Impact of NO\textsubscript{x} and OH on secondary organic aerosol formation from \(\beta\)-pinene photooxidation

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Abstract. In this study, the NO\textsubscript{x} dependence of secondary organic aerosol (SOA) formation from photooxidation of the biogenic volatile organic compound (BVOC) \(\beta\)-pinene was comprehensively investigated in the Jülich Plant Atmosphere Chamber. Consistent with the results of previous NO\textsubscript{x} studies we found increases of SOA yields with increasing [NO\textsubscript{3}] at low-NO\textsubscript{x} conditions ([NO\textsubscript{3}]\textsubscript{0} < 30 ppb, [BVOC]\textsubscript{0} / [NO\textsubscript{3}]\textsubscript{0} > 10 ppbC ppb\textsuperscript{-1}). Furthermore, increasing [NO\textsubscript{3}] at high-NO\textsubscript{x} conditions ([NO\textsubscript{3}]\textsubscript{0} > 30 ppb, [BVOC]\textsubscript{0} / [NO\textsubscript{3}]\textsubscript{0} \sim 10 to \sim 2.6 ppbC ppb\textsuperscript{-1}) suppressed the SOA yield. The increase of SOA yield at low-NO\textsubscript{x} conditions was attributed to an increase of OH concentration, most probably by OH recycling in NO + HO\textsubscript{2} \rightarrow NO\textsubscript{2} + OH reaction. Separate measurements without NO\textsubscript{x} addition but with different OH primary production rates confirmed the OH dependence of SOA yields. After removing the effect of OH concentration on SOA mass growth by keeping the OH concentration constant, SOA yields only decreased with increasing [NO\textsubscript{3}]. Measuring the NO\textsubscript{x} dependence of SOA yields at lower [NO] / [NO\textsubscript{2}] ratio showed less pronounced increase in both OH concentration and SOA yield. This result was consistent with our assumption of OH recycling by NO and to SOA yields being dependent on OH concentrations. Our results furthermore indicated that NO\textsubscript{x} dependencies vary for different NO\textsubscript{x} compositions. A substantial fraction of the NO\textsubscript{x}-induced decrease of SOA yields at high-NO\textsubscript{x} conditions was caused by NO\textsubscript{x}-induced suppression of new particle formation (NPF), which subsequently limits the particle surface where low volatiles condense. This was shown by probing the NO\textsubscript{x} dependence of SOA formation in the presence of seed particles. After eliminating the effect of NO\textsubscript{x}-induced suppression of NPF and NO\textsubscript{x}-induced changes of OH concentrations, the remaining effect of NO\textsubscript{x} on the SOA yield from \(\beta\)-pinene photooxidation was moderate. Compared to \(\beta\)-pinene, the SOA formation from \(\alpha\)-pinene photooxidation was only suppressed by increasing NO\textsubscript{x}. However, basic mechanisms of the NO\textsubscript{x} impacts were the same as that of \(\beta\)-pinene.

1 Introduction

Biogenic volatile organic compounds (BVOCs), such as monoterpenes (C\textsubscript{10}H\textsubscript{16}) are emitted in large quantities into the atmosphere (Guenther et al., 1995, 2012; Griffin et al., 1999a). These BVOCs are oxidized in the atmosphere by hydroxyl radicals (OH), ozone (O\textsubscript{3}) or nitrate radicals (NO\textsubscript{3}) resulting in the formation of secondary organic aerosol (SOA). SOA contributes to a substantial fraction of ambient organic aerosol and is known to adversely affect visibility, climate and human health (Hallquist et al., 2009).

SOA formation potentials of BVOC species are represented by SOA yields, which are generally defined as the ratio of the SOA mass produced from the oxidation of the SOA precursor to the mass of the precursor consumed (Odum et al., 1996). Despite the fact that many studies have focused on the production of SOA from a number of monoterpenes, reported SOA yields have shown high variability for a given...
precursor (Pandis et al., 1991; Hoffmann et al., 1997; Griffin et al., 1999b; Larsen et al., 2001; Presto et al., 2005; Kroll et al., 2006; Ng et al., 2007a; Mentel et al., 2009; Eddingsaas et al., 2012a). For instance, the reported SOA mass yield for α-pinene photooxidation ranges from 8 to 37% (Eddingsaas et al., 2012a). This variability is likely related to the numerous factors that influence the SOA yields, such as the inorganic and organic mass loading, particle acidity, NOx (NOx = NO + NO2) level, humidity, and temperature. Therefore, ambient SOA yields cannot be represented by a unique value for a given monoterpene as the yields are heavily dependent on the conditions under which the SOA is formed.

One of the critical factors is the impact of NOx on SOA formation. For sesquiterpenes, such as longifolene and aromadendrene, yields increase with increasing NOx (Ng et al., 2007a). However, results of the majority of studies indicate that NOx yields are lower at high-NOx levels (Hatakeyama et al., 1991; Pandis et al., 1991; Presto et al., 2005; Kroll et al., 2006; Ng et al., 2007a). It is generally assumed that the impact of NOx results from altering the balance between competing peroxy-radical (RO2) reactions and thus from the changes in the distribution of oxidation products. Reaction (R1) is the dominant pathway for RO2 radicals under low-NOx conditions, which leads to the formation of low-volatility hydroperoxides that can participate in new particle formation (NPF) and contribute to SOA mass (Johnson et al., 2005; Camredon et al., 2007).

\[ \text{RO}_2 + \text{HO}_2 \rightarrow \text{ROOH} + \text{O}_2 \]  

(R1)

Under high-NOx conditions, RO2 radicals react with NO resulting in the formation of organic nitrates (Reaction R2a) as well as alkoxy radicals (Reaction R2b) that either fragment, or react to form more volatile products. This understanding implies that higher NOx concentrations will suppress the formation of low volatility products, and thereby suppress NPF and SOA mass formation.

\[ \text{NO} + \text{RO}_2 \rightarrow \text{RONO}_2 \]  

(R2a)

\[ \text{NO} + \text{RO}_2 \rightarrow \text{RO} + \text{NO}_2 \]  

(R2b)

Despite numerous studies of SOA formation from terpene ozonolysis, the SOA formation from OH oxidation of β-pinene has been scarcely investigated. In the present study, we investigated the SOA formation from β-pinene photooxidation under varied NOx levels in the Jülich Plant Atmosphere Chamber (JPAC) to gain more insight into the impact of NOx on SOA yield and to better characterize mechanisms leading to effects of NOx on SOA yield.

2 Experimental

The experimental setup of JPAC is described in detail elsewhere (Mentel et al., 2009, 2015). The chamber is 1450 L in volume, made of borosilicate glass and set up in a climate-controlled housing. Temperature and relative humidity inside the chamber were held constant at 16 ± 1°C and 63 ± 2% respectively over the course of the experiments. The chamber was operated as a continuously stirred tank reactor with a residence time of approximately 46 min. The flow into the chamber consisted of two purified air streams. One stream was passed through an ozonator and was humidified with double distilled water. The other stream contained β-pinene emitted from a diffusion/permeation source held at 38°C. Where necessary seed particles could be generated externally and introduced using a third air stream.

The chamber was equipped with several lamps: 12 discharge lamps (HQI 400 W/D; Osram) used to simulate the solar light spectrum. Twelve discharge lamps (Philips, TL 60 W/10-R, 60 W, λmax = 365 nm) were used for NO2 photolysis. According to the spectral distribution of their light these lamps are termed as UVA lamps from here on. The TUV lamp could be shielded by glass tubes to control the amount of UV radiation entering the chamber. Thus, by altering the gap between these glass tubes, the OH production rate could be adjusted by varying the photolysis rate \( J(O_1^D) \). It has to be noted that the short wavelength cut off of the glass is around 350 nm and thus no light with wavelength short enough to produce \( O_1^D \) is in the chamber when the TUV lamp is off. Furthermore, the absorption cross section of NO2 at the wavelength of the TUV lamp is more than an order of magnitude lower than at wavelengths around 365 nm (Davidson et al., 1988). Together with the quite low energy of the TUV lamp compared to the energy of the UVA lamps, this allowed varying \( J(O_1^D) \) and \( J(NO_2) \) independent of each other.

A suite of instruments were used to measure both the gas and particle phase products. Ozone concentration was determined by UV photometric devices (Thermo Environmental 49 and Ansycr, O3 42M ozone analyzers), NO was measured by chemiluminescence (Eco Physics, CLD 770 AL ppt), NO2 by chemiluminescence after photolysis (Eco Physics, PLC 760) and relative humidity was measured by a dew point mirror (TS-2, Walz). Furthermore, a condensation particle counter (CPC; TSI 3783) and a scanning mobility particle sizer (SMPS; combination of a TSI 3081 electrostatic classifier and a TSI 3025 CPC) were used to count the total particle number greater than 3 nm and to measure the particle size distribution between 13 and 740 nm respectively. The total particle mass concentration was estimated from the measured total aerosol volume assuming a SOA density of \( \sim 1.2 \text{ g cm}^{-3} \) and spherical particles. β-pinene mixing ratio in the chamber was determined by gas chromatography–mass spectrometry (GC-MS; Agilent GC-MSD system with HP6890 GC and 5973 MSD) and a proton transfer reaction mass spectrometer (PTR-MS; Ionicon). The GC-MS and PTR-MS were switched periodically between the outlet and the inlet of the chamber to quantify concentrations of β-pinene entering and exiting the chamber. The OH concentra-
tion was estimated from the decay of β-pinene in the chamber (Eq. 2) (Kiendler-Scharr et al., 2009).

$$\frac{d[\beta p]}{dt} = \frac{F}{V} \cdot ([\beta p]_{in} - [\beta p]) - \left( k^{OH} \cdot [OH] + k^{O_3} \cdot [O_3] \right) \cdot [\beta p]$$  \hspace{1cm} (1)

$$[OH] = \frac{F \cdot [\beta p]_{in} - [\beta p]}{k^{OH}} - k^{O_3} \cdot [O_3]$$  \hspace{1cm} (2)

Equation (1) is the basic rate equation for a continuously stirred tank reactor resulting from mass balance and Eq. (2) results from Eq. (1) under steady state conditions when solving for [OH]. In Eqs. (1) and (2), V is the volume of the chamber and F is the total air flow through the chamber. [\beta p]_{in} and [\beta p] are the concentrations of β-pinene in the inlet air and in the chamber respectively. For a well-mixed continuously stirred tank reactor, [\beta p] is the concentration of β-pinene measured in the outlet flow, k^{OH} and k^{O_3} are the rate constants of reactions of β-pinene with OH and with O_3. Since β-pinene has a quite low rate constant with O_3 (k^{O_3} = 1.5 \times 10^{-17} \text{ cm}^3 \text{s}^{-1}; Atkinson and Arey, 2003), the reaction of β-pinene with O_3 could be neglected from Eq. (2) for our ozone- (50–100 ppb) and OH concentrations (9 \times 10^{-8} – 1.6 \times 10^8 \text{ cm}^{-3}). The uncertainty in OH concentration was estimated to be approximately 20% (Wildt et al., 2014).

SOA yields were determined as described in Mentel et al. (2009). Particle formation was induced by switching on ozone photolysis and thus producing OH radicals. From such a measurement the formed particle mass as well as the amount of consumed BVOC was obtained. Repeating such experiments using different amounts of BVOC gave a set of data on SOA mass and consumed BVOC. Plotting the SOA masses in dependence of consumed BVOC gave linear relationships with only small deviations from linearity. The slopes of such plots were used as the incremental yields. However, different from the procedure described in Mentel et al. (2009), here we use particle masses corrected for wall losses of extremely low volatile organic compounds (ELVOCs) that are direct particle precursors.

Details of the correction method are described in detail in the supplement. Briefly, ELVOCs were measured with a NO_3^-CIMS (Ehn et al., 2014; Mentel et al., 2015). Stopping the ELVOC production by stopping OH production allowed for the measurement of their decay rates and thus their lifetimes. In the absence of particles, the lifetimes were in the range of 2 to 3 min. The lifetimes became shorter with increasing particle surface because of condensation of the ELVOCs onto the particles. Knowing the total loss rate and the wall loss rate allowed for the determination of ELVOC condensation onto the particles, as well as the fraction of condensation $F_p$: $F_p = \frac{\text{Loss on particles}}{\text{Loss on particles + loss on walls}}$. The measured mass was then corrected accordingly, by dividing by $F_p$. We verified this correction procedure for experiments with α-pinene and β-pinene with particle surfaces varying over a wide range, including different amounts of ammonium sulfate seed aerosols. Note that the numbers obtained for wall loss correction are only valid for the chamber used in this study.

Additionally, we used another approach to determine the mass yields at steady state conditions. Correcting measured particle masses by the procedure described in the supplement, revealed that after an induction time of about 20 min, the wall loss corrected particle mass was constant as long as the OH production rate was constant. This allowed determining yields using steady state assumptions. Yields were determined by dividing the particle mass formed in the experiment by the oxidation rate of the BVOC. With our method of [OH] determination, using the BVOC consumption according to Eq. (2), and at the negligible inflow of particle mass into the chamber, this equals the simple mass balance assumption: produced particle mass divided by BVOC consumption (Eq. 3).

$$Y = \frac{\text{Particle mass}}{\text{BVOC consumption}}$$  \hspace{1cm} (3)

As was expected from the consistency of wall loss corrected particle masses, both procedures of yield determinations led to identical results. However, the method using steady state conditions had advantages since adjustments of [OH] were required during many experiments. The justification to use both type of yield determinations is given in the supplement.

**Experimental procedure**

A series of β-pinene photooxidation experiments were performed in the JPAC to investigate the SOA formation under low-NO_3 (here defined as [NO_3]_0 < 30 ppb, [BVOC]_0 / [NO_3]_0 > 10) and high-NO_3 (here defined as [NO_3]_0 > 30 ppb, [BVOC]_0 / [NO_3]_0 < 10) conditions. In these experiments, the inflow of β-pinene (95%, Aldrich) to the chamber was kept constant, leading to initial mixing ratios of 37 ± 0.6 ppb. Initial O_3 concentration was 40 ± 5 ppb. NO_2 (Linde, 104 ± 3 ppm NO_2 in nitrogen) was introduced into the β-pinene air stream. Initial NO_3 concentrations, [NO_3]_0, in the chamber were varied between < 1 and 146 ppb. The chamber was illuminated with one of the HQU lamps and all the UVA lamps, resulting in an NO_2 photolysis frequency $J(\text{NO}_2)$ of 4.3 \times 10^{-3} \text{s}^{-1}. When VOC, NO_3, and O_3 concentrations in the chamber were near to steady state, the experiment was initiated by turning on the TUV lamp resulting in OH radical production. During the described experiments, a constant $J(\text{O}^3\text{D})$ was maintained. Experiments without NO_3 addition were performed between NO_3 experiments. In these cases, residual NO_3 concentrations from chamber walls were below 1 ppb.

After initiating the OH production, β-pinene and NO_3 concentrations decreased due to their reactions with OH rad-
icals. The majority of the results presented in this study are from steady state measurements, when all physical and chemical parameters were constant in the chamber. However, for the purpose of comparison with the literature data, the initial concentration of NO$_x$, [NO$_x$], and $\beta$-pinene, [BVOC], were also used here.

To investigate the role of NO$_x$ on SOA formation in the presence of inorganic aerosol, $\beta$-pinene photooxidation / NO$_x$ experiments were repeated in the presence of seed aerosol. The seed particles were generated using a constant output aerosol generator (TSI, Model 3076) by atomizing (NH$_4$)$_2$SO$_4$ solutions (typical concentration $\sim 40$ mg L$^{-1}$) at a pressure of around 1.4 bar. The generated aerosol then passed through a silica gel diffusion drier before entering the reaction chamber. In the control experiments, distilled water was used for atomization to keep the experimental conditions constant. For these experiments, the organic particle mass was determined by subtracting the initial seed aerosol mass from the total particle mass.

3 Results and discussion

3.1 Impact of NO$_x$ on SOA formation

To determine the influence of NO$_x$ on SOA formation, a series of NO$_x$ experiments were conducted in the JPAC in which $\beta$-pinene was oxidized in the absence of inorganic seed aerosol. A summary of experimental conditions and results for the $\beta$-pinene / NO$_x$ photooxidation experiments is given in Table 1. Figure 1 shows SOA yields, calculated from wall-loss corrected maximum particle mass concentration ($\text{PM}_{\text{max}}$), as a function of [BVOC]$_0$ / [NO$_x$]$_0$ ratio and [NO$_x$]$_0$. The strong dependence of SOA yield on BVOC / NO$_x$ levels is evident. At low NO$_x$ conditions an increase in the initial NO$_x$ concentration increases the SOA yield, whereas at high-NO$_x$ concentrations the opposite SOA yield dependence on NO$_x$ was observed. Similar NO$_x$ dependencies of SOA yields have been observed in previous studies (Pandis et al., 1991; Kroll et al., 2006; Zhang et al., 1992; Camredon et al., 2007; Xu et al., 2014).

At high-NO$_x$ conditions strong depletion of SOA yield as well as NPF was observed with increasing NO$_x$ (Fig. 1). Wildt et al. (2014) made similar observations for NPF during the photooxidation of a BVOC mix emitted from Mediterranean plants. However, the NO$_x$ dependence of SOA yield was different from that shown by Wildt et al. (2014). At low-NO$_x$ concentrations we observed an increasing SOA yield with increasing NO$_x$ (Fig. 1). At high-NO$_x$ levels, the yields decreased. Having different NO$_x$ dependencies at different NO$_x$ regimes suggests multiple factors at play.

Kroll et al. (2006) suggested that the increase in SOA yield of isoprene with NO$_x$ could be due to changes in the [NO]/[HO$_2$] ratio. As experiments in batch reactors proceed, NO$_x$ concentrations decrease due to their reactions with OH resulting in a switch from high-NO$_x$ to low-NO$_x$ conditions. The lowered NO concentrations cause increasing HO$_2$ concentrations due to Reaction (R3):

\[ \text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH} \]  

(R3)

In such experiments, peroxy radicals initially react mainly with NO, whereas peroxy radicals formed later from first generation products, primarily react with HO$_2$. Although the reason for the observed increase of SOA yield with increasing NO$_x$ at low-NO$_x$ levels was not fully explored, Camredon et al. (2007) noted that this could be due to the influence of OH levels. However, in the majority of studies investigating the impact of NO$_x$ on SOA formation, OH concentration was either not measured or the potential influence of OH was not discussed in detail (Eddingsaas et al., 2012a, b; Xu et al., 2014).

As the NO$_x$ concentration is changed in this study, the concentration of OH was found to change markedly (Fig. 2). OH concentrations passed through a maximum ($\sim 3.8 \times 10^7$ molecules cm$^{-3}$) at [NO$_x$]$_{tot} \sim 40$ ppb ([NO$_x$]$_0 \sim 70$ ppb), which represented a 4-fold increase over that in the absence of NO$_x$. NO$_x$ enhanced OH production in two ways: by increasing [O$_3$] and thereby the photolytic OH source, and by recycling OH through Reaction (R3). However, at very high-NO$_x$ concentrations, NO$_x$ is acting as a sink for OH due to Reaction (R4):

\[ \text{NO}_2 + \text{OH}(+M) \rightarrow \text{HNO}_3(+M) \]  

(R4)
To examine whether or not SOA yields depend on the OH concentration, additional experiments were performed at two different OH production rates and the β-pinene variation to give a range of SOA mass. The detailed experimental conditions are summarized in Table 2. Two different J(O1D) conditions (1.9 ± 0.2 × 10−3 and 5.4 ± 0.5 × 10−3 s−1) were used to give significantly different OH production rates at otherwise unchanged conditions. Figure 3 shows particle mass as a function of consumed β-pinene ranging from 20 to 140 µg m⁻³. Approximately 90–95% of the total β-pinene was consumed in these experiments.

The OH concentrations were 4 × 10⁻⁷–1 × 10⁻⁶ molecules cm⁻³ and 1.1–1.6 × 10⁸ molecules cm⁻³ under low- and high-OH conditions respectively. The SOA yields (incremental yields; see Mentel et al., 2009, and the supplement to this paper) were higher at higher OH levels (31 ± 3 % and 20 ± 1 % for high- and low-OH conditions respectively).

Increasing yields with increasing OH concentrations have been previously observed. More efficient NPF and/or higher abundance of low volatile vapors at higher oxidant levels were suggested to be the reason. The first should lead to a larger particle surface, which allows for more semi-volatile vapors to condense on particles (Ng et al., 2007b; Healy et al., 2009). As we corrected for wall losses of ELVOCs this effect should be of minor importance in our case. Therefore, other reasons for this dependence have to be considered. Such other reasons might be the secondary reactions (Song et al., 2007; Eddingsaas et al., 2012a, b).

As an example, the rate constant for the reaction of β-pinene + OH (k ~ 7.4 × 10⁻¹¹ cm³ s⁻¹; Atkinson and Arey, 2003) is higher than that of the reaction of nopinone + OH (k ~ 1.5 × 10⁻¹¹ cm³ s⁻¹; Atkinson and Arey, 2003).
Table 2. Experimental conditions and results for β-pinene photooxidation experiments at two OH levels.

<table>
<thead>
<tr>
<th>$J(\text{O}_1\text{D}) / 10^{-3}$ (s$^{-1}$)$^a$</th>
<th>Initial β-pinene (ppb)</th>
<th>β-pinene reacted (ppb)</th>
<th>[OH] / $10^7$ (cm$^{-3}$)</th>
<th>PM$_{\text{max}}$ (µg m$^{-3}$)$^b$</th>
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</table>

$^a$ $J(\text{O}_1\text{D})$ was varied by altering the TUV gap. $^b$ Maximum formed particle mass concentration, assuming a SOA density of 1.2 g cm$^{-3}$. These values have been adjusted for wall losses and losses on particles.

Figure 3. Total aerosol mass concentration as a function of the amount of reacted β-pinene under low-[OH] (blue open circles) and high-[OH] (red open squares) conditions. The SOA yield was estimated from the aerosol mass linear regression slope as a function of consumed β-pinene, which resulted in approximately 20 ± 1 % and 31 ± 3 % for low- and high-OH conditions respectively. The error in [consumed β-pinene] was estimated to be ±10 % and the error in particle mass was estimated from the sum of the systematic error and the correction procedure error.

3.1.2 Isolate the effect of [OH] on SOA formation

To examine the impact of NO$_x$ on SOA production independent of [OH] changes, a series of experiments were performed where the steady state OH concentration was held constant by tuning the value of $J(\text{O}_1\text{D})$. This required constant [OH] monitoring as the system approached steady state, i.e., monitoring the consumption of β-pinene, to ensure the [OH] was adjusted to the desired level. Although there was a significant variation in initial OH concentrations on adding NO$_x$ if $J(\text{O}_1\text{D})$ was unchanged, it was possible to maintain the OH concentrations to within 5 % across all NO$_x$ concentrations by adjusting $J(\text{O}_1\text{D})$ (Fig. 4). Figure 5 shows the SOA yield as a function of [NO$_x$] during the steady state before and after [OH] adjustment. Before adjusting [OH] the yield profile was consistent with our previous results; SOA yield increased with increasing NO$_x$ at low-NO$_x$ levels and then dropped at high-NO$_x$ levels. After adjusting [OH], the yield revealed no increase at low-NO$_x$ levels. It was only suppressed by increasing NO$_x$. This indicated that the observed increase in SOA yield without adjusting [OH] is a result of NO$_x$ enhancing [OH]. Thus, isolating the effect of [OH] revealed that increasing [NO$_x$] only suppressed particle mass formation, and therefore also suppressed SOA mass yield.
3.2 Possible role of peroxy radical chemistry and [NO] / [NO₂] ratio in SOA formation

We also investigated the effect of the [NO] / [NO₂] ratio on SOA formation from β-pinene / NOₓ mixtures. To change this ratio we changed [O₃]. Ozone, NO and NO₂ are interrelated as illustrated in Reactions (R5) and (R6):

\[
\begin{align*}
\text{NO} + \text{O}_3 &\rightarrow \text{NO}_2 + \text{O}_2 \quad \text{(R5)} \\
\text{NO}_2 + \text{O}_2 + h\nu &\rightarrow \text{NO} + \text{O}_3 \quad \text{(R6)}
\end{align*}
\]

Hence, to a good approximation the [NO] / [NO₂] ratio is described by the photostationary steady state (Leighton, 1961):

\[
\frac{[\text{NO}]}{[\text{NO}_2]} = \frac{J(\text{NO}_2)}{k^5[\text{O}_3]},
\]

where \(J(\text{NO}_2)\) represents the photolysis rate of NO₂ and \(k^5\) is the rate coefficient of Reaction (R5). Hence, adjusting [O₃] in the chamber allowed varying [NO] / [NO₂] ratios. Here, to probe the dependency of SOA mass formation on relative NO and NO₂ concentrations, NOₓ experiments were performed with approximately 50 % higher O₃ concentration (74 ± 7 ppb, [NO] / [NO₂] = 0.018 ± 0.004 ppb ppb⁻¹) than that of previous NOₓ experiments where the [NO] / [NO₂] ratio was 0.035 ± 0.005 ppb ppb⁻¹. The remaining conditions maintained the same.

Results obtained from these experiments are shown in Fig. 6. The behavior observed in the low-O₃ experiments (equivalent to lower NO / NO₂) was different from that in the experiments with lower [O₃] (cf. Figs. 6 to 4). When not adjusted, [OH] increased with increasing NOₓ but the increase was less pronounced. With a lower [NO] / [NO₂] ratio, the maximum OH concentration increase was approximately 2-fold relative to the respective NOₓ-free experiments (Fig. 6), compared to the 4-fold increase with the higher [NO] / [NO₂] (Fig. 4). This is consistent with the assumption that Reaction (R3) recycles OH. There was also a slight increase in SOA yield when [NOₓ] increased up to ∼ 15 ppb (Fig. 7). In addition, the increase in SOA yield was less pronounced in the high-O₃ experiments again pointing to the role of [OH] in SOA formation.

After adjusting [OH] to the same level as in the NOₓ-free experiments (Fig. 6), no increase in SOA yield was observed and increasing NOₓ only suppressed SOA formation (Fig. 7). These results were consistent with those found earlier in the low-O₃ experiments indicating that, after isolating the effect of [OH], SOA yield was only suppressed with increasing NOₓ also at higher [O₃]. Comparing the yield profiles obtained from the low-O₃ and the high-O₃ experiments respectively (blue circles in Figs. 5 and 7), it can be seen that the decrease in SOA yield was ∼ 35 % in the high-O₃ experiments, whereas it was roughly 70 % in the low-O₃ experiments. This shows that NOₓ dependencies itself depend on the composition of NOₓ. As the suppression of yield was more pronounced in the low-O₃ experiments (i.e., higher [NO] / [NO₂]), it indicates that NO is the molecule mainly responsible for the SOA yield diminishing effect of NOₓ.

After separating the impacts of NOₓ on OH, there was a remaining effect on SOA formation. According to present knowledge (e.g., Hatakeyama et al., 1991; Pandis et al., 1991; Kroll et al., 2006) this effect is due to impacts of NOₓ on RO₂ chemistry. The most obvious impact of NOₓ is the change in product composition. Organic nitrates are formed as an al-
alternative to hydroperoxides and formation of organic nitrates may have an effect on the average volatility of the product mixture. Also decomposition of alkoxy radicals may play a role here. Decomposition of alkoxy radicals can lead to products with higher volatility and thus to a mixture with an average higher volatility.

We found that diminishing of SOA is more effective at higher [NO] / [NO₂] ratio. This points to NO as a major player and thus to a role of alkoxy radical decomposition. As alkoxy radicals are produced by only RO₂ + NO reactions, more effective suppression of SOA formation at higher [NO] / [NO₂] would be consistent with alkoxy radical decomposition leading to decomposition products with on average high vapor pressures. However, from our results no clear conclusion can be given in this respect.

### 3.3 Comparison of the impact of NOₓ on SOA yield from α-pinene and β-pinene photooxidation

A series of α-pinene / NOₓ experiments were performed in the same chamber to compare the NOₓ dependencies of SOA formation of α-pinene to that of β-pinene. These experiments were performed with 12 ± 1.2 ppb α-pinene, 78 ± 14 ppb O₃ and with [NOₓ]₀ up to 126 ppb.

When using α-pinene as the SOA precursor, no increase in aerosol mass formation was observed at low NOₓ, with only suppression of the particle mass formation and the SOA yield (Fig. 8). Furthermore, presumably due to the lower α-pinene concentrations, no particle formation at all was observed when [NOₓ]₀ was above 60 ppb.

At high-NOₓ levels, the differences between the NOₓ dependencies of α-pinene (Fig. 8) and β-pinene (Fig. 1) photooxidation were not very strong, both showing a decrease with increasing NOₓ. At low-NOₓ levels there were substantial differences, in that β-pinene showed a distinctive increase and maximum of the yield, while the yield of α-
pinene is almost unaffected and monotonically decreasing. A part of these differences can be explained by the differences in $[O_3]$ during $\alpha$-pinene and $\beta$-pinene photooxidation. The lower $[O_3]$ in the $\beta$-pinene experiments caused higher $[NO]/[NO_2]$ ratios and thus more effective conversion of HO$_2$ to OH by NO (Reaction R3). This is supported by the experiments with $\beta$-pinene performed at higher $[O_3]$ that caused a less NO$_x$-induced increase of $[OH]$ (Fig. 6, black squares), as well as less NO$_x$-induced increase of SOA yield (Fig. 7, black circles). Restricting focus to the same [BVOC] / [NO$_x$] where the substantial increase in $\beta$-pinene SOA yield was observed ($> 100$ to $\sim 20$ ppbC ppb$^{-1}$), such increases were neither observed for $\alpha$-pinene nor for the monoterpene mix emitted from Mediterranean species (Wildt et al., 2014). The NO$_x$ dependence of SOA formation therefore is different in different chemical systems. Different impacts of NO$_x$ superimpose each other and the net effect of NO$_x$ is determined by the strongest impact in the individual chemical system. For SOA formation from $\alpha$-pinene, the suppressing effect via impacts on peroxy radical chemistry was obviously stronger than the increases in SOA yield by NO$_x$-induced increases of [OH]. However, at high-NO$_x$ conditions, the principle behavior of all systems was identical; a general SOA yield suppression with increasing NO$_x$.

### 3.4 Impact of NO$_x$ on SOA formation in the presence of seed aerosol

From Fig. 2, it can be seen that the SOA yield measured at $[NO_\text{iso}] \sim 86$ ppb ($[NO_\text{x}]_0 \sim 146$ ppb) was lower than that at $[NO_\text{iso}] < 1$ ppb while $[OH]$ was higher. Hence, there must be another effect of NO$_x$ addition besides its impact on $[OH]$. As illustrated in Fig. 9, particle number concentrations were suppressed significantly when adding NO$_x$. The strong decrease of particle number concentration with increasing NO$_x$ indicates that NPF is suppressed by NO$_x$ (see also Wildt et al., 2014). Hence, there is a high chance that the SOA formation is hindered by low particle phase condensational sinks at high-NO$_x$ levels, and thus the observed suppression of SOA yield may be due to the lowering of available particle surface. At high-NO$_x$ conditions, particle numbers and surfaces were quite low. Therefore, high correction factors had to be used to correct the particle mass for wall losses of ELVOCs, which includes high uncertainties (see Supplement). These uncertainties can be diminished by using seed particles since they provide a surface onto which the low volatile organics may condense. In the presence of seed aerosol, the growth of particles would not be limited by the surface of particles and would be much less affected by losses of SOA precursors on the chamber walls.

Therefore, experiments with variations of [NO$_x$] were also conducted in the presence of ammonium sulfate ((NH$_4$)$_2$SO$_4$) seed particles (average seed mass and surface were approximately $9 \pm 1$ $\mu$g m$^{-3}$ and $1.3 \times 10^{-3}$ m$^2$ m$^{-3}$ respectively). These experiments were carried out in the same manner as previous experiments: by adjusting $[OH]$ during steady state to the same level as during the NO$_x$-free experiments. Figure 10 presents a comparison of SOA yield before and after $[OH]$ adjustment for seeded NO$_x$ experiments (seed mass is subtracted from the total particle mass to determine the organic mass used in the yield calculation). The results from the seeded experiments showed the same general features as the unseeded experiments. Without adjustment of $[OH]$, yields increased with increasing NO$_x$ at low levels and were slightly suppressed with further increases...
ing NO\textsubscript{x}. The most evident difference here to the experiments without seed particles is the fairly high yield at high [NO\textsubscript{x}] (Fig. 10). Even after [OH] was adjusted, the decrease in SOA yield was not as significant as in the experiments without seed particles. This suggests that in the absence of seed particles, the accumulation of mass was indeed limited by low particle surface caused by the NO\textsubscript{x}-induced suppression of NPF.

In the presence of seed particles and at constant [OH], the decrease in yield was only moderate. This indicates that other NO\textsubscript{x} impacts such as formation of organic nitrates were moderate as well. The difference between yields determined with and without addition of seed particles indicates that at very small particle surface, our correction procedure underestimates wall losses of precursors. This might be due to either possible differences in uptake of the ELVOC by particles (mainly organic particles vs. ammonium sulfate particles), or the differences in the size of particles. However, the real reason for this underestimation is not known yet.

Our correction procedure may involve uncertainties and errors. Nevertheless, it had to be applied; otherwise the NO\textsubscript{x} dependence would have been overestimated. NO\textsubscript{x} suppresses NPF and thereby limits mass formation in the absence of seed particles. As both, the impacts of wall losses and impacts of suppressed NPF on SOA mass formation are certainly diminished in the presence of seed, we assume that the experiments with seed particles give the most reliable results on NO\textsubscript{x} impacts on SOA mass formation from \(\beta\)-pinene.

4 Summary and conclusions

We investigated the effect of NO\textsubscript{x} on SOA formation from \(\beta\)-pinene photooxidation under low-NO\textsubscript{x} and high-NO\textsubscript{x} conditions and found a very similar behavior as that observed in other studies (Pandis et al., 1991; Zhang et al., 1992; Presto et al., 2005; Kroll et al., 2006; Camredon et al., 2007; Pathak et al., 2007; Chan et al., 2010; Hoyle et al., 2011; Loza et al., 2014). At low-NO\textsubscript{x} levels SOA yields increased with increasing NO\textsubscript{x} and then decreased at higher NO\textsubscript{x} concentrations. The increase of yield at low [NO\textsubscript{x}] was caused by the NO\textsubscript{x}-induced increase of [OH]. The decrease of yield at higher NO\textsubscript{x} levels was mainly a consequence of NPF suppression and thereby decreasing particle condensational sink with increasing NO\textsubscript{x}. Eliminating the impacts of NO\textsubscript{x} on NPF and on [OH], showed that the impacts of NO\textsubscript{x} on mass formation were only moderate. Even at the highest NO\textsubscript{x} level ([NO\textsubscript{x}]\textsubscript{ss} \sim 86 ppb, [BVOC]\textsubscript{ss} / [NO\textsubscript{x}]\textsubscript{ss} \sim 1.1) suppression of mass yield was only 20–30 %.

Our study also showed that SOA yield is dependent on OH concentration. Although the exact mechanism for this [OH] dependence is still unknown, our results show that besides yield dependencies on the amount of pre-existing matter and effects like partitioning there is also a dependence on reaction conditions, in particular on oxidant levels. Although SOA yields measured in laboratory chambers may not be indicative of the yields in the real atmosphere, their variations as a consequence of different conditions could provide a more comprehensive description of SOA in global and climate model.

5 Data availability

All data given in figures can be displayed in tables or in digital form. This includes the data given in the Supplement where we describe the method how the mass yields were corrected for wall losses of ELVOCs. Please send all requests for data to J.wildt@fz-juelich.de.

The Supplement related to this article is available online at doi:10.5194/acp-16-11237-2016-supplement.

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