



# Photo-oxidation of pinonaldehyde at low NO<sub>x</sub>: from chemistry to organic aerosol formation

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**Abstract.** Pinonaldehyde oxidation by OH radicals under low-NO<sub>x</sub> conditions produces significant secondary organic aerosol (SOA) mass yields. Under concurrent UV illumination, mass yields are lower than high-NO<sub>x</sub> 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<sub>x</sub>. Because pinonaldehyde is a major first-generation gas-phase product of  $\alpha$ -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  $\alpha$ -pinene. Both the general tendency for aging reactions to produce more SOA and the sensitivity of the low-NO<sub>x</sub> products to UV photolysis observed in the bulk clearly occur for this single species as well. Photochemical oxidation of pinonaldehyde and analogous first-generation terpene oxidation products are potentially a significant source of additional SOA in biogenically influenced air masses.

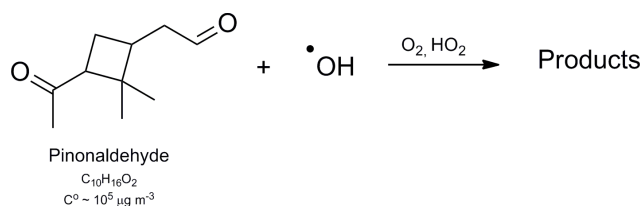
## 1 Introduction

Particulate matter can have profound impacts on human health (Pope and Dockery, 2006; Pope 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 (SOA) constitutes a significant portion of particulate matter mass (PM<sub>2.5</sub>) (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 them 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. 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 ongoing 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).

$\alpha$ -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  $\alpha$ -pinene oxidation by ozone and OH radicals, with molar yields ranging from 20–25 % (Hatakeyama et al., 1989, 1991). Pinonaldehyde is also highly reactive with the OH radical (Glaesius et al., 1997). Its structure, presented in Fig. 1, consists of a C<sub>10</sub>-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; however, there are limited data on the



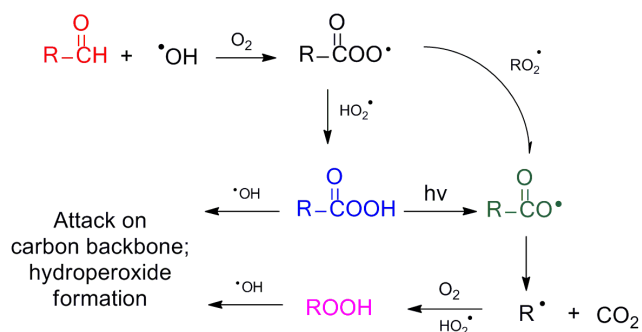
**Fig. 1.** Pinonaldehyde (C<sub>10</sub>H<sub>16</sub>O<sub>2</sub>) is a C<sub>10</sub>-keto-aldehyde structure with a characteristic cyclobutane ring. Similar structures can be found in other products of photo-oxidation from different monoterpenes. It is a highly reactive molecule, with a lifetime against reaction with OH radicals of order hours in the atmosphere.

chemistry of pinonaldehyde and similar compounds in the literature (Glasius et al., 1997).

Though we recently described SOA chemistry under high-NO<sub>x</sub> conditions (Chacon-Madrid and Donahue, 2011), it is important to explore its chemistry in low-NO<sub>x</sub> conditions because products of biogenic species are concentrated in areas where NO<sub>x</sub> concentrations are low (Atkinson and Arey, 1998; Lelieveld et al., 2008). Finally, because pinonaldehyde 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<sub>x</sub> 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.

Under high-NO<sub>x</sub> conditions, *n*-aldehyde SOA mass yields are significantly smaller than yields from similar saturation-concentration *n*-alkanes (Chacon-Madrid et al., 2010); SOA mass yields are close to those for a much more volatile *n*-alkane with 1 carbon less than the aldehyde. However, OH + hydrocarbon chemistry at low NO<sub>x</sub> is very different from that at high NO<sub>x</sub>. Notable differences are the absence of organic nitrate (R-ONO<sub>2</sub>) formation at low NO<sub>x</sub> and the strong production of hydroperoxides (ROOH) at low NO<sub>x</sub> (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 2D-NMR samples of terpene ozonolysis products formed without NO<sub>x</sub>.

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, 2003). 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 low-NO<sub>x</sub> reaction path of a generic aldehyde + OH reaction. When aldehydes are attacked by the OH radical, an acyl-hydroperoxide (RC(O)OOH; blue structure, Fig. 2), also called a 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



**Fig. 2.** A simplified aldehyde + OH radical chemical-path in the absence of NO<sub>x</sub>. After the aldehyde (red structure) is attacked, an acyl-peroxy radical is formed. In the absence of NO<sub>x</sub>, the acyl-peroxy radical forms a peroxyacid (blue structure) or an acyl-oxy radical (green structure) when reacting with HO<sub>2</sub> or RO<sub>2</sub>, respectively. The acyl-oxy radical decarboxylates quickly.

structure, Fig. 2), which can also be formed from R(O)OO + RO<sub>2</sub>. Our objective is to assess this general description in the context of low-NO<sub>x</sub> pinonaldehyde oxidation.

Here we shall present SOA mass yields under low-NO<sub>x</sub> conditions for pinonaldehyde over an atmospherically relevant range of organic aerosol concentrations (C<sub>OA</sub>) and compare results to those of *n*-tridecanal and α-pinene for similar conditions. By using both photolytic and dark OH radical sources we shall also explore the effect of photolysis on SOA formation from pinonaldehyde. We shall then explore the difference in SOA mass yields for pinonaldehyde between low- and high-NO<sub>x</sub> conditions, and show that first-generation products of biogenic photo-oxidation (such as pinonaldehyde) are significant additional contributors of SOA.

To isolate the specific effect of the aldehydic moiety at different NO<sub>x</sub> levels, we shall compare oxidation of *n*-tridecanal and pinonaldehyde. These two molecules have similar saturation concentrations and similar oxidation chemistry, and so by comparing SOA mass yield data under similar oxidation conditions for each we can also assess the repeatability of our experiments.

## 2 Experimental

The experiments were 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 had a volume capacity between 10 and 12 m<sup>3</sup>. The bag was suspended inside a temperature-controlled room, held at 295 K for all experiments described here. The experiments were conducted under low-NO<sub>x</sub> conditions (< 10 ppb). Particle number and size distributions were 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<sub>p</sub>). The concentrations of the gas-phase organic species

were monitored with a unit mass resolution proton transfer reaction mass spectrometer (PTR-MS, Ionicon GmbH). For each experiment, hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, Sigma Aldrich, 50/50 in water) photolysis was used to create OH radicals, and the relative humidity was kept under ~20%. Ammonium sulfate particles (Sigma Aldrich, 99.99%) were used as inert seeds for condensation of low-volatility organic oxidation products. These were formed from an aqueous solution with a nebulizer (TSI 3075), then dried and neutralized. We used seed concentrations of ~10<sup>4</sup> particles cm<sup>-3</sup> with mass in the range of ~10 to 20 μg m<sup>-3</sup>. UV lights (General Electric 10526 black lights) with a J<sub>NO<sub>2</sub></sub> < 3.6 h<sup>-1</sup> were used for initiation and during photo-oxidation after all the components were mixed in the chamber. For dark experiments, tetrathymethylene (TME, Aldrich, 99%) ozonolysis was employed as a source of OH radicals (Lambe et al., 2007). The organic species used were *n*-tridecanal (Alfa Aesar, 94%), pinonaldehyde (synthesized in Carnegie Mellon Laboratory, ~85%), and α-pinene (Sigma Aldrich, > 99%). These molecules were all used without further purification.

## 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

$$Y = \frac{C_{\text{OA}}}{\Delta C_{\text{prec}}} \quad (1)$$

$C_{\text{OA}}$  is the organic aerosol mass formed, and  $\Delta C_{\text{prec}}$  is the mass of the precursor organic species consumed while forming  $C_{\text{OA}}$  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 ( $C_{\text{OA}}$ ) is determined by using the ratio of suspended organic aerosol ( $C_{\text{OA}}^{\text{sus}}$ ) to suspended ammonium sulfate ( $C_{\text{seed}}^{\text{sus}}$ ) and the initial concentration of ammonium sulfate  $C_{\text{seed}}^{\text{sus}}(t=0)$ , as described by Hildebrandt et al. (2009):

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

$C_{\text{seed}}^{\text{sus}}(t)$  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  $t=0$  (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  $C_{\text{OA}}^{\text{sus}}(t)$ . To obtain the total  $C_{\text{OA}}(t)$  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 assumed aerosol density of 1 g cm<sup>-3</sup>.

The experiments described here were part of a series of experiments designed to probe the influence of precursor composition and reaction conditions on SOA mass yields, with emphasis on the competition between reaction pathways that functionalize the carbon backbone and those that fragment it. Previous studies in our laboratory have shown repeatability in SOA formation experiments via OH reaction of better than 50% ( $\times/\div 1.5$ ) at low SOA loadings (Hildebrandt et al., 2009; Henry et al., 2012; Chacon-Madrid and Donahue, 2011), including for aldehydes. We thus elected to use the available chamber time to vary reagents and conditions rather than repeat experiments, as the yield variations described below are substantially larger than those limits.

## 2.2 Measurement of reactants

The concentrations of reactants were monitored with a unit mass-resolution PTR-MS. The fragments used to track concentrations were 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.

We also used methanol as an OH radical tracer in all experiments. We measured methanol 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 were lower than or equal to

those of the precursor molecules, and methanol is also substantially less reactive with OH. Consequently the methanol had a minimal effect on the radical balance. There is no evidence for interference from isobaric ions for either the precursors or the OH tracer; they are the dominant gas-phase organics, and the observed precursor decay matches that expected based on the inferred OH concentration. This is discussed in detail in Chacon-Madrid et al. (2010) in Fig. 5 and Fig. A.

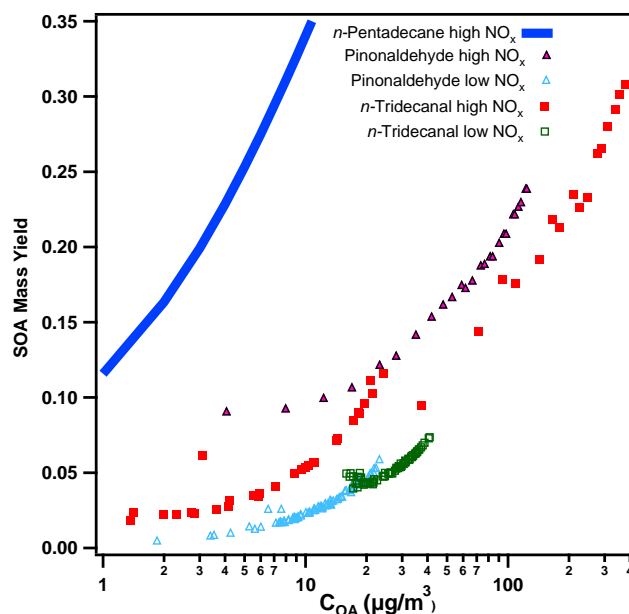
### 2.3 Synthesis of pinonaldehyde

We synthesized pinonaldehyde following McMurry and Bosch (1987), as it is not commercially available. Products were formed via ozonolysis in solution, as shown in Fig. A in the Supplement.  $\alpha$ -Pinene (Sigma Aldrich, > 99 %) was used as the parent reactant for pinonaldehyde. The synthesis started with formation of the secondary ozonide, which was kept stable by maintaining a temperature of  $-78^{\circ}\text{C}$  with a dry-ice ethanol slurry. After ozonide formation, dimethyl sulfide (DMS) was added to reduce the ozonide to pinonaldehyde. After adding DMS, the products were held at room temperature for about three hours, after which they were extracted with water to remove water-soluble contaminants. Finally, a simple distillation procedure vaporized solvents and other volatile impurities. We used Nuclear Magnetic Resonance (Proton NMR, Heteronuclear Single-Quantum Correlation, and Total Correlation Spectroscopy) to determine products and yields from the synthesis. The dominant impurity was DMSO. 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 ( $C_{\text{OA}}$ ). 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.

Matsunaga and Ziemann (2010) have shown that oxidized organic vapors may be lost to Teflon chamber walls. Losses to the walls would suppress calculated SOA mass yields. To test for this, at the beginning of each experiment the precursor concentration was monitored for 30 min before start of photo-oxidation, with no evident decay. The reproducibility and precision of the experiments can be observed in Fig. 3. In the Supplement, Fig. E, we also show a sample experiment where different *n*-aldehyde vapors were injected to the smog chamber and their concentrations remained stable for roughly 1 hour to within the precision of the PTRMS signal; we did not observe dramatic losses for these aldehydes, though very rapid equilibration with the chamber walls can-



**Fig. 3.** Pinonaldehyde and *n*-tridecanal SOA mass yields at high and low NO<sub>x</sub>. The potential to form organic aerosol from pinonaldehyde + OH and *n*-tridecanal + OH is less than that from *n*-pentadecane + OH under high and low NO<sub>x</sub>. All precursors have similar volatility. *n*-Pentadecane yields come from Presto et al. (2010). Pinonaldehyde (triangles) and *n*-tridecanal (squares), regardless of NO<sub>x</sub> concentration, suffer fragmentation paths in their first-generation chemistry, reducing their SOA formation potential. *n*-Alkanes such as *n*-pentadecane do not experience significant fragmentation in their first-generation chemistry (Lim and Ziemann, 2005).

not be ruled out. Finally, particle diameters were generally stable after the end of photo-oxidation when we were constraining particle wall deposition. We thus see no evidence for significant vapor wall losses, especially considering that the conclusions of this work derive from *relative* SOA mass yields under different conditions.

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, when OH levels were much lower, 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, despite intriguing reports of disequilibrium behavior in SOA systems (Perraud et al., 2012), we

conclude that there were no substantial mass-transfer limitations during these experiments and that an equilibrium interpretation is valid. Regardless of the theoretical context used to interpret our observations, the main issue is the relative formation of SOA under different conditions from various precursors.

SOA mass yields for pinonaldehyde and *n*-tridecanal under high- and low-NO<sub>x</sub> conditions are presented in Fig. 3. In the same figure, we present a function from Presto et al. (2010) for *n*-pentadecane (blue) SOA mass yield under high-NO<sub>x</sub>. Mass yields are plotted as a function of the organic-aerosol concentration because the products are often 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 saturation concentrations, making their SOA mass yield comparison informative. Contrasting precursors of similar saturation concentrations 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, 2003) in the pinonaldehyde + OH reaction, it was important to compare with another aldehyde with a similar saturation concentration – *n*-tridecanal. Figure 3 shows that the SOA mass yields from pinonaldehyde and *n*-tridecanal are broadly similar under low- and high-NO<sub>x</sub> conditions, supporting our conclusion that the two aldehydes have similar chemistry. Low-NO<sub>x</sub> SOA mass yields for *n*-tridecanal for C<sub>OA</sub> of <15 μg m<sup>-3</sup> are not presented due to a high degree of uncertainty and noise. The high-NO<sub>x</sub> data have been reported before (Chacon-Madrid and Donahue, 2011); the new results are the low-NO<sub>x</sub> data. For both of the aldehydes, SOA mass yields under low-NO<sub>x</sub> conditions are substantially (a factor of two) lower than under high-NO<sub>x</sub> conditions. This is in marked contrast to first-generation SOA yields from monoterpene ozonolysis, where mass yields are significantly higher under low-NO<sub>x</sub> conditions (Presto et al., 2005a; Zhang et al., 2006; Ng et al., 2007a).

## 4 Discussion

The data presented in Fig. 3 include SOA formed from several precursors under different conditions. We shall focus on several individual comparisons to highlight the important features of those data.

### 4.1 Pinonaldehyde vs. *n*-tridecanal

The similarity at low NO<sub>x</sub> between pinonaldehyde and *n*-tridecanal SOA mass yields can be explained by their similar first-generation chemistry and by the fact that both precur-

sors have similar saturation concentrations ( $\sim 10^5 \mu\text{g m}^{-3}$ ). OH abstraction from the aldehydic hydrogen drives most of the first-generation chemistry for both species, and the functional groups formed subsequently 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 cyclobutane and a carbonyl) are not sufficient to result in substantially different SOA mass yields.

### 4.2 Pinonaldehyde vs. *n*-pentadecane

These two molecules have similar saturation concentrations of about  $\sim 10^5 \mu\text{g m}^{-3}$ , but their chemistry is very different. *n*-Pentadecane, like many other large (> C<sub>7</sub>) *n*-alkanes, follows a characteristic mechanism when reacting with the OH radical; this has been studied extensively (Atkinson, 2000; Atkinson and Arey, 2003; 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 any major carbon-carbon fragmentation. This *n*-alkane mechanism results in much lower saturation concentration products than for pinonaldehyde, resulting in higher 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<sub>2</sub>– (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  $\sim 79\%$  of the time on the aldehydic hydrogen.

The OH attack on the aldehydic hydrogen leads to the eventual formation of an acyl-oxy radical (green structure, Fig. 1) either in the presence or absence of NO<sub>x</sub>. This acyl-oxy radical can fragment easily, yielding CO<sub>2</sub> and C<sub>*n*-1</sub> 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<sub>x</sub>, both mechanisms systematically cleave the aldehyde moiety. This suppresses the SOA mass yields compared to those of *n*-pentadecane, as seen in Fig. 3. While this is more or less obvious for high-NO<sub>x</sub> conditions, it is potentially more surprising under low-NO<sub>x</sub> conditions, where one might hypothesize that any SOA formation would be dominated by hydroperoxide formation from RO<sub>2</sub> species regardless of the identity of the carbon backbone.

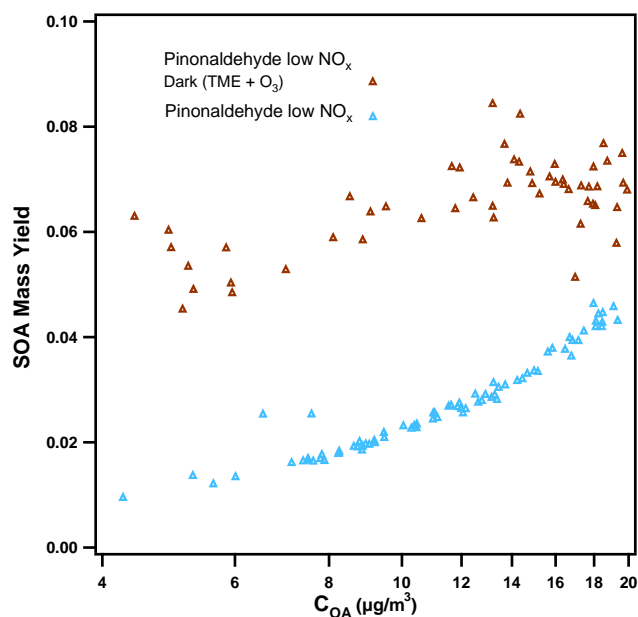
### 4.3 Pinonaldehyde: low and high NO<sub>x</sub>

Even though both high- and low-NO<sub>x</sub> pinonaldehyde oxidation experiments (Fig. 3) show lower SOA mass yields compared to *n*-pentadecane, there is a difference between them. Pinonaldehyde photo-oxidation at high NO<sub>x</sub> results in higher

SOA yields than at low NO<sub>x</sub>. 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<sub>x</sub> and the formation of organic nitrates (mainly peroxyacyl nitrates or PANs) when NO<sub>x</sub> is abundant. Either moiety, when added to a carbon backbone, can reduce its saturation concentration 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, while at least temporarily terminating the radical oxidation sequence. However, for pinonaldehyde the PAN or peroxide products are predicted to have saturation concentrations in the order of 300 μg m<sup>-3</sup>, too large to directly produce SOA in these experiments; consequently it is either subsequent chemistry or minor products that must dominate the SOA formation.

SOA formed under low-NO<sub>x</sub> conditions is sensitive to UV-light photolysis (Presto et al., 2005b; Lee et al., 2006; Park et al., 2006; Henry et al., 2012). Previous experiments in our laboratory have shown that low-NO<sub>x</sub> SOA formation from α-pinene ozonolysis is cut in half in the presence of UV illumination vs dark conditions when SOA loadings are below 10 μg m<sup>-3</sup> (Presto et al., 2005b), and also that SOA growth for the same system under further aging by OH radicals can be halted or even reversed by UV illumination (Henry and Donahue, 2012b). The UV effect is evidently rapid, occurring only if UV light is present during SOA formation from pure ozonolysis (Presto et al., 2005b) and destroying SOA at a rate of ~0.2 h<sup>-1</sup> (2% jNO<sub>2</sub>) after (or during) OH aging of α-pinene SOA (Henry and Donahue, 2012a). Similar rapid loss has also been reported for SOA formed from isoprene in the absence of NO<sub>x</sub> (Kroll et al., 2006).

In order to test the effect of photolysis on SOA formation potential for pinonaldehyde photo-oxidation, an experiment was performed under low-NO<sub>x</sub> conditions in the dark. We used ozonolysis of tetramethylethylene (TME) as a dark source of OH radicals without introducing NO<sub>x</sub>. The experimental details of TME + O<sub>3</sub> as a dark source of OH are explained in Lambe et al. (2007); TME + O<sub>3</sub> products do not contribute to SOA (Salo et al., 2011), and we did not observe any pinonaldehyde loss in the presence of ozone before TME addition. Figure 4 shows that low-NO<sub>x</sub> 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, 2012a). The difference in SOA mass yields between light and dark experiments is approximately 0.04 absolute yield units, and the dark, low-NO<sub>x</sub> yields are similar to the (illuminated) high-NO<sub>x</sub> yields. Mass yields are enhanced by roughly a factor of three at a 10 μg m<sup>-3</sup> mass loading, well above the repeatability threshold for SOA formation experiments we have conducted over the years. The UV effect we observe for pinonaldehyde SOA is consistent with the effect reported by Presto et al. (2005b) and Henry and Donahue (2012a).

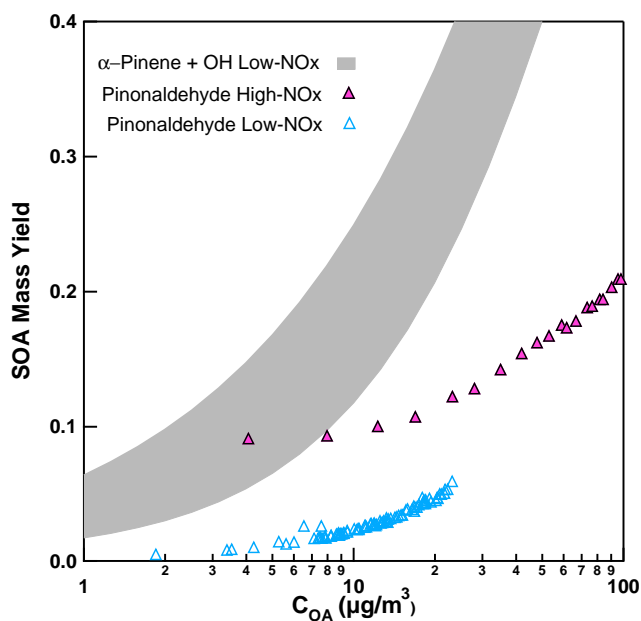


**Fig. 4.** Comparison between SOA mass yields of pinonaldehyde in the absence (brown) and presence (blue) of UV light, at low NO<sub>x</sub>. SOA formation is enhanced by approximately 0.04 (absolute units) using a dark OH source compared with OH formed from HOOH photolysis. This is consistent with UV photolysis destroying SOA-forming products.

The flat SOA mass yields vs C<sub>OA</sub> observed in Fig. 4, for the dark-pinonaldehyde low-NO<sub>x</sub> experiment (C<sub>OA</sub> > 10 μg m<sup>-3</sup>) are consistent with a system that creates a very low-volatility product and few semi-volatiles over the C<sub>OA</sub> range of the experiment. This may well be a higher molecular weight association product (oligomer) that is susceptible to photolytic cleavage. Flat SOA mass yields have been reported in other experiments such as toluene and *m*-xylene oxidation at high NO<sub>x</sub> (Ng et al., 2007b).

#### 4.4 α-pinene and pinonaldehyde

Figure 5 compares SOA mass yields from pinonaldehyde oxidation with mass yields from OH oxidation of its parent molecule, α-pinene. It is clear that first-generation α-pinene oxidation products such as pinonaldehyde are also able to contribute to organic aerosol (Henry et al., 2012; Donahue et al., 2012). Pinonaldehyde SOA mass yields, both under high and low-NO<sub>x</sub> conditions, are significant when compared to those of α-pinene + OH (Henry et al., 2012). High-NO<sub>x</sub> yields (Chacon-Madrid and Donahue, 2011) are similar to those from α-pinene, but even low-NO<sub>x</sub> illuminated conditions result in mass yields that are discernibly higher than zero (almost 1/4 of α-pinene mass yields). This shows the importance of atmospheric chemical aging to organic aerosol formation. If the most volatile first-generation product from α-pinene oxidation is able to produce significant SOA, it is



**Fig. 5.** Pinonaldehyde SOA yields in the context of  $\alpha$ -pinene SOA yields. As a first-generation product from  $\alpha$ -pinene + OH, pinonaldehyde forms SOA as well, though at lower yields than  $\alpha$ -pinene itself. Nonetheless, the yields of pinonaldehyde, including low NO<sub>x</sub>, are significant and higher than zero.

likely that later-generation products also have the potential to contribute to organic aerosol formation. This is especially important because organic aerosol can last for about a week in the atmosphere (Wagstrom and Pandis, 2009; Balkanski et al., 1993), giving it sufficient time to add oxygen containing functional groups to carbon backbones, increasing total organic aerosol mass.

## 5 Environmental significance and conclusions

Atmospheric chemical aging of organic aerosol is a challenging problem because the relatively large molecules involved lead to a huge number of products formed via complex, branched mechanisms. Aging experiments on bulk SOA are one avenue (Donahue et al., 2012), but studying selected first-generation products can give us insight as well. Pinonaldehyde is able to form SOA under low-NO<sub>x</sub> conditions, though less effectively than under high-NO<sub>x</sub> conditions. This is especially important given that pinonaldehyde is the most volatile major first-generation product of  $\alpha$ -pinene oxidation and the pinonaldehyde + OH mechanism goes through a strong fragmentation path in its first-generation chemistry. The ability of pinonaldehyde to form a significant amount of organic aerosol shows that volatile products from  $\alpha$ -pinene photo-oxidation can contribute to SOA, making a case for the importance of chemical aging for biogenic SOA. Oxidation products from many terpenes are similar, and the current results hold for both pinonaldehyde and *n*-tridecanal, which

are structurally quite different. Consequently, these conclusions should extend to terpenes as a whole.

SOA yields from pinonaldehyde + OH under UV light are lower at low NO<sub>x</sub> than at high NO<sub>x</sub>. This suppression can be explained by the susceptibility of some SOA formed at low NO<sub>x</sub> to photolysis. 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. The observed photolysis at low NO<sub>x</sub> indicates that SOA chemistry may be highly dynamic; aging reactions can enhance SOA levels, but they can also destroy SOA via fragmentation. Because the photolysis appears to be associated with low-NO<sub>x</sub> conditions, and because NO<sub>x</sub> is associated with human activity, this observation also suggests an intriguing connection between SOA formation from biogenic precursors and persistence of that SOA associated with human activity.

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<sub>x</sub> 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. Furthermore, other species from monoterpene oxidation with carboxylic acid functionality, such as *cis*-pinonic acid, should be studied in detail due to the ubiquity of acid moieties in organic aerosol (Rudich et al., 2007).

**Supplementary material related to this article is available online at:** <http://www.atmos-chem-phys.net/13/3227/2013/acp-13-3227-2013-supplement.pdf>.

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## References

- Anderson, H. R.: Air pollution and mortality: A history, *Atmos. Environ.*, 43, 142–152, 2009.
- Atkinson, R.: Atmospheric chemistry of VOCs and NO<sub>x</sub>, *Atmos. Environ.*, 34, 2063–2101, 2000.
- Atkinson, R. and Arey, J.: Atmospheric Chemistry of Biogenic Organic Compounds, *Accounts Chem. Res.*, 31, 574–583, 1998.
- Atkinson, R. and Arey, J.: Atmospheric Degradation of Volatile Organic Compounds, *Chem. Rev.*, 103, 4605–4638, 2003.
- Atkinson, R., Arey, J., and Aschmann, S. M.: Atmospheric chemistry of alkanes: Review and recent developments, *Atmos. Environ.*, 42, 5859–5871, 2008.

- Balkanski, Y. J., Jacob, D. J., Gardner, G. M., Graustein, W. C., and Turekian, K. K.: Transport and Residence Times of Tropospheric Aerosols Inferred from a Global Three-Dimensional Simulation of <sup>210</sup>Pb, *J. Geophys. Res.*, 98, 20573–20586, 1993.
- Bytnerowicz, A., Omasa, K., and Paoletti, E.: Integrated effects of air pollution and climate change on forests: A northern hemisphere perspective, *Environ. Pollut.*, 147, 438–445, 2007.
- Carlton, A. G., Bhawe, P. V., Napelenok, S. L., Edney, E. O., Sarwar, G., Pinder, R. W., Pouliot, G. A., and Houyoux, M.: Model Representation of Secondary Organic Aerosol in CMAQv4.7, *Environ. Sci. Technol.*, 44, 8553–8560, 2010.
- Chacon-Madrid, H. J. and Donahue, N. M.: Fragmentation vs. functionalization: chemical aging and organic aerosol formation, *Atmos. Chem. Phys.*, 11, 10553–10563, doi:10.5194/acp-11-10553-2011, 2011.
- Chacon-Madrid, H. J., Presto, A. A., and Donahue, N. M.: Functionalization vs. Fragmentation: *n*-Aldehyde Oxidation Mechanisms and Secondary Organic Aerosol Formation, *Phys. Chem. Chem. Phys.*, 12, 13975–13982, 2010.
- Crawford, M. A., Wallington, T. J., Szente, J. J., Maricq, M. M., and Francisco, J. S.: Kinetics and Mechanism of the Acetylperoxy + HO<sub>2</sub> Reaction, *J. Phys. Chem. A*, 103, 365–378, 1999.
- Docherty, K. S., Wu, W., Lim, Y. B., and Ziemann, P. J.: Contributions of Organic Peroxides to Secondary Aerosol Formed from Reactions of Monoterpenes with O<sub>3</sub>, *Environ. Sci. Technol.*, 39, 4049–4059, 2005.
- Donahue, N. M. and Prinn, R. G.: In Situ Nonmethane Hydrocarbon Measurements on SAGA 3, *J. Geophys. Res.*, 98, 16915–16932, 1993.
- Donahue, N. M., Henry, K. M., Mentel, T. F., Kiendler-Scharr, A., Spindler, C., Bohn, B., Brauers, T., Dorn, H. P., Fuchs, H., Tillmann, R., Wahner, A., Saathoff, H., Naumann, K.-H., Möhler, O., Leisner, T., Müller, L., Reinnig, M.-C., Hoffmann, T., Salo, K., Hallquist, M., Frosch, M., Bilde, M., Tritscher, T., Barmet, P., Praplan, A. P., DeCarlo, P. F., Dommen, J., Prévôt, A. S. H., and Baltensperger, U.: Aging of biogenic secondary organic aerosol via gas-phase OH radical reactions, *Proc. Natl. Acad. Sci.*, 109, 13503–13508 doi:10.1073/pnas.1115186109, 2012.
- Fehsenfeld, F., Calvert, J., Fall, R., Goldan, P., Guenther, A. B., Hewitt, C. N., Lamb, B., Liu, S., Trainer, M., Westberg, H., and Zimmerman, P.: Emissions of volatile organic compounds from vegetation and the implications for atmospheric chemistry, *Global Biochem. Cy.*, 6, 389–430, 1992.
- Glasius, M., Calogirou, A., Jensen, N. R., Hjorth, J., and Nielsen, C. J.: Kinetic Study of Gas-Phase Reactions of Pinonaldehyde and Structurally Related Compounds, *Int. J. Chem. Kinet.*, 29, 527–533, 1997.
- Griffin III, R. J., D. R. C., Seinfeld, J. H., and Dabdub, D.: Estimate of global atmospheric organic aerosol from oxidation of biogenic hydrocarbons, *Geophys. Res. Lett.*, 26, 2721–2724, 1999.
- Hakola, H., Arey, J., Aschmann, S. M., and Atkinson, R.: Product formation from the gas-phase reactions of OH radicals and O<sub>3</sub> with a series of monoterpenes, *J. Atmos. Chem.*, 18, 75–102, 1994.
- Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M., Dommen, J., Donahue, N. M., George, C., Goldstein, A. H., Hamilton, J. F., Herrmann, H., Hoffmann, T., Iinuma, Y., Jang, M., Jenkin, M. E., Jimenez, J. L., Kiendler-Scharr, A., Maenhaut, W., McFiggans, G., Mentel, T. F., Monod, A., Prévôt, A. S. H., Seinfeld, J. H., Surratt, J. D., Szmigielski, R., and Wildt, J.: The formation, properties and impact of secondary organic aerosol: current and emerging issues, *Atmos. Chem. Phys.*, 9, 5155–5236, doi:10.5194/acp-9-5155-2009, 2009.
- Hasson, A. S., Tyndall, G. S., and Orlando, J. J.: A Product Yield Study of the Reaction of HO<sub>2</sub> Radicals with Ethyl Peroxy (C<sub>2</sub>H<sub>5</sub>O<sub>2</sub>), Acetyl Peroxy (CH<sub>3</sub>C(O)O<sub>2</sub>), and Acetonyl Peroxy (CH<sub>3</sub>C(O)CH<sub>2</sub>O<sub>2</sub>) Radicals, *J. Phys. Chem. A*, 108, 5979–5989, 2004.
- Hatakeyama, S., Izumi, K., Fukuyama, T., and Akimoto, H. j.: Reactions of Ozone with *a*-Pinene and *b*-Pinene in Air: Yields of Gaseous and Particulate Products, *J. Geophys. Res.*, 94, 13013–13024, 1989.
- Hatakeyama, S., Izumi, K., Fukuyama, T., Akimoto, H., and Washida, N.: Reactions of OH with *a*-Pinene and *b*-Pinene in Air: Estimate of Global Co Production from the Atmospheric Oxidation of Terpenes, *J. Geophys. Res.*, 96, 947–958, 1991.
- Henry, K. M. and Donahue, N. M.: Photochemical Aging of *α*-Pinene Secondary Organic Aerosol: Effects of OH Radical Sources and Photolysis, *J. Phys. Chem. A*, 116, 5932–5940, doi:10.1021/jp210288s, 2012a.
- Henry, K. M. and Donahue, N. M.: Photochemical Aging of *α*-Pinene Secondary Organic Aerosol: Effects of OH Radical Sources and Photolysis, *J. Phys. Chem. A*, 116, 5932–5940, 2012b.
- Henry, K. M., Lohaus, T., and Donahue, N. M.: Organic Aerosol Yields from *α*-Pinene Oxidation: Bridging the Gap between First-Generation Yields and Aging Chemistry, *Environ. Sci. Technol.*, 46, 12347–12354, 2012.
- Hildebrandt, L., Donahue, N. M., and Pandis, S. N.: High formation of secondary organic aerosol from the photo-oxidation of toluene, *Atmos. Chem. Phys.*, 9, 2973–2986, doi:10.5194/acp-9-2973-2009, 2009.
- IPCC: Climate change 2007, The Physical Science Basis, Contribution of Working Group I to the Fourth Assessment Report of the IPCC, 2007.
- Jimenez, J. L., Canagaratna, M. R., Donahue, N. M., Prevot, A. S. H., Zhang, Q., Kroll, J. H., DeCarlo, P. F., Allan, J. D., Coe, H., Ng, N. L., Aiken, A. C., Docherty, K. S., Ulbrich, I. M., Grieshop, A. P., Robinson, A. L., Duplissy, J., Smith, J. D., Wilson, K. R., Lanz, V. A., Hueglin, C., Sun, Y. L., Tian, J., Laaksonen, A., Raatikainen, T., Rautiainen, J., Vaattovaara, P., Ehn, M., Kulmala, M., Tomlinson, J. M., Collins, D. R., Cubison, M. J., E, Dunlea, J., Huffman, J. A., Onasch, T. B., Alfarra, M. R., Williams, P. I., Bower, K., Kondo, Y., Schneider, J., Drewnick, F., Borrmann, S., Weimer, S., Demerjian, K., Salcedo, D., Cottrell, L., Griffin, R., Takami, A., Miyoshi, T., Hatakeyama, S., Shimojo, A., Sun, J. Y., Zhang, Y. M., Dzepina, K., Kimmel, J. R., Sueper, D., Jayne, J. T., Herndon, S. C., Trimborn, A. M., Williams, L. R., Wood, E. C., Middlebrook, A. M., Kolb, C. E., Baltensperger, U., and Worsnop, D. R.: Evolution of Organic Aerosols in the Atmosphere, *Science*, 326, 1525–1529, 2009.
- Kanakidou, M., Seinfeld, J. H., Pandis, S. N., Barnes, I., Dentener, F. J., Facchini, M. C., Dingenen, R. V., B. Ervens, A. N., Nielsen, C. J., Swietlicki, E., Putaud, J. P., Balkanski, Y., Fuzzi, S., Horth, J., Moortgat, G. K., Winterhalter, R., Myhre, C. E. L., Tsigaridis, K., Vignati, E., Stephanou, E. G., and Wilson, J.: Organic aerosol and global climate modelling: a review, *Atmos. Chem. Phys.*, 5,



- 1053–1123, doi:10.5194/acp-5-1053-2005, 2005.
- Kroll, J. H. and Seinfeld, J. H.: Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere, *Atmos. Environ.*, 42, 3593–3624, 2008.
- Kroll, J. H., Ng, N. L., Murphy, S. M., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from isoprene photooxidation, *Environ. Sci. Technol.*, 40, 1869–1877, 2006.
- Kroll, J. H., Smith, J. D., Che, D. L., Kessler, S. H., Worsnop, D. R., and Wilson, K. R.: Measurement of fragmentation and functionalization pathways in the heterogeneous oxidation of oxidized organic aerosol, *Phys. Chem. Chem. Phys.*, 11, 8005–8014, 2009.
- Kwok, E. S. C. and Atkinson, R.: Estimation of Hydroxyl Radical Reaction Rate Constants for Gas-Phase Organic Compounds Using a Structure-Reactivity Relationship: An Update, *Atmos. Environ.*, 29, 1685–1695, 1995.
- Laden, F., Schwartz, J., Speizer, F. E., and Dockery, D. W.: Reduction in Fine Particulate Air Pollution and Mortality Extended Follow-up of the Harvard Six Cities Study, *Am. J. Respir. Crit. Care Med.*, 173, 667–672, 2006.
- Lambe, A. T., Zhang, J., Sage, A. M., and Donahue, N. M.: Controlled OH Radical Production via Ozone-Alkene Reactions for Use in Aerosol Aging Studies, *Environ. Sci. Technol.*, 41, 2357–2363, 2007.
- Larsen, B. R., Di Bella, D., Glasius, M., Winterhalter, R., Jensen, N. R., and Hjorth, J.: Gas-Phase OH Oxidation of Monoterpenes: Gaseous and Particulate Products, *J. Atmos. Chem.*, 38, 231–276, 2001.
- Lee, A., Goldstein, A. H., Kroll, J. H., Ng, N. L., Varutbangkul, V., Flagan, R. C., and Seinfeld, J. H.: Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes, *J. Geophys. Res.*, 111, D17305, doi:10.1029/2005JD006437 2006.
- Lelieveld, J., Butler, T. M., Crowley, J. N., Dillon, T. J., Fischer, H., Ganzeveld, L., Harder, H., Lawrence, M. G., Martinez, M., Taraborrelli, D., and Williams, J.: Atmospheric oxidation capacity sustained by a tropical forest, *Nature*, 452, 737–740, 2008.
- Lim, Y. B. and Ziemann, P. J.: Products and Mechanism of Secondary Organic Aerosol Formation from Reactions of n-Alkanes with OH Radicals in the Presence of NO<sub>x</sub>, *Environ. Sci. Technol.*, 39, 9229–9236, 2005.
- Logan, J. A., Prather, M. J., Wofsy, S. C., and McElroy, M. B.: Tropospheric Chemistry: A Global Perspective, *J. Geophys. Res.*, 86, 7210–7254, 1981.
- Maksymiuk, C. S., Gayahtri, C., Gil, R. R., and Donahue, N. M.: Secondary organic aerosol formation from multiphase oxidation of limonene by ozone: mechanistic constraints via two-dimensional heteronuclear NMR spectroscopy, *Phys. Chem. Chem. Phys.*, 11, 7810–7818, 2009.
- Matsunaga, A. and Ziemann, P. J.: Gas-Wall Partitioning of Organic Compounds in a Teflon Film Chamber and Potential Effects on Reaction Product and Aerosol Yield Measurements, *Aerosol Sci. Tech.*, 44, 881–892, 2010.
- McMurry, J. E. and Bosch, G. K.: Synthesis of macrocyclic terpenoid hydrocarbons by intramolecular carbonyl coupling: bicyclogermacrene, lepidozene, and casbene, *J. Org. Chem.*, 52, 4885–4893, 1987.
- Moortgat, G. K., Veyret, B., and Lesclaux, R.: Kinetics of the reaction of HO<sub>2</sub> with CH<sub>3</sub>C(O)O<sub>2</sub> in the temperature range 253–368 K, *Chem. Phys. Lett.*, 160, 443–447, 1989.
- Ng, N. L., Chhabra, P. S., Chan, A. W. H., Surratt, J. D., Kroll, J. H., Kwan, A. J., McCabe, D. C., Wennberg, P. O., Sorooshian, A., Murphy, S. M., Dalleska, N. F., Flagan, R. C., and Seinfeld, J. H.: Effect of NO<sub>x</sub> level on secondary organic aerosol (SOA) formation from the photooxidation of terpenes, *Atmos. Chem. Phys.*, 7, 5159–5174, doi:10.5194/acp-7-5159-2007, 2007a.
- Ng, N. L., Kroll, J. H., Chan, A. W. H., Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol formation from m-xylene, toluene, and benzene, *Atmos. Chem. Phys.*, 7, 3909–3922, doi:10.5194/acp-7-3909-2007, 2007b.
- Odum, J. R., Hoffmann, T., Bowman, F., Collins, D., Flagan, R. C., and Seinfeld, J. H.: Gas/Particle Partitioning and Secondary Organic Aerosol Yields, *Environ. Sci. Technol.*, 30, 2580–2585, 1996.
- Pankow, J. F. and Asher, W. E.: SIMPOL.1: a simple group contribution method for predicting vapor pressures and enthalpies of vaporization of multifunctional organic compounds, *Atmos. Chem. Phys.*, 8, 2773–2796, doi:10.5194/acp-8-2773-2008, 2008.
- Park, J., Gomez, A. L., Walsler, M. L., Lin, A., and Nizkorodov, S. A.: Ozonolysis and photolysis of alkene-terminated self-assembled monolayers on quartz nanoparticles: implications for photochemical aging of organic aerosol particles, *Phys. Chem. Chem. Phys.*, 8, 2506–2512, 2006.
- Perraud, V., Bruns, E. A., Ezell, M. J., Johnson, S. N., Yu, Y., Alexander, M. L., Zelenyuk, A., Imre, D., Chang, W. L., Dabdub, D., Pankow, J. F., and Finlayson-Pitts, B. J.: Nonequilibrium atmospheric secondary organic aerosol formation and growth, *P. Natl. Acad. Sci. USA*, 109, 2836–2841, 2012.
- Pierce, J. R., Engelhart, G. J., Hildebrandt, L., Weitkamp, E. A., Pathak, R. K., Donahue, N. M., Robinson, A. L., Adams, P. J., and Pandis, S. N.: Constraining Particle Evolution from Wall Losses, Coagulation, and Condensation-Evaporation in Smog-Chamber Experiments: Optimal Estimation Based on Size Distribution Measurements, *Aerosol Sci. Tech.*, 42, 1001–1015, 2008.
- Pope, C. A. and Dockery, D. W.: Health Effects of Fine Particulate Air Pollution: Lines that Connect, *J. Air Waste Manage. Assoc.*, 56, 709–742, 2006.
- Pope, C. A., Burnett, R. T., Thun, M. J., Calle, E. E., Krewski, D., Ito, K., and Thurston, G. D.: Lung Cancer, Cardiopulmonary Mortality, and Long-term Exposure to Fine Particulate Air Pollution, *JAMA*, 287, 1132–1141, 2002.
- Presto, A. A., Hartz, K. E. H., and Donahue, N. M.: Secondary Organic Aerosol Production from Terpene Ozonolysis. 2. Effect of NO<sub>x</sub> Concentration, *Environ. Sci. Technol.*, 39, 7046–7054, 2005a.
- Presto, A. A., Huff Hartz, K. E., and Donahue, N. M.: Secondary Organic Aerosol Production from Terpene Ozonolysis. 1. Effect of UV Radiation, *Environ. Sci. Technol.*, 39, 7036–7045, 2005b.
- Presto, A. A., Miracolo, M. A., Donahue, N. M., and Robinson, A. L.: Secondary Organic Aerosol Formation from High-NO<sub>x</sub> Photo-Oxidation of Low Volatility Precursors: n-Alkanes, *Environ. Sci. Technol.*, 44, 2029–2034, doi:10.1021/es903712r, 2010.
- Rudich, Y., Donahue, N. M., and Mentel, T. F.: Aging of Organic Aerosol: Bridging the Gap Between Laboratory and Field Studies, *Ann. Rev. Phys. Chem.*, 58, 321–352, 2007.
- Salo, K., Hallquist, M., Jonsson, A. M., Saathoff, H., Naumann, K.-H., Spindler, C., Tillmann, R., Fuchs, H., Bohn, B., Rubach, F., Mentel, T. F., Müller, L., Reinnig, M., Hoffmann, T., and

- Donahue, N. M.: Volatility of secondary organic aerosol during OH radical induced ageing, *Atmos. Chem. Phys.*, 11, 11055–11067, 10, <http://www.atmos-chem-phys.net/11/11055/10/.5194/acp-11-11055-2011>, 2011.
- Wagstrom, K., and Pandis, S.: Determination of the age distribution of primary and secondary aerosol species using a chemical transport model, *J. Geophys. Res.*, 114, 1-12, 2009.
- Watson, J. G.: Visibility: Science and Regulation, *J. Air & Waste Manage. Assoc.*, 52, 628–713, 2002.
- Zhang, J., Huff Hartz, K. E., Pandis, S. N., and Donahue, N. M.: Secondary Organic Aerosol Formation from Limonene Ozonolysis: Homogeneous and Heterogeneous Influences as a Function of NO<sub>x</sub>, *J. Phys. Chem. A*, 110, 11053–11063, 2006.