene oxidation. These compounds are of great interest to atmospheric chemistry scientists because they are valuable markers for aerosol sources and indicators of its growth and transformation processes (i.e. aging).

The purpose of this dissertation was to provide a set of the physical and chemical parameters, as well as reactivity of selected α -pinene SOA components using various research tools, including aerosol chambers, mass spectrometry techniques and quantum chemical calculations.

Research in this dissertation included (i) improved synthesis of selected model compounds, (ii) examining the impact of relative humidity on the formation of α -pinene SOA in reaction of α -pinene with OH radicals (photooxidation processes) and ozone (ozonolysis processes) in LEAK chamber (iii) examining the behavior of ultra-fine aerosol particles derived from MBTCA, terebic and *cis*-norpinic acid in photooxidation processes in the FORTH aerosol chamber. (iv) determination of water solubility parameters and constant acidity of the studied α -pinene oxidation products (v) determination of fragmentation products and energy of decay of *cis*-norpinonic acid, as well as - reactivity of its fragments in reaction with simple atmospheric reagents (CO₂, CS₂, CH₃SSCH₃, CH₃SCN, CH₂Cl₂, CHCl₃, CHBr₃) using mass spectrometry techniques and calculation methods.

The synthetic methods used as part of the doctoral dissertation have enabled to obtain the investigated compounds with good efficiency and purity. The structures and purity of these compounds were confirmed by spectral and spectrometric data (NMR, IR and MS).

The results of experiments in the LEAK aerosol chamber showed that relative humidity does not affect the SOA yield in the reaction of α -pinene with OH radicals, while with ozone - the SOA yield clearly increases with increasing humidity. In addition, during chamber experiments, I described a number of products formed in the gas phase using the PTR-ToF-MS technique. Then, I conducted a quantitative analysis of the composition of the aerosol phase collected after each of the experiments. This analysis confirmed that all compounds selected for testing are oxidation products of α -pinene. Of all the compounds analyzed, *cis*-pinonic and *cis*-norpinonic acids dominated - as reaction products of α -pinene with OH and/or ozone radicals. In addition, obtained results confirmed that the shares of terebic, *cis*-pinic, MBTCA and *cis*-norpinic acid in the mass of SOA increased with the increase in relative humidity of the α -pinene oxidation process using OH radicals.

In the next part of the research, I determined several important physicochemical parameters of the ultra-fine aerosol derived from MBTCA, terebic and *cis*-norpinic acids, including volatility, density, enthalpy of evaporation and saturation concentration. The results showed that the saturation concentration at 298 K is $(1.76 \pm 1.3) \times 10^{-3} \mu\text{g}/\text{m}^3$ (MBTCA), $35 \pm 1.3 \mu\text{g}/\text{m}^3$ (terebic acid) and $40 \pm 10.3 \mu\text{g}/\text{m}^3$ (*cis*-norpinic acid, respectively). The low MBTCA value places this compound in a group of compounds with extremely reduced volatility. In contrast, the values obtained for the other acids allow them to be assigned to the group of semivolatile, which means that, these acids can be present in the atmosphere both in the particle and gas phase. In addition, in my research I measured for the first time the reference mass spectra of AMS for these acids, and additionally - for diaterpenylic acid acetate. Mass signal analysis showed that m/z 141 corresponding mainly to the composition of C₇O₃H₉⁺ can be used as the diagnostic ion MBTCA in AMS aerosol measurements. I received interesting results in the study of MBTCA reaction with OH radicals. Under these conditions, this compound was mainly fragmented, while until now it was considered a thermodynamically stable marker of α -pinene aerosol. I received a different result in the photooxidation reaction of terebic acid aerosol particles: the aerosol mass [$\mu\text{g}/\text{m}^3$] dropped rapidly after the start of the reaction at the constant value

of the O:C and H:C ratios during the experiment, which suggests that this acid is a volatile compound, and it quickly evaporates from the aerosol phase to the gas phase.

An important point of work was also the determination of the solubility parameters of the tested compounds in water. In addition, during this part I examined a number of physical parameters, such as: acidity constants, glass transition temperatures, melting points, as well as heat and enthalpy of melting. Physical and chemical studies on the solubility of α -pinene SOA components have shown that the solubility of the tested compounds in water varies in the series: *cis*-pinic acid > *cis*-norpinic acid > \geq DTAA \geq MBTCA > *cis*-pinonic acid > *cis*-norpinonic acid > terebic acid. Analysis of the results also showed no correlation between the solubility of the compounds tested and their increasing O:C ratio. For *cis*-norpinonic and *cis*-pinonic acids, I determined water solubility parameters depending on the pH of the solution. The results showed that the solubility

of the tested compounds increases with increasing pH of the solution. The measured acidity constant of the investigated compounds ranged from 3.7 for terebic acid to 6.63 for MBTCA.

In the last part of the work I described the results of fragmentation products of the *cis*-norpinonic acid and its potential reactions with simple atmospheric reagents. As part of this project, I described possible *cis*-norpinonic acid fragmentation processes and determined the energy of these decays using tandem mass spectrometry techniques and quantum chemical calculations. I also examined the reactivity of the fragments obtained by conducting simulation reactions in the environment of a specially modified Q-ToF mass spectrometer. In these experiments, I introduced selected volatile reagents directly into the collision cell of the spectrometer. I showed that the degradation products of norpinonic acid are reactive and undergo secondary reactions with selected reagents, which has led to a number of new products. These results showed that the chemical compounds present in the aerosol particles can undergo fragmentation, leading to the formation of low-molecular secondary products, and these products can further react with other air pollutants. The latter processes can be one of the ways of functionalizing the aerosol composition.

To sum up, in my work I have determined a number of interesting physical and chemical parameters of seven α -pinene oxidation products and examined their potential reactivity in the lower layers of the atmosphere. During the research, I used various research tools, including aerosol chambers, mass spectrometry, quantum chemical calculations and organic synthesis.

A detailed description of the physical and chemical parameters of the tested compounds and their possible transformation paths is the key to a fundamental understanding of the processes of secondary organic atmospheric aerosol formation and its impact on human health and quality of life. The collected results also allow to broaden the base of input parameters of known atmospheric models.

1. Hallquist, M., *et al.*, The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos. Chem. Phys.* **2009**, 9 (14), 5155-5236.

2. Seinfeld, J. H. *et al.*, *Atmos. Chem. Phys.*, - *From Air Pollution to Climate Change*. John Wiley & Sons: **2006**.