Atmospheric Environment xxx (2015) 1–7

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

A detailed MS^n study for the molecular identification of a dimer formed from oxidation of pinene

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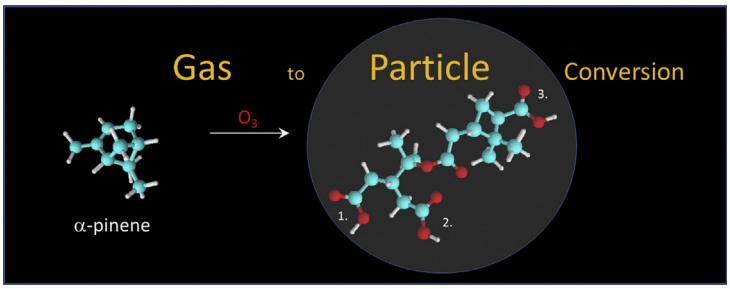
HIGHLIGHTS

- A two step approach is used for the molecular identification of biogenic SOA dimers.
- A functional group derivatization method is applied to quantify carboxylic acid groups.
- Cationization reagents enable multiple fragmentation of the target molecule.
- MS^n (n = 7) spectra of the derivatized product have been recorded and interpreted.
- The target dimer likely contains a terpenylic acid and a pinic acid building block.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 9 July 2015
Received in revised form
2 September 2015
Accepted 2 September 2015
Available online xxx

Keywords:
Natural aerosol formation
Biogenic secondary organic aerosol (BSOA)
Product studies
Structure elucidation
High molecular weight compounds
Mass spectrometry
Functional group derivatization
MS/MS

ABSTRACT

Dimeric products formed in the oxidation of α- and β-pinene have been frequently observed in laboratory and field studies of biogenic SOA formation. While their existence is undoubted, their exact chemical structures remain unclear. This study uses a combined two step approach aiming on the molecular identification of the most important of the various dimers that have been observed in biogenic secondary organic aerosol formation, a dimer with the molecular weight 358 g mol^{-1}. The first step is the application of a functional group derivatization technique (esterification) to quantify the number of carboxylic acid groups in the target molecule. Based on the detailed interpretation of the MS^n spectra (up to n = 7) of the derivatized product further information about the exact structure of the compound of interest is compiled. To increase the intensity of precursor ions for the MS^n-studies and especially to facilitate successive fragmentation of the target molecule, which yields structurally informative product spectra, cationization reagents (Li^+, NH_4^+) are introduced. The results clearly point to the formation of a dimer containing three carboxylic acid groups and a structure containing a terpenylic acid building block and a pinic acid building block, strongly supporting a structure suggestion by Claeys and coworkers (Yasmeen et al., 2010).

1. Introduction

The formation of higher-molecular weight products from the oxidation of biogenic VOCs (volatile organic compounds) is an important aspect of SOA formation and is intensively discussed

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http://dx.doi.org/10.1016/j.atmosenv.2015.09.012
1352-2310/

during the last few years. The main motivation is their drastically decreased vapor pressure, which is highly relevant for gas/particle partitioning as well the formation and growth of new particles in the atmosphere (Kroll and Seinfeld, 2008; Boy et al., 2004; Claeys et al., 2009; Yasmeen et al., 2010). One recently discovered pathway to form higher molecular weight products is the introduction of multiple oxygen atoms into the products, thus the formation of highly oxidized multifunctional products (HOMs) (Ehn et al., 2014, 2012; Mentel et al., 2015). Another pathway that leads to higher molecular weight products is oligomerisation of primary products (either radicals or closed shell molecules), in which the monomeric units preserve the carbon skeleton (or a fraction of it) of the precursor VOC (Hallquist et al., 2009). Obviously the first and most important step of oligomerization is the dimerization reaction. Although the first observation of such dimers in the α-pinene oxidation system is more than a decade ago (Hoffmann et al., 1998), their exact chemical structures and thus the formation pathways as well as the question whether SOA dimers are formed in the gas or condensed phase remain unanswered. One reason for this lack of understanding is the fact that SOA precursors typically produce a large range of oxidation products, resulting in a considerable number of possible reaction pathways and chemical functionalities. This is especially true for oligomerization reactions since cross reactions of different monomeric building blocks have to be considered (Hallquist et al., 2009). One subgroup of possible dimeric products are hydrogen-bonded dimers of organic acids, which are likely to exist in the particle phase and may also be involved in the early steps of new particle formation processes (Hoffmann et al., 1998; Claeys et al., 2009; DePalma et al., 2013). However, since several BSOA dimers have been shown to sustain ultrasonification in methanolic/aqueous solutions, which is very unlikely for non-covalently bonded oligomers, also covalently bonded dimers must exist (Reinnig et al., 2008; Mueller et al., 2009). One group of potential covalently bounded dimeric compounds are peroxidic products, such as oligoperoxides, peroxyhemiacetals or alkoxyhydroperoxides (Rissanen et al., 2014; Ziemann, 2002, 2003; Sadezky et al., 2008; Docherty et al., 2005). Also carbonyl chemistry (acetal formation/aldol condensation) has been suggested to be responsible for larger organic molecules from α-pinene oxidation (Gao et al., 2004; Iinuma et al., 2004). Another possible subgroup of oligomeric products contains esters, which are often suggested to be formed in large amounts in laboratory studies of SOA formation (Mueller et al., 2008; Hallquist et al., 2009 Kourtchev et al., 2014). Classical esterification reactions between an alcohol moiety and a carboxylic acid group could be a pathway for ester formation (Surratt et al., 2006; Szmigielski et al., 2007).

Most of the research on SOA dimers formed from biogenic VOC oxidation has been performed on dimers from α-pinene oxidation due to the high quantity in which this monoterpene is emitted into the atmosphere. Various dimeric products have been observed, but most of the work has been done on a dimeric compound with the molecular mass 358 g mol^{-1}. Several different formation pathways and chemical structures are suggested in the literature (Mueller et al., 2009; Yasmeen et al., 2010).

Structures A and B in Fig. 1, as suggested by Hoffmann and coworkers (Mueller et al., 2009), both contain a peroxy functional group. Claeys and coworkers proposed structure C for the dimer (Yasmeen et al., 2010), which is a simple ester. One option to unambiguously identify the α-pinene dimer 358 would be the chemical synthesis of reference compounds, e.g., those shown in Fig. 1. Unfortunately a traditional synthesis of structures A and B is almost impossible. Likewise structure C could only be synthesized by a time-consuming multistep synthesis. Other structure elucidation techniques, such as NMR and IR, cannot be easily utilized since the product samples are not only complex multicomponent product mixtures but the target analyte is present only in trace amounts. However, a significant difference between structures A/B and structure C is the different number of carboxylic acid groups. Therefore, it should be possible to verify the structure suggestions shown above by the application of a functional group specific derivatization technique (Elgstoen, 2008). The purpose of this work is to supply further evidence for the exact molecular structure and chemical functionality of high molecular weight compounds in biogenic VOC oxidation systems by applying a detailed mass spectrometric study combined with a specific derivatization step.

2. Materials and methods (experimental)

Filter samples from a typical ozonolysis experiment of α-pinene in the atmospheric simulation chamber of Mainz were used. The chamber and experimental settings are similar to those described by Reinnig et al., 2008. The samples were collected on PTFE-coated fiber filters (45 mm PALLFLEX, Pall Life Science, USA). Additional blank filters were also investigated in order to exclude potential contaminations. The filter samples were split into two halves. One half was extracted three times for about 30 min with 2 mL of a methanol/water solution (1:10) by ultrasonification. The extracts were filtered (Sartorius Minisart SRP4, PTFE membrane, 0.45 μm) and unified. The remaining solution was reduced to dryness under a gentle stream of nitrogen and mild heating (60 °C).

The derivatization was performed, similar to the procedure of Elgstoen (Elgstoen, 2008). One milliliter of a 10% acetyl chloride solution in butanol was added aiming on the conversion of all carboxylic acid groups to the corresponding butyl esters (see Scheme 1). In principle the reaction operates for most of the smaller, none-aromatic alcohols. The sample was heated several minutes and then again reduced to dryness. The residue was dissolved in water/methanol 1:1. A second series of experiments were performed with the same kind of samples. The only difference for this second series was that the residues were dissolved in water/methanol solutions containing small amounts of LiBr or NH_4Cl. The motivation for the addition of these cations will be explained below. All solutions were measured via direct-infusion-ESI-IT-MS^n (Bruker Daltonics HCT-Plus).

As already mentioned above, the suggested dimer structures A and B have only two carboxylic acid groups, whereas C possesses three groups. The derivatization by butylation as described above should therefore result in an increasing molecular mass of 56 g mol^{-1} per carboxylic acid group. Consequently, the resulting molecular weight after derivatization would be 470 g mol^{-1} and 526 g mol^{-1} for two and three carboxylic acids groups, respectively, and the expected masses in the mass spectrum in the positive ion mode the protonated molecular ions $[M + H]^+$ *m/z* 471 and *m/z* 527, although possible Na^+-, Li^+- and NH_4^+-adducts have to be taken into account, which are the most common adducts in ESI-MS experiments. The use of an ion trap-MS provides the opportunity to perform MS^n experiments. The MS-parameters are controlled via the software esquireControl from Bruker Daltonik. The ion source was set to following main parameters: dry temperature 350 °C, dry gas 5.0 L/min, nebulizer 20.0 psi and high voltage capillary 5000 V. The MS^n parameters are mostly pre-defined by the software. One of the adjustable parameter is the “Fragmentation Amplitude”, which was set manually to one Volt for all MS^n experiments.

3. Results

3.1. Determination of the number of carboxylic acid groups

When the extracted filter samples were analyzed, which were

Please cite this article in press as: Beck, M., Hoffmann, T., A detailed MS^n study for the molecular identification of a dimer formed from oxidation of pinene, Atmospheric Environment (2015), http://dx.doi.org/10.1016/j.atmosenv.2015.09.012