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Photo-oxidation of pinonaldehyde at low NO$_x$: from chemistry to organic aerosol formation

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Abstract

Pinonaldehyde oxidation by OH radicals under low-NO_x conditions produces significant secondary organic aerosol (SOA) mass yields. Under concurrent UV illumination, mass yields are lower than high-NO_x yields published earlier by our group. However, when OH radicals are produced via dark ozonolysis the SOA mass yields are comparable at high and low NO_x. Because pinonaldehyde is a major first-generation gas-phase product of α-pinene oxidation by either ozone or OH radicals, its potential to form SOA serves as a molecular counterpoint to bulk SOA aging experiments involving SOA formed from α-pinene. Both the general tendency for aging reactions to produce more SOA and the sensitivity of the low-NO_x products to UV photolysis observed in the bulk clearly occur for this single species as well. Photochemical oxidation of pinonaldehye and analogous first-generation terpene oxidation products are potentially a significant source of additional SOA in biogenically influenced air masses.

1 Introduction

Particulate matter can have profound impacts on human health (Pope III and Dockery, 2006; Pope III et al., 2002) and mortality (Laden et al., 2006; Anderson, 2009), climate (IPCC, 2007), visibility (Watson, 2002) and ecosystems (Bytnerowicz et al., 2007). Secondary organic aerosol constitutes a significant portion of particulate matter mass ($PM_{2.5}$) (Kanakidou et al., 2005; Hallquist et al., 2009) and is a very dynamic part of the atmospheric aerosol system.

Organic aerosols are dynamic in part because the organic compounds that comprise it can undergo multiple generations of oxidation in the atmosphere. At each step, the reaction products will depend on ambient conditions, and yet most attention to date has focused on first-generation oxidation products. α-Pinene is the monoterpene with the highest estimated emissions (Griffin et al., 1999), and pinonaldehyde is one of the highest yield yet most volatile products of α-pinene oxidation by ozone and OH radicals, with molar yields ranging from 20–25 % (Hatakeyama et al., 1989; Hatakeyama et al., 1991). Pinonaldehyde is an excellent first-generation product to study because it can give insight into the chemistry and additional SOA formation potential of other products from monoterpene photo-oxidation. C_{10}-keto-aldehydes are one such example, since most have very similar chemical structures (Atkinson and Arey, 2003b, 1998; Grosjean et al., 1992; Larsen et al., 2001). There are also limited data on the chemistry of pinonaldehyde and chemically similar compounds in the literature (Glasius et al., 1997), though we recently described SOA chemistry under high-NO_x conditions (Chacon-Madrid and Donahue, 2011). It is also important to explore its chemistry in low-NO_x conditions, given that products of biogenic species are concentrated in areas where NO_x concentrations are low (Atkinson and Arey, 1998; Lelieveld et al., 2008). That is the focus here.

1.1 Pinonaldehyde as a key molecule

Due to the significant amount of non-methane hydrocarbon emissions in the form of monoterpenes (Fehsenfeld et al., 1992), it is important to study their later-generation photo-oxidation products and their ongoing contributions to organic-aerosol formation. By doing so, we can develop a better understanding of photo-chemical aerosol aging, which we define as the continuous photochemistry of progressively oxidized material either as vapors or part of aerosols (Chacon-Madrid and Donahue, 2011; Kroll et al., 2009; Jimenez et al., 2009; Rudich et al., 2007). Chemical Transport Models (CTMs) can benefit greatly by properly including SOA formation from biogenic later-generation products, especially since there has been an underestimation of organic aerosol formation from computer simulations (Carlton et al., 2010).

We concentrate on pinonaldehyde because of its high-yield formation as a product of α-pinene and its fast reactivity with the OH radical (Glasius et al., 1997). Its structure, presented in Fig. 1, consists of a C_{10}-keto-aldehyde constructed around a substituted cyclobutane. Similar structures can be found in other products of oxidation from different monoterpenes, such as caronaldehyde and limononaldehyde, among others

(Larsen et al., 2001; Lee et al., 2006; Hakola et al., 1994). Pinonaldehyde can therefore give us an understanding of SOA formation potential from other similar first-generation products of biogenic nature. Because it is relatively volatile and prone to fragmentation, it is in some sense a worst-case example of aging chemistry; if pinonaldehyde produces substantial SOA under both high- and low-NO_x conditions, it is extremely likely that many other less volatile first-generation α-pinene oxidation products will be as or more effective as sources of additional SOA.

1.2 Chemistry of aldehydes under low-NO_x conditions

OH + hydrocarbon chemistry at low NO_x is very different that at high NO_x. Notable differences are the absence of organic nitrate (R-ONO_2) formation at low NO_x and the strong production of hydroperoxides (ROOH) (Kroll and Seinfeld, 2008; Logan et al., 1981; Donahue and Prinn, 1993). Evidence of ROOH formation has been presented by Docherty et al. (2005) as well by Maksymiuk et al. (2009) in 2-D-NMR samples of terpene ozonolysis products, absent of NO_x.

The aldehydic hydrogen is the most reactive site in the pinonaldehyde molecule when attacked by the OH radical (Chacon-Madrid et al., 2010; Atkinson and Arey, 2003a). According to structure-reactivity relationships from Kwok and Atkinson, (1995), OH attacks the aldehydic hydrogen ∼79 % of the time versus ∼21 % in the rest of the molecule. Figure 2 presents a simplified reaction path of a generic aldehyde + OH. When aldehydes are attacked by the OH radical, an acyl-hydroperoxide (RC(O)OOH; blue structure, Fig. 2), also called peroxyacid, can be formed (Hasson et al., 2004; Crawford et al., 1999; Moortgat et al., 1989). Photolysis can then play an important role, however, breaking the acyl-hydroperoxide into an acyl-oxy radical (green structure, Fig. 2), which can also be formed from R(O)OO + RO_2.

The important characteristic of aldehyde + OH photo-oxidation, in the presence or absence of NO_x, is that it systematically forms first-generation products with one fewer carbon atoms. Under high-NO_x conditions *n*-aldehyde SOA mass yields are significantly smaller than yields from a similar vapor pressure *n*-alkane (Chacon-Madrid et al., 2010); yields are close to those for a much more volatile *n*-alkane with 1 carbon less than the aldehyde. It is one of our objectives to understand the importance of this fragmentation path under low-NO_x conditions.

1.3 Objectives

Our goals are to a) present SOA mass yields under low-NO_x conditions for pinonaldehyde over an atmospherically relevant range of organic aerosol concentrations (C_{OA}) and compare results to those of *n*-tridecanal and α-pinene for similar conditions, b) understand the difference in SOA mass yields for pinonaldehyde between low- and high-NO_x conditions, and c) determine whether first-generation products of biogenic photo-oxidation (such as pinonaldehyde) are significant additional contributors of SOA.

Comparison of *n*-tridecanal and pinonaldehyde gives us insight into the aldehydic moiety and its ability to form SOA under different concentrations of NO_x. α-Pinene and pinonaldehyde yields are compared to infer how much SOA is formed by first-generation products. We also determine SOA mass yields of pinonaldehyde in the dark, using tetramethylethylene (TME) + O_3 as a source of OH radical. A dark experiment allows us to determine the effect of UV lights on pinonaldehyde photo-oxidation.

2 Experimental

The experiments are conducted in the Carnegie Mellon University smog-chamber. The details of experimental procedures are described elsewhere (Hildebrandt et al., 2009). The FEP Teflon (Welch Fluorocarbon) chamber has a volume capacity between 10 and 12 m^3. The bag is suspended inside a temperature-controlled room, which is held at 295 K for all experiments described here. The experiments are conducted under low-NO_x conditions (< 10 ppb). Particle number and size distributions are monitored with a scanning mobility particle sizer (SMPS) operating in recirculation mode (TSI classifier model 3080, CPC model 3772 or 3010, 15–700 nm D_p). The concentrations of the gas-phase organic species are monitored with a unit mass-resolution proton transfer reaction-mass spectrometer (PTR-MS, Ionicon GmbH). For each experiment, hydrogen peroxide (H_2O_2, Sigma Aldrich, 50/50 in water) photolysis is used to create OH radicals, and the relative humidity is kept under ~20 %. Ammonium sulfate particles (Sigma Aldrich, 99.99 %) are used as inert seeds for condensation of low-volatility organic oxidation products. These are formed from an aqueous solution with a nebulizer (TSI 3075), then dried and neutralized. We use seed concentrations of $\sim 10^4$ particles cm^{-3} with mass in the range of ~10 to 20 $\mu\text{g m}^{-3}$. The organic species used are *n*-tridecanal (Alfa Aesar, 94 %), pinonaldehyde (synthesized in Carnegie Mellon Laboratory, ~85 %), and α-pinene (Sigma Aldrich, > 99 %). These molecules are all used without further purification. UV lights (General Electric 10526 black lights) with a $J_{\text{NO}_2} < 0.06\,\text{min}^{-1}$ are used for initiation and during photo-oxidation after all the components are mixed in the chamber. For dark experiments, tetratmethylethylene (TME, Aldrich, 99 %) ozonolysis was performed as a source of OH radicals (Lambe et al., 2007).

2.1 SOA mass yields and wall loss calculations

The SOA mass yield from a chemical precursor is calculated as the ratio of organic aerosol mass formed divided by the mass of precursor consumed (Odum et al., 1996),

$$Y = \frac{C_{\text{OA}}}{\Delta C_{\text{precursor}}} \tag{1}$$

C_{OA} is the organic aerosol mass formed, and $\Delta C_{\text{precursor}}$ is the mass of the precursor organic species consumed while forming C_{OA} and other, gas-phase products. We determined SOA mass yields for the different organic precursors based on volume growth of organic aerosol, measured with the SMPS, during each oxidation experiment.

Because Eq. (1) is a mass balance, one must account for organic aerosol mass losses during an experiment – especially wall losses. Suspended particles can deposit to the chamber walls, and condensable organic vapors can either condense onto those deposited particles, or they can be lost to the chamber walls. Here we assume that condensable vapors interact with particles deposited on the chamber walls, and that the mass growth of those deposited particles follows that of the suspended particles. In this case the total SOA production (C_{OA}) is determined by using the ratio of suspended organic aerosol ($C_{\mathrm{OA}}^{\mathrm{sus}}$) to suspended ammonium sulfate ($C_{\mathrm{seed}}^{\mathrm{sus}}$) and the initial concentration of ammonium sulfate $C_{\mathrm{seed}}^{\mathrm{sus}}(t=0)$, as described by Hildebrandt et al. (2009):

$$C_{\mathrm{OA}}(t) = \frac{C_{\mathrm{OA}}^{\mathrm{sus}}(t)}{C_{\mathrm{seed}}^{\mathrm{sus}}(t)} C_{\mathrm{seed}}^{\mathrm{sus}}(t=0) \qquad (2)$$

$C_{\mathrm{seed}}^{\mathrm{sus}}(t)$ is obtained by fitting an exponential decay to the ammonium sulfate volume concentration (measured with the SMPS and verified with a High Resolution-Aerosol Mass Spectrometer) over the interval between seed injection (and mixing) in the chamber and the onset of photo-oxidation. Extrapolation of this signal after the photo-oxidation process starts defines the seed mass concentration as a function of time.

At time 0 (onset of photo-oxidation) and later, the difference between the total aerosol mass concentration in the chamber (measured with an SMPS) and the extrapolated ammonium sulfate mass concentration is considered $C_{\mathrm{OA}}^{\mathrm{sus}}(t)$. To obtain the total $C_{\mathrm{OA}}(t)$ from the suspended mass concentration, we correct for wall losses, assuming that organic particles lost to the wall are in equilibrium with the suspended particles and vapor-phase species, and also that the organic to seed mass ratio remains the same for suspended and deposited particles. This is the upper-limit estimate for SOA production. There is approximately a 15 % difference in SOA mass yields for each species studied when assuming particles lost to the walls are in equilibrium with the suspended particles (upper limit) versus assuming that no further condensation occurs once particles have deposited (lower limit). This percentage has been observed in current and past experiments (Chacon-Madrid et al., 2010; Chacon-Madrid and Donahue, 2011).

The SOA mass yields in this work are presented using an aerosol density of unity ($1\,\mu g\,m^{-3}$).

2.2 Measurement of reactants

The concentrations of reactants are monitored with a unit mass-resolution PTR-MS. The fragments used to track concentrations are those of the MW + 1 or MW + 1–18 (dehydrated form) for *n*-tridecanal, pinonaldehyde and α-pinene. The PTR-MS sensitivity at these fragment masses was previously calibrated with those species. A key assumption is that interferences from other species were minimal.

We also use methanol as an OH radical tracer in all experiments. We measure it with the PTR-MS (at *m/z* 33) to determine the concentration of OH radicals during the experiments. OH concentrations and kinetic rate constants allow us to predict concentrations of the different precursors and compare with the initial decay of their respective MW + 1 or MW + 1–18 (dehydrated form). Methanol concentrations in all experiments are lower or equal to those of the precursor molecules, and methanol is also substantially less reactive with OH. Consequently the methanol has a minimal effect on the radical balance.

2.3 Synthesis of pinonaldehyde

We synthesize pinonaldehyde following McMurry et al. (1987), as it is not commercially available. Products are formed via ozonolysis in solution, as shown in Fig. A in the Supplement. α-Pinene (Sigma Aldrich, > 99 %) is used as the parent reactant for pinonaldehyde. The synthesis starts with formation of the secondary ozonide, which is kept stable by maintaining a temperature of −78 °C with a dry-ice ethanol slurry. After the ozonide is formed, dimethyl sulfide (DMS) is added to reduce the ozonide to pinonaldehyde. After adding DMS, the products are held at room temperature for about three hours, after which they are extracted with water to remove water-soluble contaminants. Finally, a simple distillation procedure vaporizes solvents and other volatile impurities.

We use Nuclear Magnetic Resonance (H NMR, HSQC and Tocsy) to determine products and yields from the synthesis. The spectra are shown in the Supplement, Figs. B and C.

3 Results

Following Odum et al. (1996), we plot SOA mass yields vs. the organic aerosol concentration (C_{OA}). In all experiments presented here there was no evidence for precursor decay before the onset of photochemistry and there was no evidence for delayed condensation of organic aerosol after the cessation of photochemistry. Both issues are important for the interpretation of accurate equilibrium mass yields. We observed no evidence of precursor wall losses, in contrast to the results presented in Matsunaga and Ziemann (2010). After injection into the smog chamber, precursor concentrations were monitored for about a half an hour before start of photo-oxidation with no evident decay. This is important because losses to the walls would suppress calculated SOA mass yields. The reproducibility and precision of the experiments can be observed in Fig. 3.

All experiments presented in this manuscript reached equilibrium between the organic aerosol-phase and the gas-phase within the experimental time frame. Specifically, particles grew rapidly during the first hour of each experiment due to the high OH radical concentration, but after the first hour or two of photo-oxidation, the particles stopped growing. There was no evidence for any substantial delay in condensational growth that would be associated with a significant delay in equilibration. The median particle diameters were thus stable following completion of the oxidation chemistry, and so we conclude that the gas and condensed-phases were in equilibrium, as any disequilibrium would constitute a driving force for condensation (or evaporation). This is consistent with other experiments performed in our laboratories (Pierce et al., 2008; Presto et al., 2005b). Consequently, we believe that there were no substantial mass-transfer limitations during these experiments that would affect our conclusions regard-

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ing the competition between fragmentation, functionalization and accretion effects on SOA formation.

SOA mass yields for pinonaldehyde and *n*-tridecanal under high- and low-NO_x conditions are presented in Fig. 3. In the same figure, a function from Presto et al. (2010) for *n*-pentadecane (blue) SOA mass yield under high-NO_x is presented for comparison. Mass yields are plotted as a function of the organic-aerosol concentration because the products are semi-volatile. The equilibrium partitioning between the gas and condensed phases drives yields up with increasing loading, as described by Odum et al. (1996). *n*-Pentadecane, pinonaldehyde, and *n*-tridecanal have similar vapor pressures, making their SOA mass yield comparison instructive. Contrasting species of similar vapor pressure can provide information regarding chemical paths, more specifically the competition between fragmentation, functionalization and accretion (Chacon-Madrid and Donahue, 2011; Kroll et al., 2009).

Because of the unusually high reactivity of the aldehydic moiety (Chacon-Madrid et al., 2010; Atkinson and Arey, 2003a) in the pinonaldehyde + OH reaction, it was important to compare with another aldehyde with similar vapor pressure – *n*-tridecanal. Low-NO_x yields for *n*-tridecanal for C_{OA} of $< 15\,\mu g\,m^{-3}$ are not presented due to a high degree of uncertainty and noise. An important feature of Fig. 3 is the similarity between the yields of pinonaldehyde and *n*-tridecanal under low- and high-NO_x conditions, supporting our conclusion that the two aldehydes have comparable chemistry. For both of the aldehydes discussed here, high-NO_x conditions enhance SOA yields with respect to low NO_x. This is in marked contrast to first-generation SOA yields from monoterpene ozonolysis, where yields are significantly higher under low-NO_x conditions (Presto et al., 2005a; Zhang et al., 2006; Ng et al., 2007).

4 Discussion

We shall start with a comparison of various precursors in Fig. 3, as this highlights the important similarities and differences of the chemistry.

4.1 Pinonaldehyde vs. *n*-tridecanal

The similarity at low NO_x between pinonaldehyde and *n*-tridecanal SOA yields can be explained by their similar first-generation chemistry and by the fact that both species possess similar vapor pressures ($\sim 10^5\,\mu g\,m^{-3}$). This similarity has also been observed under high-NO_x levels (Chacon-Madrid and Donahue, 2011), as shown in the Fig. 3 as well. The aldehydic hydrogen drives most of the first-generation chemistry for both species by OH abstraction, and the functional groups formed in subsequent chemistry are likely to be similar as well. Because the aldehydic moiety dominates the initial chemistry, structural differences between *n*-tridecanal (straight chain) and pinonaldehyde (characteristic cyclo-butane and a carbonyl) are not sufficient to result in different SOA mass yields.

4.2 Pinonaldehyde vs. *n*-pentadecane

These two molecules have similar vapor pressures of about $\sim 10^5\,\mu g\,m^{-3}$, but their chemistry is very different. *n*-Pentadecane, like many other large ($> C_7$) *n*-alkanes, goes through a similar mechanistic path when reacting with the OH radical; this path has been studied extensively (Atkinson, 2000; Atkinson and Arey, 2003a; Atkinson et al., 2008; Lim and Ziemann, 2005). The main feature of *n*-alkane first-generation chemistry is the efficient addition of oxygen to the carbon backbone by way of functionalization, mainly with carbonyls and alcohols, without suffering any major carbon-carbon fragmentation. This *n*-alkane mechanism results in products of much lower vapor pressure, enhancing SOA mass yields.

Aldehyde + OH chemistry is very different from that of *n*-alkanes. The first key difference is the high reactivity of the aldehydic hydrogen compared to $-CH_2-$ (methylene) groups in *n*-alkane carbon backbones. Consequently, most of the first-generation chemistry occurs by abstraction of the aldehydic hydrogen. According to Kwok and Atkinson (1995), the first-generation attack from the OH radical on pinonaldehyde occurs ~ 79 % of the time on the aldehydic hydrogen.

The OH attack on the aldehydic hydrogen leads to the eventual formation of an acyloxy radical (green structure, Fig. 2) either in the presence or absence of NO_x. This acyloxy radical can fragment easily, yielding CO_2 and C_{n-1} products (species with one less carbon). Our main conclusion is that even though there are differences in the pinonaldehyde + OH chemistry in the presence or absence of NO_x, both mechanisms systematically fragment the aldehyde precursor. This systematic fragmentation happens rapidly, suppressing SOA mass yields when compared to those of *n*-pentadecane, as seen in Fig. 3.

4.3 Pinonaldehyde: low and high NO_x

Even though both high- and low-NO_x pinonaldehyde experiments (Fig. 3) show lower SOA yields compared to *n*-pentadecane, there is a difference between them. Pinonaldehyde photo-oxidation at high NO_x results in higher SOA yields than at low NO_x. In order to understand this difference, it is important to distinguish between the products likely to be obtained in each case.

Major differences are the creation of hydroperoxides in the absence of NO_x and the formation of organic nitrates (mainly peroxyacyl nitrates or PANs) when NO_x is abundant. These two moieties, when added to a carbon backbone, can reduce its vapor pressure by roughly a factor of 300 (Pankow and Asher, 2008). They are both exceptions to the rule that aldehyde oxidation results in loss of a carbon atom, as both moieties protect the terminal carbon. However, for pinonaldehyde the PAN or peroxide products are predicted to have saturation concentrations in the order of $300\,\mu g\,m^{-3}$; too large to directly produce SOA in these experiments.

A major difference is that hydroperoxides (especially peroxyacids) are sensitive to UV-light photolysis (Presto et al., 2005b; Park et al., 2006; Henry and Donahue, 2012). When photolysis of a hydroperoxide bond occurs, an alkoxy radical is formed, which has the ability to fragment a C–C bond. Such fragmentation can increase the vapor pressure of products when compared to the products of high-NO_x chemistry. In order to test the effect of photolysis on SOA formation potential for pinonaldehyde photo-oxidation, an experiment was performed under low-NO_x conditions in the dark. A tetramethylethylene (TME) + O_3 reaction was used as a dark source of OH radical without introducing NO_x. The experimental details of TME + O_3 as a dark source of OH radical are explained in Lambe et al. (2007); TME + O_3 products do not contribute to SOA (Salo et al., 2011).

Figure 4 shows that low-NO_x pinonaldehyde SOA mass yields are higher in the dark than in the presence of ~350 nm UV light from our black lights (Presto et al., 2005b; Henry and Donahue, 2012). The difference in SOA mass yields between light and dark experiments is approximately 0.04 absolute yield units, and the dark, low-NO_x yields are similar to the (illuminated) high-NOx yields. A similar yield suppression by UV light was reported in Presto et al. (2005b) for α-pinene ozonolysis, and recently Henry and Donahue (2012) reported significant loss of later-generation low-NO_x SOA from α-pinene in the presence of the same UV lights (Henry and Donahue, 2012). The yield disparity shown here supports the hypothesis that hydroperoxide photolysis forms alkoxy radicals that can fragment carbon-carbon bonds, creating products of higher volatility.

4.4 α-pinene and pinonaldehyde

Figure 5 compares pinonaldehyde SOA yields to those from its parent molecule, α-pinene. This figure shows the importance of atmospheric chemical aging. It is clear that first-generation products such as pinonaldehyde are able to contribute to organic aerosol (Henry and Donahue, 2012; Donahue et al., 2012). Pinonaldehyde yields, both under high and low-NO_x conditions, are significant when compared to those of α-pinene + OH (Henry et al., 2012). High-NO_x yields (Chacon-Madrid and Donahue, 2011) are comparable to α-pinene, but even low-NO_x illuminated conditions result in yields that are discernibly higher than zero (almost 1/4 of α-pinene yields). This shows the importance of atmospheric chemical aging to organic aerosol formation. If a first-generation product from α-pinene + OH is able to produce significant SOA, it is likely that later-generation ones have also the potential to contribute to organic aerosol formation. This is especially important because organic aerosol material can last for about a week in the atmosphere (Wagstrom and Pandis, 2009; Balkanski et al., 1993), giving it sufficient time to add oxygens to carbon backbones, increasing total organic aerosol mass.

5 Environmental significance and conclusions

Atmospheric chemical aging mechanisms are challenging to understand due to their dynamic nature, but studying first-generation products can give us insight. Pinonaldehyde is able to form SOA under low-NO_x conditions, though less effectively than under high-NO_x conditions. This is especially important given that the pinonaldehyde + OH mechanism goes through a strong fragmentation path in its first-generation chemistry. The ability of pinonaldehyde to form organic aerosol shows that volatile products from α-pinene photo-oxidation can contribute to SOA, making a case for the importance of biogenic chemical aging. This is especially true since many monoterpene + OH products share similar chemical structures. Oxidation products from many terpenes are similar, and the current results hold for both pinonaldehyde and *n*-tridecanal, which are structurally quite different. Consequently, we are confident extrapolating our conclusions to terpenes as a whole.

SOA yields from pinonaldehyde + OH under UV light are lower at low NO_x than at high NO_x. This suppression can be explained by the susceptibility of hydroperoxides and peroxyacids – formed under low-NO_x conditions – to fragment, creating products of higher volatility. Strong evidence of this susceptibility to fragment in the presence of UV light was shown by performing an experiment in the dark, which produced more organic aerosol and higher yields.

In order to improve our understanding of atmospheric chemical aging from biogenic material, many more chemical species should be studied, especially later-generation products of monoterpene photo-oxidation. Studying the effect of NO_x and UV light on SOA formation is also important in order to understand the susceptibility of hydroperoxides and peroxyacids to fragment and suppress SOA yields in systems other than pinonaldehyde. Species from monoterpene oxidation with carboxylic acid functionality, such as *cis*-pinonic acid, should be studied in detail due to the ubiquity of such a moiety (Rudich et al., 2007).

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/12/7727/2012/ acpd-12-7727-2012-supplement.pdf.

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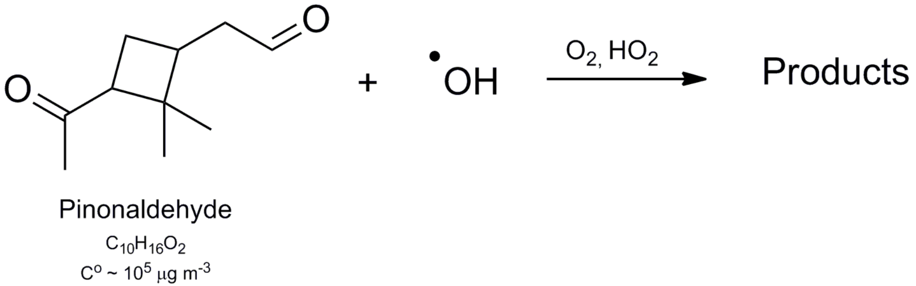

Fig. 1. Pinonaldehyde ($C_{10}H_{16}O_2$) is a C_{10}-keto-aldehyde structure with a characteristic cyclobutane. Similar structures can be found in other products of photo-oxidation from different monoterpenes. It is a highly reactive molecule, with an OH-radical lifetime in the order of hours.

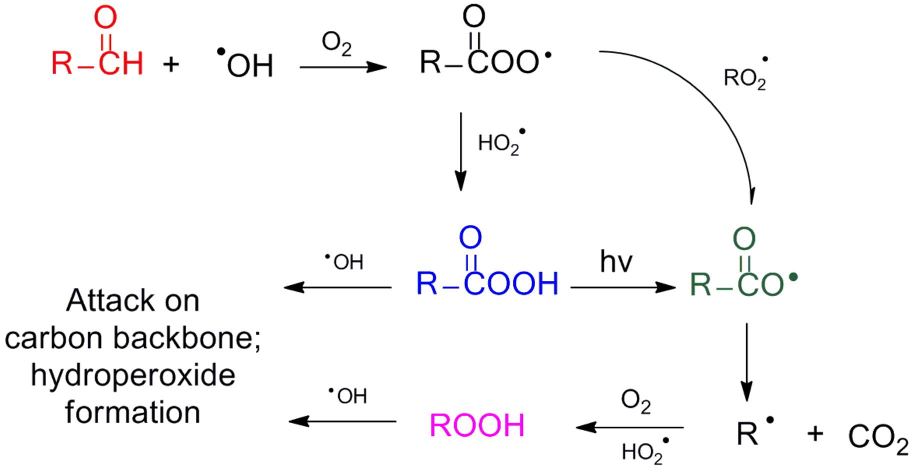

Fig. 2. A simplified aldehyde + OH radical chemical-path in the absence of NO_x. After the aldehyde (red structure) is attacked, an acyl-peroxy radical is formed. In the absence of NO_x, the acyl-peroxy radical forms a peroxyacid (blue structure) or an acyl-oxy radical (green structure) when reacting with HO_2 or RO_2, respectively. The acyl-oxy radical decomposes quickly, losing one carbon.

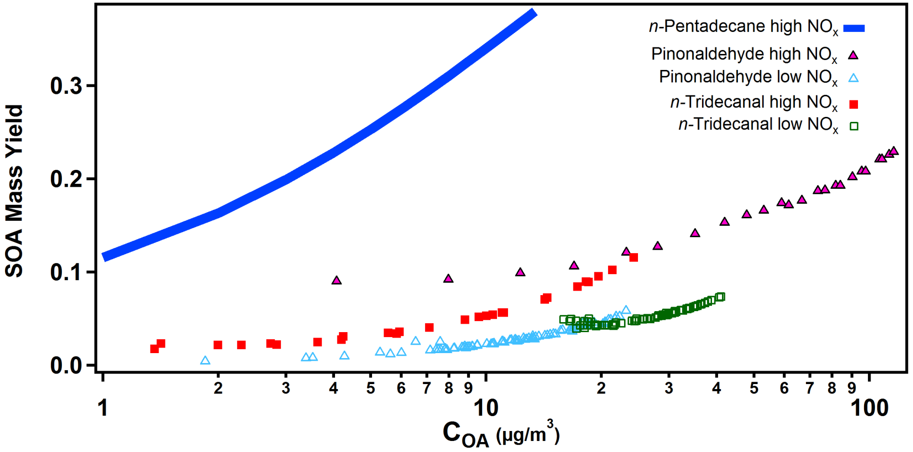

Fig. 3. Pinonaldehyde and *n*-tridecanal SOA mass yields at high and low NO_x. The potential to form organic aerosol from pinonaldehyde + OH – and *n*-tridecanal – is less than that from *n*-pentadecane + OH under high and low NO_x. *n*-Pentadecane yields come from Presto et al. (2010). Pinonaldehyde (triangles) and *n*-tridecanal (squares), independent from NO_x concentration, suffer fragmentation paths in its first-generation chemistry that limits its SOA formation potential. *n*-Alkanes such as *n*-pentadecane do not experience significant fragmentation in their first-generation chemistry (Lim and Ziemann, 2005).

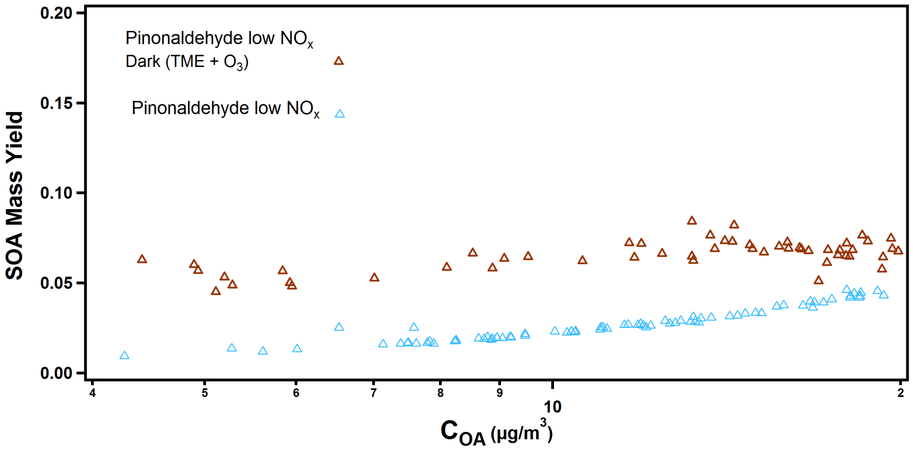

Fig. 4. Comparison between SOA mass yields of pinonaldehyde in the absence (brown) and presence (blue) of UV light, under low NO_x. In order to understand if the difference in pinonaldehyde SOA yields between low and high NO_x is due to photolysis of hydroperoxides and subsequent fragmentation, an experiment in the dark is performed. The dark experiment (no UV light) produces more SOA than the one where the oxidation reaction is exposed to UV lights. We can infer that UV light is responsible for fragmentation paths, and it is likely that the fragmentation happens on hydroperoxide moieties since the experiments are performed under low NO_x.

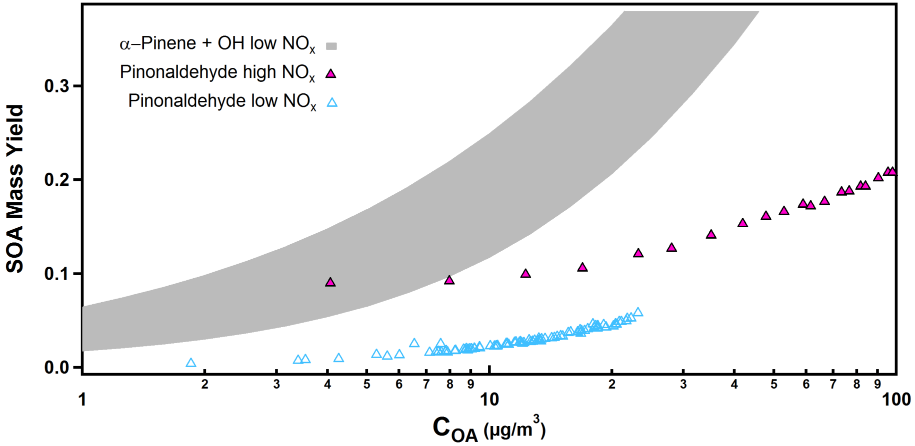

Fig. 5. Pinonaldehyde SOA yields in the context of α-pinene SOA yields. As a first-generation product from α-pinene + OH, pinonaldehyde can form SOA at lower yields than α-pinene itself. Nonetheless, the yields of pinonaldehyde, including low NO_x, are significant and higher than zero. This figure shows how later-generation species from α-pinene photo-oxidation are capable of forming SOA, making atmospheric chemical aging an important source of SOA.