Formation of highly oxygenated organic molecules from chlorine atom initiated oxidation of alpha-pinene

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Abstract

Highly oxygenated organic molecules (HOMs) from atmospheric oxidation of alpha-pinene can irreversibly condense to particles and contribute to secondary organic aerosol (SOA) formation. Recently, the formation of nitryl chloride (ClNO₂) from heterogeneous reactions, followed by its subsequent photolysis is suggested to be an important source of chlorine atoms in many parts of the atmosphere. However, the oxidation of monoterpenes such as alpha-pinene by chlorine atoms has received very little attention, and the ability of this reaction to form HOM is completely unstudied.

Here, chamber experiments were conducted with alpha-pinene and chlorine under low and high nitrogen oxide (NOₓ) conditions. A NO₃-based CI-API-TOF was used to measure HOM products. Clear distributions of monomers with 9-10 carbon atoms and dimers with 18-20 carbon atoms were observed under low NOₓ conditions. With increased concentration of NOₓ within the chamber, the formation of dimers was suppressed due to the reactions of peroxy radicals with NO. We estimated the HOM yields from chlorine-initiated oxidation of alpha-pinene under low-NOₓ conditions to be around 1.8 %, though with a substantial uncertainty range (0.8-4 %) due to lack of suitable calibration methods. Corresponding yields at high NOₓ could not be determined because of concurrent ozonolysis reactions. Our study demonstrates that chlorine atoms also initiated oxidation of alpha-pinene and yields low volatility organic compounds.
1. Introduction

Highly oxygenated organic molecules (HOMs) have been identified as key species in the formation of new atmospheric aerosol particles and secondary organic aerosol (SOA) (Ehn et al., 2014, 2017; Kulmala et al., 2013; Bianchi et al., 2019). Recently, the formation of HOMs in the gas phase was described as an autoxidation process of peroxo radicals (RO$_2$) via multiple intramolecular H atom shifts (Crounse et al., 2013; Jokinen et al., 2014b; Mentel et al., 2015; Rissanen et al., 2014). Oxygen-containing moieties such as carbonyl, carboxylic acid and hydroxyl groups can weaken nearby C-H bonds, making H-abstraction and autoxidation competitive with bimolecular RO$_2$ reactions, e.g. with NO (Crounse et al., 2013; Praske et al., 2018). Until now, all studies on the formation of HOMs have focused on reactions initiated by oxygen-containing oxidants (O$_3$, OH and NO$_3$).

Increasing evidence indicates that the chlorine atom (Cl) may also play an important role in transforming atmospheric organics. (Tham et al., 2016; Thornton et al., 2010). Chlorine atoms have the greatest reactivity toward volatile organic compounds (VOC), with rate constants that are, with some exceptions, an order of magnitude higher than those of hydroxyl radicals (OH) (Riva et al., 2015). Historically, chlorine atoms were thought to be formed primarily from heterogeneous reaction cycles involving sea salt, and its concentration estimated to be around 1-10% of that of OH. Therefore, the role of chlorine atoms in atmospheric oxidation processes has traditionally been thought to be limited to the marine boundary layer only. In recent years, ClNO$_2$, as a significant chlorine atom source, was found in continental regions of America, Canada and Germany, and high concentrations of ClNO$_2$ were also detected in the urban atmosphere in China (Reyes-Villegas et al., 2018; Tham et al., 2016; Thornton et al., 2010; Wang et al., 2017). The new findings have expanded the potential importance of chlorine atoms from coastal areas to continental urban areas. A recent study also reported that chlorine atoms can be more important than OH radicals for the oxidation of alkanes in...
the North China Plain (Liu et al., 2017). Therefore, it is desirable to probe the role of chlorine radicals in the degradation of VOCs and related SOA formation.

Emission of biogenic volatile organic compounds (BVOC) to the atmosphere dominates total hydrocarbon emissions on a global scale, with methane, isoprene and terpenes having the highest source strengths (Guenther et al., 2012). Alpha-pinene is the most abundant monoterpene in the atmosphere and its oxidation products from ozonolysis and photooxidation contribute to a substantial fraction of SOA mass (Riccobono et al., 2014; Zhang et al., 2018). Chlorine atom initiated reactions of alpha-pinene have also been shown to contribute to the formation of SOA, which implies that low volatile compounds are efficiently produced also in this process (Cai and Griffin, 2006; Ofner et al., 2013).

Similar to the reaction with OH radicals, the reaction of VOCs with chlorine atoms may proceed either via addition of Cl to unsaturated bonds or via H-abstraction. Wang et al (2017) found that the Cl addition to isoprene can lead to the formation of low volatility organic compounds. In principle, Cl-initiated reactions could form HOMs in a similar manner as OH-initiated reactions (Berndt et al., 2016a), as the initial addition or abstraction step is comparable for both oxidants. In view of the increased understanding of the importance of chlorine atoms in atmospheric chemistry, it is desirable to investigate the formation of HOMs from reactions of common atmospheric VOC with Cl.

Here, a laboratory chamber experiments were performed to investigate the ability of chlorine atom to form HOMs from the oxidation of alpha-pinene. HOMs were characterized using a nitrate-based chemical ionization mass spectrometer, under both low and high NOx conditions. The yields of these HOMs were determined under the low NOx conditions, and the atmospheric implications of this study are discussed.
2. Experiment and method

2.1 experimental setup

The experiments were conducted in the “COALA” chamber at the University of Helsinki (Peräkylä et al., 2019; Riva et al., 2019). It is a 2 m$^3$ Teflon chamber, run as a continuously stirred tank reactor, used with a flow of 45 liter per minutes (LPM), resulting in an average residence time of about 45 minutes. The chamber is surrounded by housing to provide dark conditions. No water vapor was added to the chamber, and the temperature was the same as the temperature of the room, around 25°C. A general schematic of the chamber facility is shown in Figure 1. Our experiment was aimed to probe chlorine atom initiated formation of HOMs under low/high NO$_x$ conditions. We use 400 nm LED lights to photolyze chlorine and NO$_2$ and produce chlorine atoms and NO as following:

$\text{NO}_2 \rightarrow \text{NO} + \text{O}$

$\text{Cl}_2 \rightarrow \text{Cl} + \text{Cl}$

The concentration of Cl atoms was varied by changing the amount of 400 nm light. In practice this was done by turning on different amounts of the available lights, with the maximum corresponding to seven. We will refer below to the number of lights that were turned on, although each “light” corresponds to a group of LED strips.

2.2 Instrumentation and data analysis

A nitrate ion (NO$_3^-$) based chemical ionization atmospheric pressure interface long time-of-flight (CI-API-L-TOF) mass spectrometer was used for measuring HOMs. The instrument has been shown to be sensitive towards such group of compounds, detecting them as adducts with the nitrate ion. Due to a lack of suitable calibration methods, the CI-API-L-TOF was not calibrated for HOMs during this study. In order to estimate rough HOM concentrations, we directly use the calibration coefficient ($C = 1.6 \times 10^4$) utilized by Ehn et al. (2014), which is very close to values utilized in several other
studies using a CI-APi-TOF (Jokinen et al., 2014a; Riva et al., 2019). This approach obviously brings large uncertainties when estimating HOM concentrations, which we estimate to be at least -50 %/+100 %. More detailed information about the instrument can be found in (Jokinen et al., 2012), noting that compared with the CI-APi-TOF used before, the long time-of-flight mass spectrometer used here has a doubled mass resolving power enabling a more accurate assignment of molecular formulas. Simultaneously, we also used a high-resolution long time-of-flight aerosol mass spectrometer (HR-L-TOF-AMS) to measure bulk aerosol chemical properties (Decarlo et al., 2006). As no seed aerosol particles were added to the chamber, the VOC oxidation products lead to new particle formation and growth to large enough sizes to be measured by the AMS. We also periodically used a filter in front of the AMS inlet to see the influence of the background signal to measured aerosol mass concentration. There were 10 minutes of filter measurements per hour during our experiments. A PTR-TOF-MS (TOF-8000, Ionicon) was used to measure the concentration of alpha-pinene in the chamber. The instrument background was determined every day for 20 mins by guiding the chamber air through a catalytic converter, which removes the VOCs. Then, the background corrected signals were used to obtain alpha-pinene mixing ratios by using the calibration coefficient determined before the experiments. A description of the used setup employed for the calibration and zero air measurements have been introduced earlier (Schallhart et al., 2018). A custom-built DMPS system was used to measure the particle number size distribution from 10 nm to 400 nm in the chamber. The NO concentration was measured with an ECO-PHYSICS CLD 780 TR instrument with a detection limit of 3 ppt. NOx (=NO+NO2) concentrations were determined by using a Thermo-Fisher 42i analyzer. O3 concentration was measured with a Thermo-Fisher 49i analyzer.

2.2 Estimation of chlorine atom concentrations

During steady state in the chamber, average concentrations of chlorine atom was calculated using the rate coefficients (4.6±1.3) • 10^-10 cm^3 molecule^-1 s^-1 of Cl atoms
with alpha-pinene (Finlayson-Pitts et al., 1999), as following:

\[
\frac{d[AP]}{dt} = Q_{in} - k \cdot [Cl] \cdot [AP] - Q_{out}
\]

where \( Q_{in} \) is the concentration of alpha-pinene continuously injected into the chamber, and \( Q_{out} \) is the concentration that exited the chamber. The term \( Q_{in} \) was 13.3 ppb, while the term \( Q_{out} \) varied depending on the conditions, and is calculated as \( [AP]/45 \) min. During steady state, \( \frac{d[AP]}{dt} \) is zero, and then \([Cl]\) concentration is calculated accordingly. As shown in Figure 2, the concentration of HOMs decreased and alpha-pinene increased as the number of lights switched on changed from 7 to 4, 2 and 1. We use the variation of alpha-pinene and HOM concentrations during this run to calculate both chlorine atom concentrations and HOM yields. Each change in alpha-pinene concentration was due to the change in Cl atom concentration, and with knowledge of the reaction rate, the concentration of Cl atoms as a function of the number of lights turned on was determined (Figure 3). The calculated \([Cl]\) concentrations are in the range of \((1-5) \times 10^5\) molecules cm\(^{-3}\), which is within atmospheric relevant concentration ranges (Tham et al., 2016). Raw data from the CI-API-L-TOF were recorded in 10s resolution in HDF format. We used Toftools for data analysis and detailed protocols of the software have been introduced by Junninen et al. (2010).

### 2.3 HOMs molar yield

The change of HOM concentration with time can be described as follows, in analogy with Ehn et al. (2014):

\[
\frac{d[HOMs]}{dt} = k_1 \cdot [pinene][Cl] \cdot k_{loss}[HOMs]
\]

(1)

\[
= \frac{k_{loss}[HOMs]}{k_1[pinene][Cl]}
\]

(2)
Here, $k_1$ is the reaction rate coefficient of alpha-pinene with chlorine atoms and $\gamma$ is the molar yield of HOMs, i.e., the fraction of alpha-pinene + Cl reactions that produced HOMs. $k_{\text{loss}}$ is the loss rate of HOMs to the chamber walls and particles, though the latter was negligible in this study due to the low aerosol loadings. We used 300 s as a lifetime of HOMs, i.e., $k_{\text{loss}} = 1/300$ s$^{-1}$, in our previous study in the COALA chamber (Riva et al., 2019).

3. Results and discussion

3.1 Formation of HOMs under low NO condition

Figure 4 (a, b, c and d) shows mass spectra measured by the NO$_3$-Cl-API-TOF during steady state alpha-pinene oxidation with different amounts of lights switched on. The x-axis represents mass to charge ratio, in units of Thomson (Th). The y-axis represents signals in units of counts per second. As we can see, both monomers (280-400 Th) and dimers (440-580 Th) showed increased signals with increased number of lights, and consequently increased [Cl]. The most abundant peaks are labeled in Figure 4d, with some of the largest signals in the monomer range attributed to C$_9$H$_{12}$O$_7$ and C$_{10}$H$_{14}$O$_{8,9,10}$. During the oxidation of C$_{10}$H$_{16}$, in the absence of NO, the fate of RO$_2$ radicals depends on the concentrations of HO$_2$ and RO$_2$. Autoxidation competes with bimolecular reactions, becoming more likely at lower RO$_2$ and HO$_2$ concentrations. At high oxidation rates, autoxidation is likely inhibited compared to actual atmospheric conditions.

As we show in the Figure 4(d), C$_{10}$H$_{14}$O$_{8-12}$ compounds are large peaks in the monomer range observed with the NO$_3$-Cl-API-TOF. These compounds with 14 hydrogens may come from decomposition of C$_{10}$H$_{15}$O$_8$ peroxy radicals via loss of OH or HO$_2$, or following reactions with other RO$_2$, as depicted schematically in Figure 5. Another
abundant group is C_{10}H_{16}O_{6-12}, which may result from RO₂ terminated by HO₂. In the
dimer range, the most abundant compounds are C_{19}H_{28}O_{8-14} and C_{20}H_{30}O_{11-14}. These
compounds come from RO₂ cross reactions, as has been shown in multiple earlier
studies. The C_{20}H_{30}O₆ dimers are most likely formed from reactions of two C_{10}H_{15}Oₓ
radicals, as were many abundant monomers. As noted earlier, Cl oxidation of alkenes
may occur via a Cl addition (forming an initial radical containing 16 H-atoms and one
Cl atom) or via an H-abstraction reaction (forming a radical with 15 H-atoms and no
Cl) (Figure 5). Based on our HOM spectra, the abstraction reaction would seem to
completely dominate the reaction, as only a few minor peaks in the spectrum could be
identified to contain Cl. Alternatively, only the abstraction pathway leads to HOM
formation, or the Cl atom is lost during the subsequent reaction in the oxidation
processes. With our data, we cannot rule out either of these explanations for this
surprising result. Loss of HCl from alpha-pinene products from Cl oxidation have, to
our knowledge, only been reported to take place in the aerosol phase (Ofner 2013).

Figure 6 shows the variation of several closed-shell HOM products and the peroxy
radical C_{10}H_{15}O₉ measured by NO₃-CI-API-TOF when we changed the lights from
dark conditions to 1, 2, 4 and 7 lights switched on. Given the low Cl atom concentration,
it is expected that no multi-generation oxidation by Cl can take place, and the behavior
of all closed shell oxidation products should follow similar patterns. As seen in Figure
6, this was the case both for monomers and dimers. The less steep increase of the radical
is also according to expectations, as the formation of RO₂ is linear with the alpha-pinene
oxidation rate, but the loss rate (when dominated by RO₂ cross reactions) is proportional
to (RO₂)². For closed shell species, the wall loss-driven loss rate stays constant
throughout the experiment, and therefore they increase linearly with the alpha-pinene
oxidation rate while the RO₂ radicals increase as the square root of the oxidation rate.
For more detailed discussion on RO₂ dynamics in a steady state chamber, see Ehn et al.
(2014).
In Figure 7, we plotted time series of the particle number size distribution and the total number concentration, together with mass concentrations of particulate chloride and organic acids as we changed the number of lights. Particle formation was detected even at the lowest Cl atom concentration, as indicated by the increases in aerosol number concentration. An increased in aerosol mass concentration as detected by the AMS only took place at the two highest Cl atom concentrations, when the particles were able to grow into a size range measurable by the AMS. Particulate chloride mass concentrations also increased relatively linearly with the concentration of organic acids as we increased the number of lights. The Chl/Org ratio was only around 3 %, suggesting that the majority of condensed OVOC did not contain Cl atoms. Some part of the chloride signal may also result from adsorption of HCl to particles.

3.2 Formation of HOMs at high NOx

Anthropogenic emission have a significant influence on the formation of SOA, to a large part due to the influence of NOx on the atmospheric oxidation chemistry (Lee et al., 2016). In general, the fate of peroxo radicals in chamber experiments can be dominated by reactions with other RO2, HO2 or NO, depending on the exact conditions. In our experiments without NOx addition, RO2 was expected to be the main terminator, as also supported by the high number of detected ROOR dimers. In the atmosphere, all of the three mentioned reaction partners may be relevant at the same time. However, with increased anthropogenic influence, the reaction of RO2 with NO will often become dominant. Therefore, we added NOx to the chamber as it allowed for the isolation of the formation pathways leading to HOMs in cases where NO was the main terminator for RO2 radicals. Figure 8 depicts a HOM mass spectrum at steady state during alpha-pinene oxidation by chlorine radicals in the presence of ~10 ppb NOx, with the maximum 7 lights turned on. As anticipated, the dimers above 440 Th were greatly reduced compared to the runs without NOx. As more lights were turned on, both the Cl atoms and NO formation increased, as the 400 nm lights photolyze both Cl2 and NO2.
This coupling, together with the fact that the NO\textsubscript{2} photolysis leads to ozone formation, which subsequently can react with alpha-pinene to form HOMs, limits our quantitative analysis of these experiments. However, we conclude that efficient HOM formation took place also under these high-NOx conditions, and thus the autoxidation occurs rapidly enough to still compete with RO\textsubscript{2} termination reactions. The NO\textsubscript{x} addition also formed an abundance of organonitrate compounds like C\textsubscript{10}H\textsubscript{15}NO\textsubscript{8},\textsubscript{9,10,11,12}, as shown in Figure 8. This family of compounds may form from H-abstraction by the chlorine radical, followed by autoxidation and finally radical termination by NO. The concurrent formation of ozone means that also some alpha-pinene ozonolysis reaction will take place, though oxidation by Cl atoms was still the main loss for alpha-pinene also under these conditions.

Figure 9 shows variation of some nitrogen-containing HOMs and variation of alpha-pinene, ozone, NO and NO\textsubscript{x}, as we changed the lights from dark conditions to 1, 2, 4 or 7 lights switched on. The concentrations of alpha-pinene and NO\textsubscript{2} decreased because of the consumption by chlorine radicals and photolysis of NO\textsubscript{2} into NO. Importantly, we did not observe any SOA when we had NO in the chamber. NO may have suppressed the particle formation by suppressing the dimer formation, as these have been shown to be important for initial particle formation (Tröstl et al., 2016).

### 3.2 Estimated HOMs production yields

Quantifying the molar yields of HOMs is essential to know their potential importance from a specific system. We attempt to estimate the molar yield in the case of Cl oxidation of alpha-pinene in the absence of NO\textsubscript{x}. The initial C\textsubscript{10}H\textsubscript{16} concentration is around 13.3 ppb without any UV lights switched on in the chamber. As we changed the lights, alpha-pinene and HOM concentrations varied as we showed in Figure 3. In addition, we calculated the concentration of Cl radicals as introduced in the Methods section. With this information, we can calculate the formation rate of HOM, which in
steady state equals the HOM loss rate $[\text{HOM}] \times k_{\text{loss}}$. We can also calculate the oxidation rate of alpha-pinene as $[\text{alpha-pinene}] \times [\text{Cl}] \times k_{\text{AP-CI}}$. The ratio of these two numbers corresponds to the HOM molar yield. We selected the same runs as in Fig. 3, used also for calculating the chlorine radical concentration, and calculated the ratio as a linear fit to these four conditions (Figure 10). We get a slope of 0.018, meaning a HOM yield of 1.8%. Considering the uncertainty in estimating absolute HOM concentrations, we conservatively estimate that the molar HOM yield from alpha-pinene + Cl is within the range of 0.8-4%. These values are similar to HOM yields reported for alpha-pinene oxidation by ozone and OH (Berndt et al., 2016; Ehn et al., 2014).

4. Conclusion

We have systematically explored the reactions of alpha-pinene with chlorine atoms in a simulation smog chamber under atmospherically relevant conditions. We measured substantial amounts of highly oxidized organic molecules (HOM) with a NO$_3$-CI-API-TOF. With increasing UV lights, and consequently higher chlorine radical concentrations, the concentrations of both HOM and secondary organic aerosol increased. With addition of NOx, HOM monomer formation was still efficient, but the particle formation decreased greatly. We estimated HOM molar yields of around 1.8% (0.8-4%) from the reaction of alpha-pinene with Cl atoms. Our study thus indicates that in regions where chlorine atom oxidation is of importance, its possible reactions with monoterpenes can be an important source of HOM, and consequently, SOA.

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Competing financial interests

The authors declare no competing financial interests.

Author contributions

Y. H. W, H. B. X and M. E had the original idea of the study. Y. H. W, M. R and H. B. X conducted the chamber experiments. Y. H. W, M. R, H. B. X, L.H and M. E interpreted the data. Y.H.W plotted the figures, wrote the manuscript with comments and suggestions from all co-authors.
Reference


Schallhart, S., Rantala, P., Kajos, M. K., Aalto, J., Mammarella, I., Ruuskanen, T. M.


Figure 1 A schematic of the chamber setup and instruments used in the experiment.
Figure 2. The variation of total HOM concentration and alpha-pinene during four experiments where the 400 nm lights were decreased stepwise from 7 lights to 4, 2 and 1 light, respectively.
Figure 3. The variation of chlorine radical concentration as a function of lights. The input alpha-pinene concentration was kept constant throughout the experiments.
(a) 1 light

(b) 2 lights

(c) 4 lights
Figure 4. The mass spectra obtained by NO$_3$-CI-API-TOF during steady state with 1(a), 2(b), 4(c) and 7(d) lights. All peaks are detected as clusters with NO$_3$-. The spectra are plotted as unit mass resolution, with background signals removed, but the peak identifications (labeled in panel d) are based on high resolution analyses. The spectra correspond to the same four steady state conditions depicted in Fig. 2.
Figure 5. Proposed chemical pathways for chlorine radical oxidation of alpha-pinene, and subsequent autoxidation and HOM formation. The upper path shows the chlorine radical addition pathway, while the lower chain shows hydrogen atom abstraction pathway. In both cases, initially a C-centered radical forms (\(\text{C}_{10}\text{H}_{16}\text{Cl}\) or \(\text{C}_{10}\text{H}_{15}\)) to which \(\text{O}_2\) adds to form an initial peroxy radical. This peroxy radical may then undergo multi-step autoxidation to reach the example molecules \(\text{C}_{10}\text{H}_{16}\text{ClO}_{10}\) or \(\text{C}_{10}\text{H}_{15}\text{O}_{10}\) before termination. The observed HOM spectra in this study suggest a completely dominant role of the lower, H-abstraction, pathway for HOM formation.
Figure 6. Time series of selected closed-shell HOM monomers, dimers and an RO$_2$ radical (C$_{10}$H$_{15}$O$_{10}$) detected by NO$_3$-Cl-API-TOF as the lights increased from 0 to 1, 2, 4 and 7.
Figure 7. (a) Particle number size distribution measured by DMPS from 10 nm to 400 nm when the lights varied from 1 to 2, 4 and 7. (b) Time series of total number concentration (black) measured by DMPS, organic aerosol concentration (green) and particulate chloride concentration (pink) measured by AMS.
Figure 8. HOM mass spectrum during steady state alpha-pinene oxidation in the presence of 10 ppb NOx, with 7 lights switched on. In addition to molecules detected also in the experiments without NOx, several abundant organ nitrate peaks are formed. Note that a fluorinated compounds (FC) overlaps with the organ nitrate C\textsubscript{10}H\textsubscript{15}O\textsubscript{8}N at 339Th. All peaks are detected as clusters with NO\textsubscript{3}-.
Figure 9. Time series of (a) selected HOMs measured by NO$_3$-CI-L-API-TOF and (b) NO$_x$, a-pinene, ozone and NO, as the lights switched on from zero to 2, 4, and 7.
Figure 10. HOM loss rate ([HOM]*Kloss) as a function of the alpha-pinene oxidation rate. In steady state the loss rate equals the formation rate, and thus the slope of the points gives the molar yield of HOM from the alpha-pinene + Cl reaction. The data corresponds to the conditions with 1, 2, 4 and 7 lights switched on in the chamber, respectively. The slope indicates an average molar yield of HOMs of 1.8%.