



Composition and
clustering of
 α -pinene oxidation
products

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Elemental composition and clustering of α -pinene oxidation products for different oxidation conditions

A. P. Praplan¹, S. Schobesberger¹, F. Bianchi^{2,3}, M. P. Rissanen¹, M. Ehn¹, T. Jokinen¹, H. Junninen¹, A. Adamov¹, A. Amorim⁴, J. Dommen², J. Duplissy⁵, J. Hakala¹, A. Hansel^{6,7}, M. Heinritzi^{8,6}, J. Kangasluoma¹, J. Kirkby^{9,8}, M. Krapf², A. Kürten⁸, K. Lehtipalo¹, F. Riccobono², L. Rondo⁸, N. Sarnela¹, M. Simon⁸, A. Tomé⁴, J. Tröstl², P. M. Winkler¹⁰, C. Williamson⁸, P. Ye¹¹, J. Curtius⁸, U. Baltensperger², N. M. Donahue¹¹, M. Kulmala^{1,5}, and D. R. Worsnop^{1,12}

¹Department of Physics, P.O. Box 64, 00014 University of Helsinki, Finland

²Laboratory of Atmospheric Chemistry, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

³Institute for Atmospheric and Climate Science, ETH Zurich, 8092 Zurich, Switzerland

⁴Laboratory for Systems, Instrumentation, and Modeling in Science and Technology for Space and the Environment (SIM), University of Lisbon and University of Beira Interior, 1749-016 Lisbon, Portugal

⁵Helsinki Institute of Physics, University of Helsinki, Helsinki, Finland

⁶University of Innsbruck, Institute for Ion Physics and Applied Physics, Technikerstrasse 25, 6020 Innsbruck, Austria

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⁷ Ionicon Analytik, Eduard Bodem-Gasse 3, 6020 Innsbruck, Austria

⁸ Institute for Atmospheric and Environmental Sciences, Goethe University Frankfurt am Main, Altenhöferallee 1, 60438 Frankfurt am Main, Germany

⁹ CERN, CH1211, Geneva, Switzerland

¹⁰ Faculty of Physics, University of Vienna, Boltzmanngasse 5, 1090 Wien, Austria

¹¹ Center for Atmospheric Particle Studies, Carnegie Mellon University, 5000 Forbes Ave, Pittsburgh, PA 15213, USA

¹² Aerodyne Research Incorporated, Billerica, MA 01821, USA

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Correspondence to: A. P. Praplan (arnaud.praplan@gmail.com)

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This study presents the difference between oxidised organic compounds formed by α -pinene ozonolysis and hydroxyl radical (OH) oxidation in the CLOUD environmental chamber. The results from three Atmospheric Pressure interface Time-Of-Flight (APi-TOF) mass spectrometers measuring simultaneously the composition of naturally charged, as well as neutral species (via chemical ionisation with nitrate) are discussed. Natural chemical ionisation takes place in the CLOUD chamber and organic oxidised compounds form clusters with nitrate, bisulphate, bisulphate/sulphuric acid clusters, ammonium, and dimethylammonium, or get protonated. This process is selective towards various oxidised organic compounds, so that in order to get a comprehensive picture of the elemental composition of oxidation products, several instruments must be used. A comparison between oxidation products containing 10 and 20 carbon atoms is presented. Oxidation products from ozonolysis showed a higher oxidation state than the ones from OH oxidation. Also, highly oxidised organic compounds are shown to be formed in the early stages of the oxidation, for low α -pinene levels.

1 Introduction

Oxidation reactions of organic vapours in the atmosphere and the subsequent condensation of their products is a source of secondary organic aerosol (SOA, see e.g. Kanakidou et al., 2005; Fuzzi et al., 2006; Hallquist et al., 2009 and references therein). Because of the vast number of different compounds in the atmosphere, with various structures and functionalities, detailed oxidation mechanisms are usually insufficiently understood and poorly represented in atmospheric chemical models, especially for larger and complex molecules (Goldstein and Galbally, 2007; Kroll and Seinfeld, 2008). Traditionally, oxidised organic compounds have been considered condensing on small pre-existing particles (few nanometres in diameter) to make them grow up to cloud condensation nuclei sizes (larger than 50 to 100 nm diameter). In general, the more oxi-

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dised these products, the lower is their volatility and therefore can condense on smaller particles (Pankow, 1994; Seinfeld and Pankow, 2003; Donahue et al., 2006). However, new studies have shown that α -pinene oxidation products (and organic oxidised compounds in general) do not only participate in particle growth, but also directly influence particle formation rates (Riccobono et al., 2012; Kulmala et al., 2013). It has been shown that sulfuric acid form clusters, which are stabilised by oxidised organic compounds participating directly in the nucleation process (Metzger et al., 2010; Riccobono et al., 2014). Other compounds such as ammonia (Kirkby et al., 2011; Schobesberger et al., 2014) or amines (Almeida et al., 2013; Kürten et al., 2014) can promote sulfuric acid nucleation as well due to an efficient acid-base stabilization mechanism.

Monoterpenes ($C_{10}H_{16}$) are a family of biogenic volatile organic compounds. In boreal forests α -pinene is the most abundant monoterpene. It has been extensively studied in laboratory experiments during the past decades due to its large SOA formation potential (Hoppel et al., 2001; Lee and Kamens, 2005; Eddingsaas et al., 2012a). Two oxidation pathways are known (see Fig. 1):

- Ozonolysis, in which ozone (O_3) reacts with the α -pinene double bond, forming a primary ozonide, which will decompose in Criegee intermediates (Ma et al., 2008; Novelli et al., 2014). These can form carboxylic acids (via rearrangement of dioxiranes) or vinylhydroperoxides that, upon hydroxyl radical (OH) loss, lead to carbonyl compounds.
- OH oxidation, in which the radical adds to the α -pinene double bond (or abstracts an hydrogen atom from α -pinene) resulting in the formation of an alkyl radical. This radical reacts immediately under atmospheric conditions with molecular oxygen (O_2) forming a peroxy radical (RO_2). This peroxy radical can react with various species including other peroxy radicals.

This figure is discussed more extensively in Sect. 3.3. Both gas phase and particulate α -pinene oxidation products were investigated and more detailed chemical analysis became available as analytical methods progressed (Hatakeyama et al., 1989; Ka-

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mens et al., 1999; Claeys et al., 2009; Eddingsaas et al., 2012a, b; Winkler et al., 2012). Products such as the dicarboxylic acid *cis*-pinic acid ($C_9H_{14}O_4$, Christoffersen et al., 1998), the tricarboxylic acid 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA, $C_8H_{12}O_6$, Szmigielski et al., 2007) and oligomeric compounds (Tolocka et al., 2004; Müller et al., 2009) were identified. Ehn et al. (2012, 2014) and Schobesberger et al. (2013) have recently observed highly oxidised multifunctional organic compounds (i. e. extremely low volatility organic compounds (ELVOCs), already predicted by Kulmala et al., 1998) in laboratory experiments and in Hyytiälä, Finland, with oxygen-to-carbon ratios (O : C) larger than 1. The more oxidised the compounds the lower their volatility and hence their contribution to SOA (Donahue et al., 2011). As an alternative to O : C, Kroll et al. (2011) use the average oxidation state of carbon \overline{OS}_C as a metric for the degree of oxidation of atmospheric organic compounds. It can be estimated by $\overline{OS}_C \approx 2(O : C) - H : C$.

As the formation of newly observed compounds from field studies or from laboratory experiments could not be explained with “traditional” atmospheric chemistry (Atkinson, 2000), new suggestions for mechanisms have been published. Intramolecular reactions seem to play an especially important role in the formation of highly oxidised compounds (Peeters et al., 2001; Vereecken and Peeters, 2004; Ma et al., 2008; Ehn et al., 2014). However, current atmospheric chemical models include only few such non-traditional oxidation mechanisms (e.g. intramolecular reactions).

Building on this knowledge, experiments have been conducted within the CLOUD project at CERN to investigate the formation of new particles from organic vapours under various oxidation regimes (ozone and hydroxyl radical oxidation). The CLOUD chamber (described in more detail in the next section) has extremely low background contamination levels, and therefore provides excellent conditions for unperturbed nucleation experiments (Schnitzhofer et al., 2014). Additionally, CLOUD makes use of CERN’s Proton Synchrotron (PS) facility in order to simulate various galactic cosmic ray (GCR) intensities (increased ion pair concentration).

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The results presented in this manuscript focus on the underlying chemistry of α -pinene oxidation, based on mass spectrometry measurements. The study investigates positive, negative and neutral species present in the CLOUD chamber during α -pinene oxidation at a given relative humidity and temperature. Two different oxidation pathways have been investigated: Ozonolysis in the presence of an OH scavenger and OH oxidation with only background levels of ozone. We first present the general differences between both systems before focussing on a subset of oxidised organic compounds, to show how the elemental composition of oxidation products varies. The interactions of these various compounds with inorganic ions and clusters is discussed and their temporal evolution is presented in order to investigate formation mechanisms.

2 Experimental

The CLOUD (Cosmics Leaving OUTdoor Droplets) facility is located at CERN (Meyrin, Switzerland) and consists of a 26.1 m^3 stainless steel reactor in a temperature-controlled enclosure. The facility is described in more detail by Kirkby et al. (2011). Thorough cleaning with ultra pure water and heat (373 K) decreases contaminant levels to a minimum. The chamber is used as a continuously stirred reactor. It is constantly flushed with ultrapure air produced from cryogenic molecular nitrogen (N_2) and oxygen (O_2) in a 79 : 21 ratio. Trace gases are carefully adjusted and monitored. An optical fibre ultra-violet (UV) irradiation setup (Kupc et al., 2011) produces hydroxyl radicals from nitrous acid (HONO) photolysis for the OH oxidation experiments (Cox, 1974). HONO is generated continuously from sodium nitrite and sulphuric acid solutions according to the method described in Taira and Kanda (1990). An additional strong UV source, a factor-100 higher intensity UV-source installed in a quartz tube inserted into the chamber (called “UV sabre”) is used to increase OH levels in the OH experiment presented in this manuscript. Additionally, field cage electrodes situated at the top and bottom of the chamber, respectively, generate an electric field (20 kV m^{-1}) that removes existing ions in less than one second. This enables the investigation of nucleation under

neutral conditions. The use of a pion beam from CERN's Proton Synchrotron increases the amount of ions present in the chamber. When neither the electrodes nor the beam are used, the ions in the chamber arise from the natural galactic cosmic rays penetrating the chamber.

The CLOUD7 campaign was conducted between September and December 2012. Table 1 summarises the conditions of representative experiments for ozonolysis and OH oxidation used in this analysis. For the ozonolysis experiment ozone was set to about 22 ppbv and the oxidation was triggered by the injection of α -pinene. For the OH oxidation experiment HONO and α -pinene were introduced until they reached stable concentrations (about 1.9 ± 0.7 ppbv and 1250 pptv, respectively). In this case the oxidation was triggered by turning on the UV lights.

State of the art particle counters and sizers were deployed, as well as recently developed mass spectrometers. The instrumentation is described in detail in Almeida et al. (2013). We present in this manuscript results from three high-resolution mass spectrometers:

- an Atmospheric Pressure interface Time-Of-Flight (APi-TOF) mass spectrometer in positive mode,
- an APi-TOF mass spectrometer in negative mode (Junninen et al., 2010),
- and a Chemical Ionisation APi-TOF (CI-APi-TOF) using nitrate (NO_3^-) as ionising reagent (Jokinen et al., 2012)

Both APi-TOF mass spectrometers measure ions and charged molecular clusters as present in the chamber, whereas the CI-APi-TOF measures neutral molecules and clusters charged by NO_3^- (either by proton transfer or by forming an adduct). High-resolution spectra acquired with these instruments were analysed using the *tofTools* data analysis software (Junninen et al., 2010).

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3 Results and discussion

3.1 Mass defect plots

Mass defect plots are a convenient way to visualise high-resolution mass spectral data (Kendrick, 1963; Sleno, 2012). The difference between the exact mass and the integer (nominal) mass of a detected compound (i. e. its mass defect) is plotted against its exact mass.

Figure 2 presents the mass defect plots from three different instruments (positive and negative APi-TOFs, as well as nitrate CI-APi-TOF) for the two different oxidation conditions. The mass spectra have been averaged over the time periods when sulfuric acid reached a stable concentration.

All plots show a similar structure, as the signals tend to be organised in “bands”, resembling clouds of markers oriented diagonally (from upper left to lower right). They are the most pronounced in mass defect plots for anions (middle column). The first band is located on the left with lower mass defect values and the following bands are placed more on the right and higher on the mass defect axis. The size of the markers is proportional to the natural logarithm of the peak area in the mass spectra ($> 0.01 \text{ s}^{-1}$ in this study) and they have been coloured according to the retrieved elemental composition (gray points have unidentified composition). The organic compounds in the first band are predominantly species with 10 carbon atoms (“C₁₀”), while in the second band they are mainly compounds with 20 carbon atoms (“C₂₀”), but also compounds with a different number of carbon atoms are detected (“C₈”, “C₉”, “C₁₉”, etc.).

The elemental compositions are not fully unambiguous due to O₆ and SO₄ having nearly identical masses (95.969 and 95.952 amu, respectively), requiring even higher resolution to distinguish between them. Nevertheless, based on previous studies, isotopic patterns, and assumptions on chemical reactions, the elemental composition of most compounds could be retrieved. For signals with low intensity, the elemental composition could sometimes be inferred by extending a pattern (e.g. increas-

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ing or decreasing the number of oxygen atoms or adding sulfuric acid molecules to ($C_{10}H_bO_c$) HSO_4^-).

In the mass defect plots from negative and neutral species the markers in red represent the clusters containing only sulfuric acid molecules ($(H_2SO_4)_nHSO_4^-$ ($n = 1, 2$)) and blue points represent nitric acid clusters ($(HNO_3)_nNO_3^-$ ($n = 1, 2$)). Ammonia-sulfuric acid clusters are present in the negative spectra. They are the points marked in pink with mass-to-charge ratio larger than 400 Th and mass defect smaller than -0.1 (Bianchi et al., 2014). Some compounds are deprotonated (dark green) and, because of the presence of NO_x in the OH oxidation experiment some compounds are organonitrates (bound to NO_3^- , light blue). At higher masses, the bands contain clusters of organic molecules and inorganic ions ($(H_2SO_4)_nHSO_4^-$ ($n = 0, 1, 2$) or NO_3^-). The binding to sulfuric acid clusters ($(H_2SO_4)_nHSO_4^-$ ($n = 1, 2$)) is more pronounced for the ozonolysis-only experiment, even though H_2SO_4 levels are similar in both experiments (within a factor of 2).

Clusters detected in the positive spectra almost exclusively consist of an α -pinene oxidation product and a cation (either a proton (H^+), an ammonium (NH_4^+), or a dimethylaminium ($C_2H_8N^+$)), even for the higher masses. They rarely contain neutral ammonia (NH_3) or dimethylamine (C_2H_7N) molecules. In Fig. 2, no distinction is made between NH_4^+ and $C_2H_8N^+$ containing clusters.

The third band (“ C_{30} ”) is not evident in spectra of anions and the fourth band (“ C_{40} ”) is absent. These have been observed by Schobesberger et al. (2013), though in a different reaction system (OH oxidation of pinanediol, a first generation oxidation product of α -pinene). This suggests that OH oxidation of first generation products of α -pinene ozonolysis is conducive to the binding of H_2SO_4 for the compounds of the third and fourth band in the negative spectra. Nevertheless, “ C_{30} ” and “ C_{40} ” bands are seen in spectra of positive clusters in both cases with a weaker signal for the third and fourth bands compared to the first two. However, as none of these bands is observed for the neutral clusters for either oxidation conditions, these large compounds evidently do not form stable clusters with NO_3^- . This means that if large oxidised organic compounds

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are formed in the gas phase before being protonated or binding to ions, their functionalities favour binding with NH_4^+ or $\text{C}_2\text{H}_8\text{N}^+$ rather than with NO_3^- or $(\text{H}_2\text{SO}_4)_n\text{HSO}_4^-$ ($n = 0, 1, 2$), pointing towards compounds with acidic (carboxylic) functionalities.

3.2 Average carbon oxidation state, $\overline{\text{OS}}_{\text{C}}$

5 The average carbon oxidation state ($\overline{\text{OS}}_{\text{C}}$) of the identified oxidised organic compounds in the clusters for both oxidation conditions is presented in Fig. 3. The results from all three instruments are combined and weighted averages for bands are shown as large gray symbols (“ C_0 ” for $\text{C} < 8$, “ C_{10} ” for $\text{C} = 8\text{--}12$, “ C_{20} ” for $\text{C} = 18\text{--}20$, “ C_{30} ” for $\text{C} = 28\text{--}30$, and “ C_{40} ” for $\text{C} = 38\text{--}40$).

10 The $\overline{\text{OS}}_{\text{C}}$ trends are similar for both oxidation conditions. The values for the “ C_0 ” band are high (i.e. compounds are more oxidised) for negative and neutral species but below zero (i.e. compounds are less oxidised) for the positive species. The compounds detected in the neutral channel are slightly more oxidised. These values converge (decreasing for negative and neutral species and increasing for positive species) and are
15 about the same for the “ C_{20} ” band. Averaged $\overline{\text{OS}}_{\text{C}}$ for the “ C_{20} ” band is about -0.3 in the ozonolysis-only experiment and about -0.7 in the OH oxidation experiment, independent of which ions the oxidised organic compounds are bound to.

Note that $\overline{\text{OS}}_{\text{C}}$ neglects the effect of peroxide functionalities, which one expects to be abundant for low NO_x levels as it is the case in the ozonolysis-only experiment. Taking this effect into account would lower the averaged $\overline{\text{OS}}_{\text{C}}$ values for this experiment, reducing the difference between the oxidation conditions. The present comparison is
20 biased, though, as it should be performed with experiments at similar NO_x levels, but such data are not available within this study. However, $\overline{\text{OS}}_{\text{C}} \approx 2(\text{O} : \text{C}) - \text{H} : \text{C}$ remains a useful, operationally defined quantity.

25 The next sections focus on the differences in elemental composition and clustering behaviour of newly formed compounds for either oxidation conditions. For the sake

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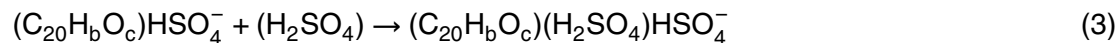
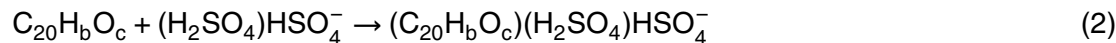
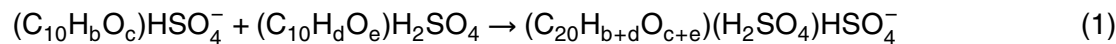
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Pure ozonolysis leads to mostly $C_{20}H_{30}O_c$ products, with higher signals for compounds with an even number of oxygen atoms in the positive spectra, whereas OH oxidation leads to $C_{20}H_{30,32,34}O_c$ without preference for compounds with even numbers of oxygen atoms. In the negative spectra, the preference for compounds with even number is less evident and the range of O : C is broader. In the ozonolysis experiment, it remains ambiguous if $(C_{20}H_bO_c)(H_2SO_4)_nHSO_4^-$ ($n = 1, 2$) are formed by aggregation of two C_{10} containing clusters (neutral and negative, Eq. 1), or by the reaction of a formed C_{20} compound with a sulphuric acid cluster (Eq. 2). The addition of a sulfuric acid molecule to an existing bisulphate cluster (Eq. 3) is also possible. The reaction pathways do not exclude each other and might coexist (see also Sect. 4).



It remains unclear why such clusters with additional neutral molecules are not observed in the OH oxidation experiment. This may be due to the lower concentration of H_2SO_4 in this experiment, or because their signals are low and hidden by isobaric clusters of a different composition.

These results illustrate how the oxidation processes modify the proton affinity and the clustering behaviour of the oxidation products of α -pinene. The addition of functional groups modifies the interaction with protons, ions and ionic clusters. Figure 1 presents an overview of both oxidation pathways (with examples of possible structures for the observed products). Despite different mechanisms in the early steps, peroxy radicals are produced under both oxidation conditions and will react in a similar way with various present reaction partners (numbered 1 to 5) independent of their formation pathway. Decomposition reaction of alkyloxy radicals (from reaction 4) and intramolecular H-abstractions followed by reaction with O_2 (reaction 5) lead again to peroxy radicals (and acylperoxy radicals), which can again react via reactions 1 to 5 in an iterative manner (red arrows). Terminal reactions lead to (extremely) low volatility organic compounds

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((E)LVOCs). In our experiments, NO_x is only relevant for the OH oxidation pathway. No explicit structure is given for products of intramolecular H-abstraction, as it is yet unknown, which H atom would be abstracted first. Termination reaction branching ratios leading to the various functionalities are influenced by HO_2 , RO_2 and NO_x levels.

Therefore, there is a minor difference in functional groups for species with a lower number of oxygen atoms: ozonolysis favours carbonyl functional groups (ketones, aldehydes), while OH oxidation produces hydroxyl (alcohols) functionalities (Atkinson, 2000; Vereecken et al., 2012; Taatjes et al., 2013). However, for multifunctional species (more than 5 oxygen atoms, ELVOCs), no particular functional group is dominant.

Bipolar charging probabilities determined for aerosol particles are sometimes extrapolated down to 1 nm diameters (e.g. Jiang et al., 2011) ignoring the role of chemical composition. Although the present results do not necessarily apply to all types of clusters, they do suggest that this extrapolation is valid down to around 1.5 nm in mobility diameter, which is roughly the size of the detected C_{20} containing clusters (Ehn et al., 2011). Below this size, compounds clearly behave differently depending on polarity and charger ion composition.

Ehn et al. (2012) identified $\text{C}_{10}\text{H}_{14}\text{O}_{7-11,13}$, $\text{C}_{10}\text{H}_{16}\text{O}_{7-11}$, $\text{C}_{20}\text{H}_{30}\text{O}_{12-16,18}$, and $\text{C}_{20}\text{H}_{32}\text{O}_{11,13,15}$ in α -pinene ozonolysis chamber experiments (and a subset of these in the boreal forest site in Hyytiälä, Finland). All of these, were also identified during our study in either experiment.

3.3.2 Neutral species

The clusters containing C_{10} and C_{20} oxidised compounds from the ozonolysis only experiment (top) and the OH oxidation (bottom), respectively, is depicted in the right columns of Figs. 4 and 5.

$\text{C}_{10}\text{H}_{15}\text{O}_{8,10}$ (bound to NO_3^-) are seen in the neutral spectra of the OH oxidation experiment (Fig. 4, bottom right). They are also seen in the negative spectra (bottom middle).

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Comparing the mass spectra of the neutral species with the previously discussed plots from the negative clusters, it appears that the natural ionisation happening in the chamber with HSO_4^- is less selective than the chemical ionisation with NO_3^- in the CI-API-TOF ion source. Therefore, not all the neutral species appear in the spectra of the neutral clusters. The detected compounds represent ELVOCs though and were shown to be proportional to the (total) amount of oxidised compounds (Ehn et al., 2014). Therefore, for a comprehensive detection of α -pinene oxidation products and their mechanistic interpretation, HSO_4^- seems to perform better than NO_3^- as an ionisation reagent.

Schobesberger et al. (2013) presents a similar analysis for oxidation reactions of pinanediol with OH (and high H_2SO_4 levels). No CI-API-TOF was used for those experiments and the authors claim that the composition of neutral clusters is similar to that of negatively charged clusters. Even though this statement may be true, it cannot be shown with only one type of chemical ionisation.

While the distribution of clusters in the neutral spectra compared to the positive and negative spectra is different for C_{10} compounds, it is almost identical for the C_{20} compounds. Therefore, C_{20} compounds independently of their formation pathways display a similar reactivity towards NH_4^+ , $\text{C}_2\text{H}_8\text{N}^+$, HSO_4^- and NO_3^- , even though the distribution is shifted towards slightly more oxidised compounds in the neutral spectra, especially for $\text{C}_{20}\text{H}_{30,32}\text{O}_c$. In our experiments, the negative spectra is sensitive to a broader range of O : C, in particular for $\text{C}_{20}\text{H}_{30}\text{O}_c$.

4 Clusters time series

Normalised time series have been derived for all three instruments to investigate formation mechanisms. The time series varies from 1 min (positive data) to 5 min (negative OH oxidation data). The other time series have a 2 min time resolution. These have been set in order to optimise the signal-to-noise ratio in each of the spectra.

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Analysis of positive C_{20} containing clusters in the ozonolysis experiment shows that most oxidised compounds (up to O_{18} , not shown) appear almost immediately after the beginning of the experiment (vertical black line) and reach their maximum concentration the earliest (Fig. 6). This is observed for clusters of $C_{20}H_{30}O_c$ with either NH_4^+ or $C_2H_8N^+$. The signals of the clusters containing the most oxidised compounds decrease after reaching their maximum, whereas the signals of the other clusters level off. This corresponds to the mixing ratio of α -pinene slowly reaching its equilibrium concentration towards the end of the run, stabilizing the oxidation conditions. This indicates that when α -pinene is very low, fewer termination reactions (with RO_2) happen, allowing further oxidation by successive intramolecular H-shifts as suggested by Ehn et al. (2014), see Fig. 1. This observation is in line with smog chamber experiments (Pfaffenberger et al., 2013), showing that higher O : C of SOA is achieved with low α -pinene levels. This result contrasts with the view that the most oxidised organic compounds are formed only after long oxidants exposure time. Highly oxidised organic compounds can also be formed very quickly, depending on the oxidation conditions.

For the OH oxidation experiment the α -pinene concentration is high from the beginning of the run and OH is produced from HONO photolysis by UV light. In this case the signals for the presented positive clusters containing $C_{20}H_{32}O_c$ (with either NH_4^+ or $C_2H_7N^+$) rise almost simultaneously, so that no similar conclusion can be drawn, even at 1 min time resolution. Trying to increase the time resolution to observe which signals increase first would lead to a too low signal-to-noise ratio. A similar (but less clear) trend is observed as well in neutral spectra (Fig. 7).

The analysis of time series for the negative spectra is not straightforward, due to the lower signal and isobaric species. Nevertheless, Fig. 8 shows the time series for selected clusters containing $C_{20}H_{30}O_c$ species for the ozonolysis-only experiment and containing $C_{20}H_{28}O_c$ species for the OH oxidation experiments. The data show that, in the ozonolysis-only experiment, the clusters with an additional neutral sulfuric acid molecule are formed later. Therefore, the mechanism suggested earlier as Eq. (3) is the most likely to happen. It remains unclear, though, if the cluster contains one covalently

bound C_{20} oxidised compound or two C_{10} compounds. The slight decrease of averaged OS_C from the “ C_{10} ” to the “ C_{20} ” band discussed earlier suggests that two C_{10} peroxy radicals probably react together (losing oxygen atoms) before binding to HSO_4^- .

5 Conclusions

Oxidation of α -pinene was conducted in the CLOUD chamber. The simultaneous use of three different mass spectrometers provides a unique insight of the chemical reaction mechanisms happening in the early stage of α -pinene oxidation and molecular cluster formation.

Charged clusters consist of oxidised organic compounds binding to a core ion (bisulfate or nitrate for negative clusters and hydronium, ammonium, or aminium for positive clusters). Molecular clusters including additional sulfuric acid molecules have also been detected in the negative spectra for ozonolysis, while in the positive spectra, even clusters with high masses rarely contain neutral ammonia or dimethylamine molecules. The results show the selectivity of this chemical ionisation process. Especially the difference between ionisation with NO_3^- and HSO_4^- can be seen from the broader range of C_{10} oxidised compounds observed in the negative spectra compared to the neutral one. The cluster distribution of the C_{20} is very similar for all instruments, showing that due to the many functional groups of these species, their affinities towards the various ions present is similar. This also implies that for the analysis of atmospheric clusters containing oxidised organic clusters, the combination of API-TOF and CI-API-TOF mass spectrometers with varying ionisation reagent is important in order to capture a comprehensive picture of formed products, in particular for low molar mass products. Heavier oxidised organic compounds (C_{20}), due to their many functional groups can be similarly charged by various ions, suggesting that the ionisation starts to be independent of the charging mechanism. Even if both oxidation mechanisms differ in their first step, they both lead to the formation of peroxy radicals, which produce multifunctional oxidised organic compounds. For compounds containing a low number of oxygen

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Table 1. Conditions of selected runs. The given values correspond to the period with constant $[\text{H}_2\text{SO}_4]$.

Run	α -pinene (pptv)	O_3 (ppbv)	SO_2 (ppbv)	HONO (ppbv)	H_2 (%)	UV	$[\text{H}_2\text{SO}_4]$ cm^{-3}
1070.02	660	22	69	0	0.1	no	1.91×10^7
1100.02	1250	0.8	1.1	1.2–2.6	0	yes	1.03×10^7

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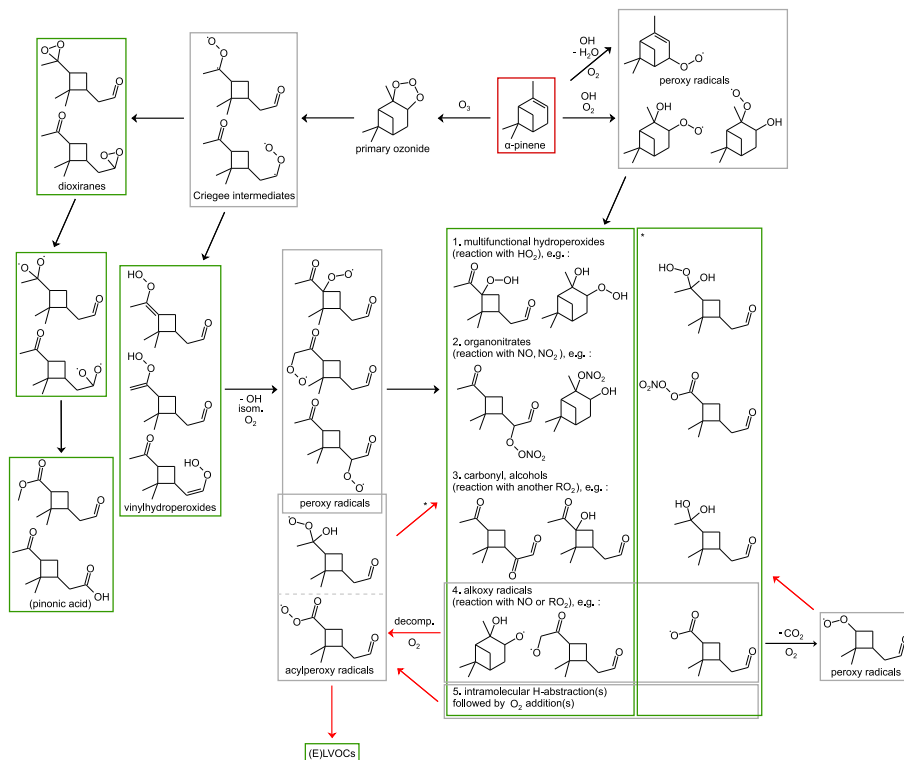


Figure 1. Non-exhaustive summary of α -pinene ozonolysis (left) and OH oxidation (right) reaction pathways. Not all possible reaction pathways and final products are displayed, but only representative examples. The box marked with a star (*) corresponds to products formed from (acyl)peroxy radicals via reactions 4 and 5. See main text and discussion for details.

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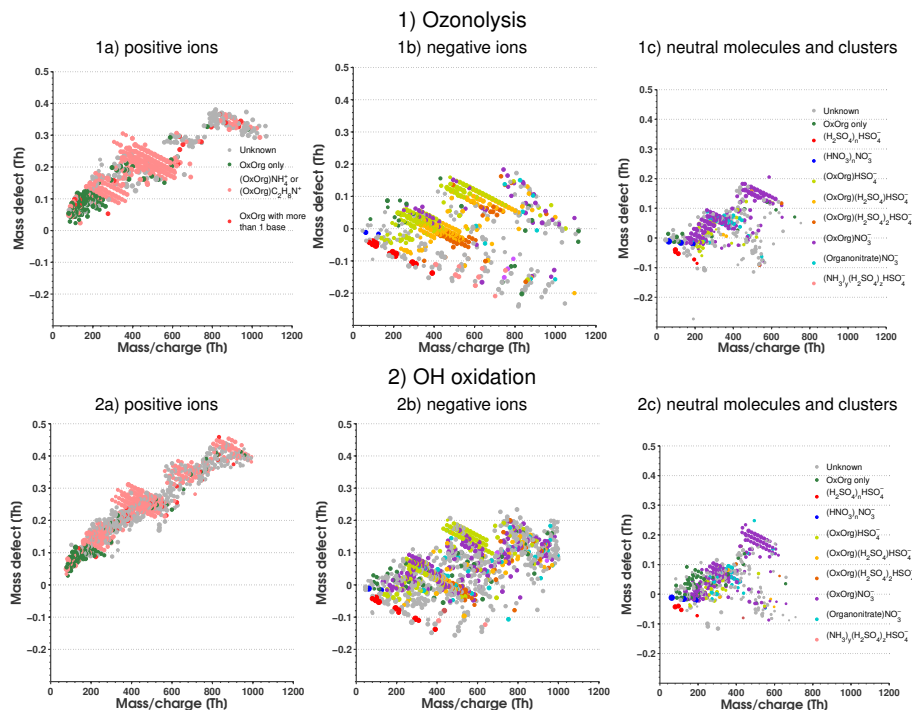


Figure 2. Mass defect plots derived from detected cations (positive APi-TOF, left column), anions (negative APi-TOF, middle column), and neutral molecular clusters (CI-APi-TOF, right column) of α -pinene ozonolysis with OH scavenger (top row) and α -pinene oxidation by OH only (bottom row). The legend on the top left panel applies to the left column (positive clusters), while the legend on the top right panel applies to the middle and right columns (negative and neutral clusters).

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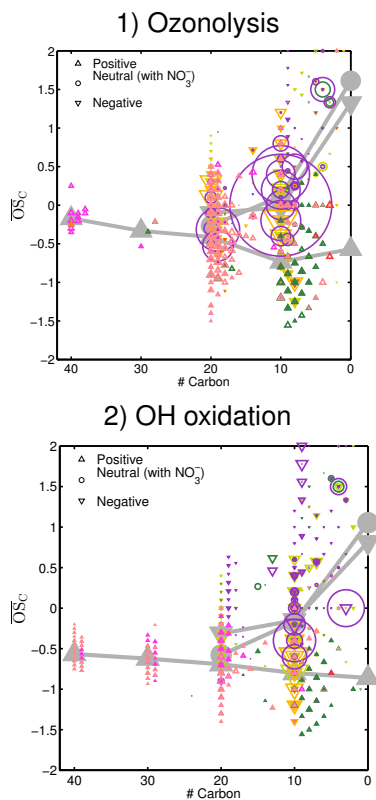


Figure 3. Mean carbon oxidation state (\overline{OS}_C) as a function of the number of carbons for each identified oxidised organic compound in clusters for all three instruments. The shape of the markers indicate which type of clusters is depicted and the colors are the same as in Fig. 2. The weighted mean for the various bands ($C < 8$, $C = 8-12$, $C = 18-20$, $C = 28-30$, and $C = 38-40$) is indicated with large gray symbols.

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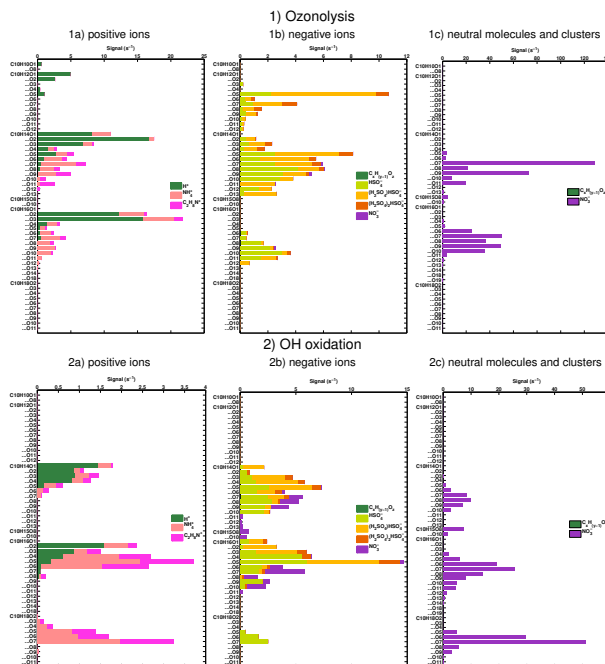


Figure 4. Stacked peak area for observed clusters containing $C_{10}H_bO_c$ according to core ion(s) of positive (left column), negative (middle column), and neutral (right column) clusters obtained from α -pinene ozonolysis with OH scavenger (top row) and α -pinene oxidation by OH only (bottom row).

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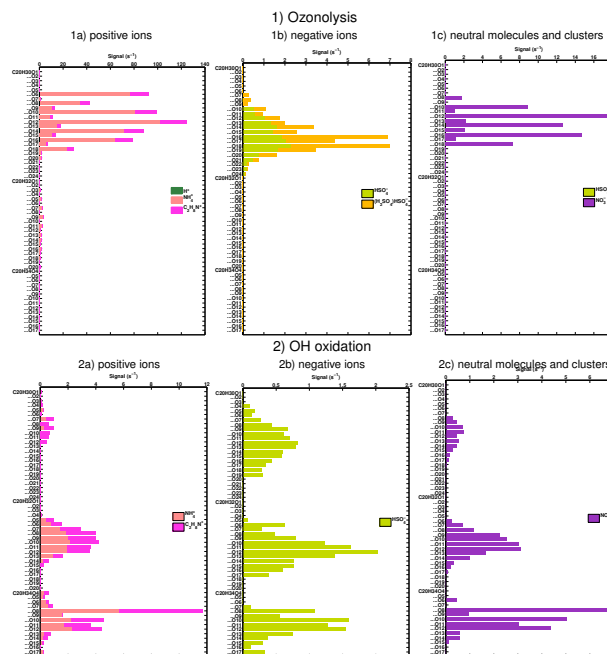


Figure 5. Stacked peak area for observed clusters containing $\text{C}_{20}\text{H}_b\text{O}_c$ according to core ion(s) of positive (left column), negative (middle column), and neutral (right column) clusters obtained from α -pinene ozonolysis with OH scavenger (top row) and α -pinene oxidation by OH only (bottom row).

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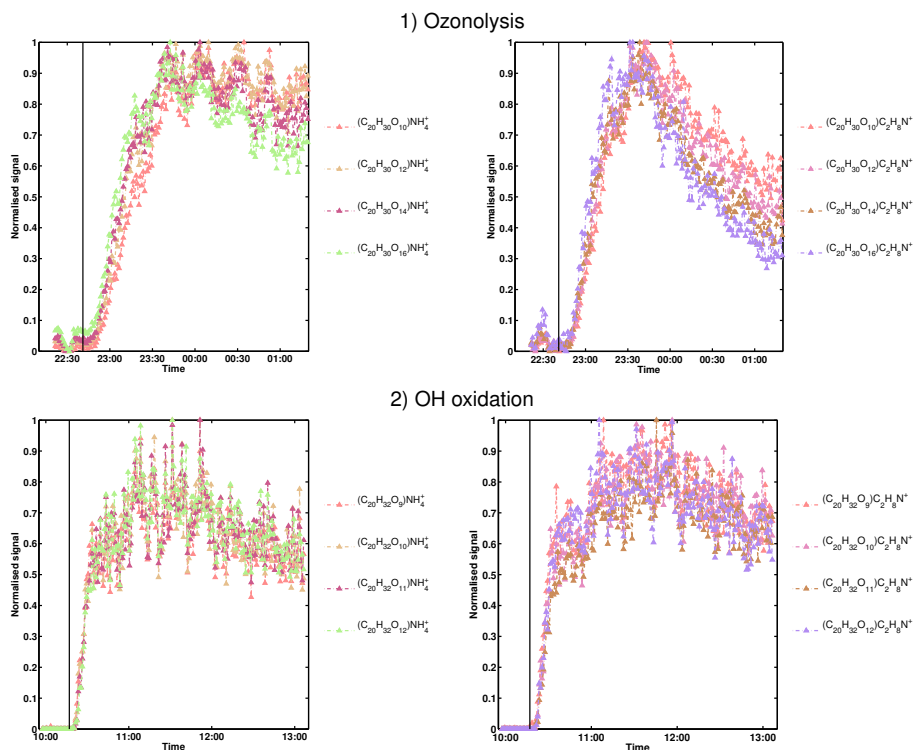


Figure 6. Time series of observed positive clusters containing $\text{C}_{20}\text{H}_{30,32}\text{O}_2$ oxidised compounds bound to NH_4^+ (left) and $\text{C}_2\text{H}_8\text{N}^+$ (right) for α -pinene pure ozonolysis (top row) and pure OH oxidation (bottom row). The vertical black line marks the beginning of the experiment.

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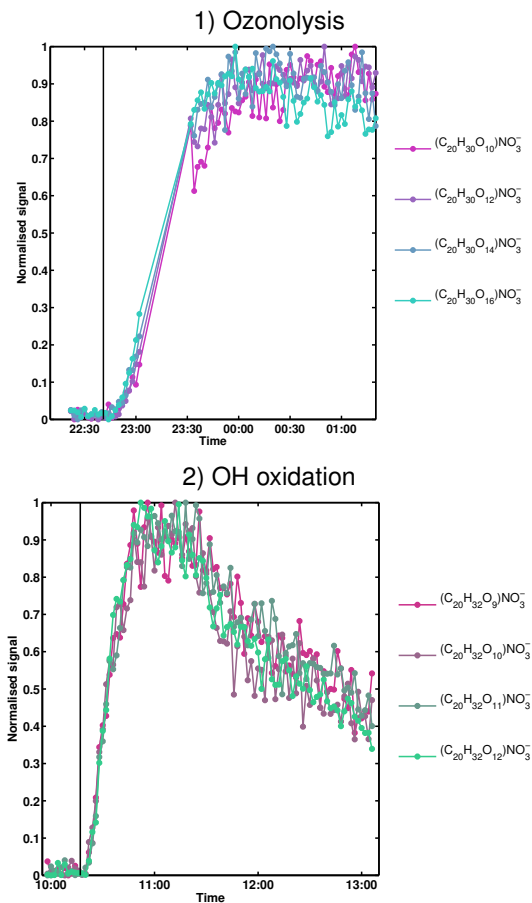


Figure 7. Time series of observed neutral clusters containing $C_{20}H_{30}O_z$ oxidised compounds for α -pinene pure ozonolysis (top row) and containing $C_{20}H_{32}O_z$ for pure OH oxidation (bottom row). The vertical black line marks the beginning of the experiment.

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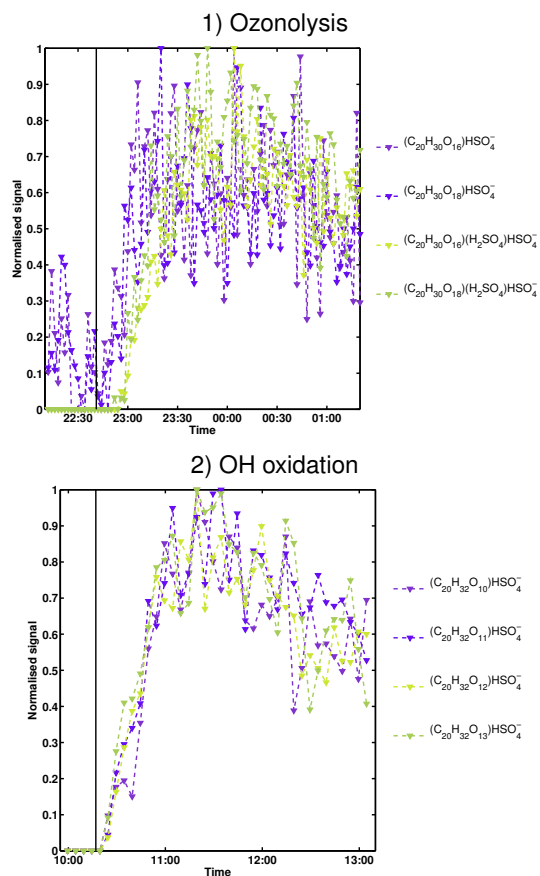


Figure 8. Time series of some observed negative clusters containing $C_{20}H_{30}O_2$ oxidised compounds for α -pinene pure ozonolysis (top row) and containing $C_{20}H_{32}O_2$ for pure OH oxidation (bottom row). The vertical black line marks the beginning of the experiment.