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Dear Prof. Nizkorodov:

We are submitting our revised manuscript (acp-2016-301-version4) for publication in *Atmospheric Chemistry and Physics*. We have revised the manuscript with consideration of all the comments from reviewer #3. Please see our response to the reviewer below for details. We also have attached a copy of the manuscript with all the changes tracked for other minor corrections. We hope that this paper will be accepted in your journal soon. Thank you very much for editing the paper.

Sincerely yours,
Yuemei Han and coauthors

Response to referee #3: “The effect of particle acidity on secondary organic aerosol formation from α -pinene photooxidation under atmospherically relevant conditions”

Yuemei Han et al.

(The blue, green, and black fonts represent the referee’s comments, the associated revised text in the manuscript, and the authors’ responses, respectively.)

This paper explores the effect of aerosol acidity on alpha-pinene SOA formation under low- and high-NO_x conditions. Although this system has been examined by prior studies, only a few studies (research groups) have really investigated this question but under varying reaction conditions (i.e., oxidant type, mixing ratios of alpha-pinene, NO, NO₂, and NO_x, as well as inorganic seed aerosol composition and RH). This has made the interpretation of the effect of acidity on alpha-pinene unclear. As the authors rightly point out in their reply to one of the initial reviewer comments, just because this topic has been examined before doesn't mean the scientific question under study is fully addressed. I think the most important results from this study include, (1) a stronger effect of aerosol acidity on alpha-pinene SOA formation under high-NO_x conditions, especially early in the reaction (first hour), compared to low-NO_x conditions. The authors suggest that since the SOA yields are larger under low-NO_x conditions (even with less acidic aerosol present), it is possible that organic coatings form on the inorganic core and thus prevent later generation products from interacting with the acidic media to undergo acid-catalyzed particle-phase reactions; (2) Under the low-NO_x condition, the authors did find if they initially conducted the photooxidation without seed aerosol they didn't see significant nucleation of SOA. This is important as they waited a few hours later to

inject inorganic seed aerosol and found the more acidic inorganic seed aerosol yielded more SOA, suggesting that later-generation products produced under low-NOx conditions could in fact reactively uptake onto these acidic particles. To me, this is one of the most interesting and significant findings of these studies conducted here. I think the authors may want to highlight this effect in the abstract! One could imagine the potential implications of this. For example, if NOx conditions are low enough and alpha-pinene produces later-generation products from a forested area that are then transported near a power plant plume or urban area, you might have acid enhancement of alpha-pinene SOA as a result; and (3) I think the acid enhancement of organic nitrates in the aerosol phase in the high-NOx experiments is quite interesting and potentially important! For example, Surratt et al. (JPCA, 2008) showed the the presence of acidic sulfate aerosol yielded significant quantities of nitrated organosulfates. It is possible that high-volatility organic nitrate products are converted into lower volatility products (like organosulfates), especially if the nitrate group is on a favorable carbon type (i.e., primary, secondary, or tertiary). Professor Matthew Elrod's group at Oberlin College has published work on how stable different organic nitrates are stable in acidic aqueous media. These studies might be helpful in supporting your results or at least provide insights into which types of organic nitrates remain unhydrolyzed in the SOA particles. Overall, I think this is a well-written paper that warrants publication in ACP after the authors consider my specific comments below. I think the authors did a great job citing all of the relevant published work.

Response: We greatly appreciate the reviewer for the insightful comments in regards to our study. We have carefully considered all the issues addressed by the reviewer and revised the manuscript accordingly, as described below.

Regarding the acidity effect on the later-generation SOA, we have highlighted it by adding the following statement in the Abstract and Implications sections of the revised manuscript:

“This effect could be important in the atmosphere under conditions where α -pinene oxidation products in the gas-phase originating in forested areas (with low NO_x and SO_x) are transported to regions abundant in acidic aerosols such as power plant plumes or urban regions.” (Lines 19–21 and 407–410)

We have addressed the possible acid-catalyzed formation of organic nitrates as proposed by Surratt et al. (JPCA, 2008) in the manuscript as follows:

“One possible reaction is the acid-catalyzed formation of sulfated organic nitrates through α -pinene oxidation products such as nitroxyl alcohols and carbonyls reacting with sulfuric acid (Surratt et al., 2008).” (Lines 356–358)

In addition, Bleier and Elrod (JPCA, 2013) reported that there were no long-lived organic nitrate species observed from aqueous phase reactions of α -pinene oxides, suggesting the quick hydrolysis of organic nitrate species in bulk aqueous solutions. However, given that the chamber reaction system in our study is quite different than a bulk solution, we did not include the discussions regarding the stability of the organic nitrates in our study compared to that of Bleier and Elrod (JPCA, 2013).

Specific Comments to Consider Before Publication:

1.) There is concern that H_2O_2 used in low- NO_x chamber experiments may bias a larger production of organic hydroxyhydroperoxides than what might actually occur in the atmosphere. This has been recently discussed in recent results published on isoprene SOA by Liu et al. (2016, ES&T). The reason this matters is this may make SOA yields much higher than expected in the atmosphere since many of these hydroperoxides are multifunctional and are ELVOC like. Thus, you may make a lot of SOA in chamber experiments due to the high HO_2 levels but maybe not a lot in the atmosphere through these compounds. This is not answered question, but I think the authors may want to put some word of caution on the use of H_2O_2 in chamber studies.

Response: We agree that the H₂O₂ level is possibly an important factor affecting the SOA yield derived from laboratory experiments. The following statement has been added in the revised manuscript:

“The oxidant used in laboratory studies is also possibly one of the important factors affecting SOA formation. For example, a positive dependence of SOA yield on H₂O₂ level has been reported for the photooxidation of isoprene (Liu et al., 2016).” (Lines 77–79)

2.) Coatings - I agree that organic coatings could be a major reason for the observed effects you reported. I noticed that the authors probably didn't cite a recent paper that wasn't published at the time of this submission that demonstrated that α -pinene SOA coatings derived from α -pinene ozonolysis suppressed the reactive uptake of isoprene epoxydiols (IEPOX) (Riva et al, 2016, ES&T). Although only a minor point in this prior study, Lin et al. (2014, ES&T) did demonstrate that acid-catalyzed reactive uptake of IEPOX could be self-limiting depending on the initial inorganic seed aerosol. Specifically, when they injected the same amount of IEPOX into a chamber filled with either MgSO₄ + H₂SO₄ or (NH₄)₂SO₄ + H₂SO₄ they found that the SOA yield was MUCH MUCH lower for the former case due to the production of light-absorbing oligomers. It appeared that these oligomers may have formed a diffusion barrier for further uptake of IEPOX. Furthermore, Professor Faye McNeill's group at Columbia University demonstrated that the reactive uptake of α -pinene oxide is also self-limiting (Drozd et al., 2014, ACP). The point of me in raising these studies is I think it provides more credibility for the interpretation of your results.

Response: We thank the reviewer for raising this good point in support of the coating theory in this study. We have added the following statements regarding the organic coating and the self-limiting of their reactive uptake in the revised manuscript:

“A possible interpretation for such a decrease in yield is that acidic particles (i.e., the inorganic core) were gradually less accessible with increased organic coating on acidic particles. **This assumes that a phase separation of particulate organic and inorganic components occurred, from which a core-shell morphology is inferred (Drozd et al., 2013), and that** the diffusion of organic molecules into the inorganic core was considerably slowed.” (Lines 248–252)

“It is expected that further reactive uptake of α -pinene SOA to acidic particles might have been suppressed due to a phase separation, as has been reported by other studies (Drozd et al., 2013; Lin et al., 2014; Riva et al., 2016).” (Lines 255–257)

3.) Vapor losses to Chamber - The time scale of your chamber experiments is quite long, which could be a problem for low vapor pressure products in a small chamber like yours. How might wall losses of ELVOC-like species (Ehn et al., 2014, Nature) affect the SOA yields you report here? It is becoming more common practice now to use CIMS instruments to measure wall losses of gaseous species in order to provide more accurate estimates of SOA yields (Zhang et al., PNAS, 2015). The question I'm posing to the authors is since you focus on reporting SOA yields, couldn't the yields you report actually be an underestimate due to wall loss issues related to "sticky" vapors? I think this has to be acknowledged in the text.

Response: We agree that the SOA yield reported in our study might have been somewhat underestimated due to vapor wall loss. This has been addressed in the manuscript:

“The calculated SOA yield could have been affected by the wall loss of semi-volatile vapors at low α -pinene loadings, whereas this effect was not taken into account herein.”

Also, in the high NO_x case we expect that the formation of ELVOC will be highly diminished, since RO₂ + NO reactions will dominate over auto-oxidation. Nevertheless, we have reworded this sentence slightly to highlight the vapor wall loss effect as follows:

“The calculated SOA yield could have been affected by the wall loss of vapors at low α -pinene loadings, in particular for low- and semi-volatile gaseous species (Ehn et al., 2014); however, such an effect was not taken into account herein.” (Lines 154–156)

4.) Something remains unclear to me. In the experiments using pure ammonium sulfate seed aerosol, do the authors think these particles effloresced? If so, how can you accurately calculate the acidities of these particles? Further, if they did efflorescence, do you think the lack of aerosol water on these particles could have affected the potential multiphase chemistry?

Response: We did not report the particle acidity for the experiments using pure ammonium sulfate seed particles (as seen in Table 1 of the manuscript), since there was no aqueous phase based on the estimation with the E-AIM model. Given that the efflorescence relative humidity for ammonium sulfate particles with a dry diameter of 150 nm is approximately 30% (e.g., Gao et al., 2006; Saukko et al., 2015), the efflorescence of these particles possibly occurred to a degree at the studied RH. Previous studies have demonstrated that α -pinene SOA yield increased with the increase in RH (e.g., Jonsson et al., 2006; Kristensen et al., 2014; Zhang et al., 2015). The lack of aerosol water could increase the timescale of particle-phase diffusion and the mean molecular weight of the particulate organic species, and also possibly affect the reactive uptake of certain compounds. This is an open question which warrants further investigations. However, the particle water content likely did not contribute substantially to the observed increase in α -pinene SOA yield with acidity in this study, as discussed in section 3.2.1.

Gao, Y., Chen, S. B., and Yu, L. E.: Efflorescence relative humidity for ammonium sulfate particles, *J. Phys. Chem. A*, 110(24), 7602–7608, doi:10.1021/jp057574g, 2006.

Saukko, E., Zorn, S., Kuwata, M., Keskinen, J., and Virtanen, A.: Phase state and deliquescence hysteresis of ammonium-sulfate-seeded secondary organic aerosol, *Aerosol Sci. Technol.*, 6826(June 2015), 00–00, doi:10.1080/02786826.2015.1050085, 2015.

Zhang, X., McVay, R. C., Huang, D. D., Dalleska, N. F., Aumont, B., Flagan, R. C., and Seinfeld, J. H.: Formation and evolution of molecular products in α -pinene secondary organic aerosol., *Proc. Natl. Acad. Sci. U. S. A.*, 112, 14168–73, doi:10.1073/pnas.1517742112, 2015.

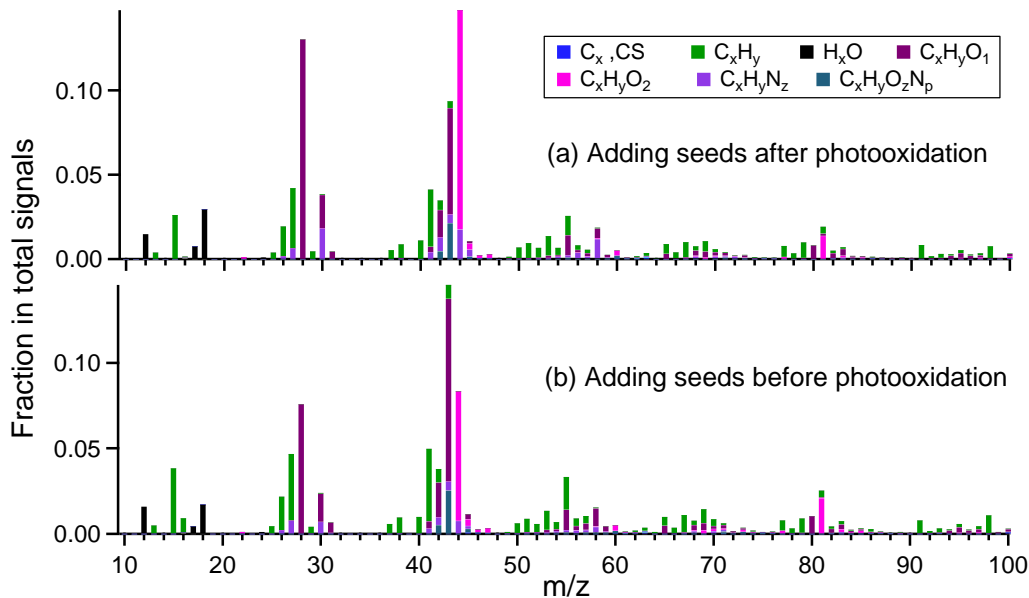
5.) Lack of acidity effect under low-NO_x conditions: The lack of an acidity effect is interesting! Recent work by Liu et al. (2015, PCCP) demonstrated the hydroperoxides might react on acidic particles and off gas more volatile products? Do you think this could be happening here? One way to check is to examine your data where you conduct the photooxidation experiments without seed aerosol but later add in the acidic aerosol. Does your PTR-MS reveal enhanced volatile product formation after this introduction of seed aerosol under low-NO_x conditions? Further, I wonder if you see changes in the aerosol composition with the AMS? That might reveal something about potential multiphase chemistry? It's possible with the AMS you see very different OA mass spectra when you add in the seed aerosol, suggesting something is occurring. This kind of connection to the chemical data you have could provide more insights into the SOA yields you report.

Response: The dependence of reactive uptake on neutralization (i.e., aerosol acidity) varies by species, as reported by Liu et al. (2016, PCCP). It is possible that certain organic compounds such as hydroperoxides might react on acidic particles and produce volatile products. This would be a plausible explanation for the different acidity effects between high- and low-NO_x conditions observed here.

Further studies are warranted to elucidate the gas-phase chemistry in this reaction system. It is a challenge to provide a detailed characterization of the gas-phase oxidation products here, as there is no quantitative measurement of those species by the PTR-MS in this study, and the normalized PTR-MS spectra were not significantly different regardless. However, we have compared the mass spectra of α -pinene SOA between the experiments with and without acidic seed particles under low-NO_x conditions. As seen from the figure below, the mass spectra from the two conditions are quite different, and it seems that the α -pinene SOA formed by adding acidic seed particles after photooxidation are more oxygenated than those of adding acidic seed particles before photooxidation. This could suggest that volatile organic species are possibly produced in the presence of acidic particles under low-NO_x conditions. Therefore, we have added the following statement in the revised manuscript:

“In addition, some oxidation products such as hydroperoxides might have reacted on the acidic particles and produced more volatile products (Liu et al., 2016), which may manifest as a decrease in the acidity effect (i.e., lower yield) for α -pinene SOA under low-NO_x conditions.” (Lines 334–336)

Liu, Y. J., Kuwata, M., McKinney, K. A., and Martin, S. T.: Uptake and release of gaseous species accompanying the reactions of isoprene photo-oxidation products with sulfate particles, *Phys. Chem. Chem. Phys.*, 18(3), 1595–1600, doi:10.1039/C5CP04551G, 2016. (Lines 570–572)



(This Figure presents the high-resolution mass spectra of α -pinene SOA for low- NO_x experiments with adding acidic seed particles (molar ratio of $\text{NH}_4/\text{SO}_4 = 0.5$) (a, Exp. 12 in Table 1) after and (b, Exp. 7 in Table 1) before the photooxidation. The mass spectra were averaged in the first two hours of the reactive uptake of oxidation products after seed particles were added.)

6.) The authors say the particles were coated with SOA. How is this known? Are you assuming this based on prior studies that related phase separation to O:C ratios (which is fine, but wanting to make sure I'm clear on how you know it is a coating versus mixture). Or did you conduct microscopy measurements to know this?

Response: The coating theory in our study is an assumption based on previous studies and we did not conduct aerosol microscopy measurements. This was partly explained in the previous version. We have provided more explanations to make this point clearer in the revised manuscript as follows:

“A possible interpretation for such a decrease in yield is that acidic particles (i.e., the inorganic core) were gradually less accessible with increased organic coating on acidic particles. **This assumes that a phase separation of particulate organic and inorganic components occurred, from which a core-shell morphology is inferred (Drozd et al., 2013), and that** the diffusion of organic molecules into the inorganic core was considerably slowed.” (Lines 248–252)

7.) Is it possible to show average mass spectra from each condition in the SI? I'm curious to know if the authors find any marker ions at higher m/zs that could potentially be used as tracers? For example, Lin et al. (2012, ES&T) and Budisulistiorini et al. (2013, ES&T) showed that m/z 82 could be a direct marker ion for the acid-catalyzed reactive uptake of IEPOX. This has been later confirmed by Hu et al. (2015, ACP).

Response: The average mass spectra of α -pinene SOA under different experimental conditions (see below) have been presented in Figure S2 of the supplement. We did not find strong evidence of specific tracer ions related to acid-catalyzed α -pinene SOA in this study. The high-resolution organic fragment families showed an apparent variation pattern with the increase in particle acidity under high-NO_x conditions, as discussed in sections 3.3 and 3.4 of the manuscript. We have added a statement regarding Figure S2 in the revised manuscript:

“The effect of particle acidity on the chemical composition of α -pinene SOA in high- and low-NO_x experiments is examined from the distribution of organic fragments in the high-resolution organic aerosol mass spectra (see **Figure S2 in the Supplement**).” (Lines 302–304)

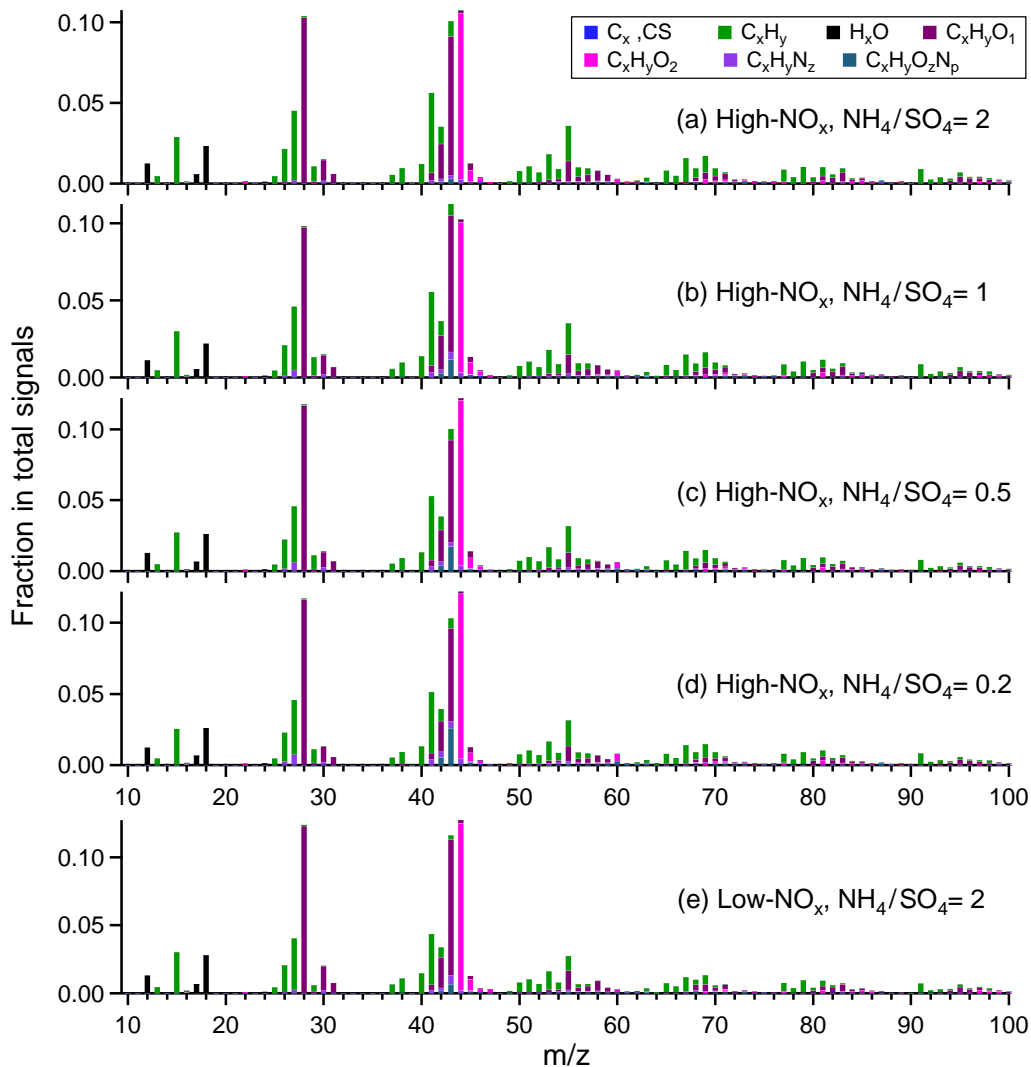


Figure S2. High-resolution mass spectra of α -pinene SOA under (a–d) high- and (e) low- NO_x conditions. The mass spectra were averaged on the irradiation times of 1–5 h and 2–12 h under high- and low- NO conditions, respectively. The mass spectra of α -pinene SOA under low- NO_x conditions for acidic particles, which are not presented here, resemble that of ammonium sulfate particles in (e).

Minor Comments:

1.) Page 2, Line 35: Need citation to literature here for this sentence.

The sentence referred to: “The effect of aerosol acidity on SOA formation is one of the scientific questions currently under open debate.”

Response: This sentence was followed by detailed explanation regarding “the scientific questions currently under open debate” in the rest of this paragraph. Therefore, rather than adding a citation here, we have revised the original sentence slightly as follows to make it clearer:

“The effect of aerosol acidity on SOA formation is one of the scientific questions currently under open debate, **as described below.**” (Lines 36–37)

2.) Page 2, Line 38: Do the authors mean the use of "e.g." instead of "i.e." when citing these prior studies on acid-catalyzed chemistry?

Response: Yes, the “i.e.” has been corrected to “e.g.”.

3.) Page 2, Line 39: The authors may want to cite Lin et al. (2012, ES&T) from the Surratt group here.

Response: We have added Lin et al. (2012) as one of the references:

“The presence of acidic aerosol particles has been reported to enhance the reactive uptake of gas phase organic species and increase SOA yields due to acid-catalyzed reactions (e.g., Garland et al., 2006; Jang et al., 2004; Liggió and Li, 2006; **Lin et al., 2012**; Northcross and Jang, 2007; Surratt et al., 2010; Xu et al., 2015a).” (Lines 39–41)

“Lin, Y.-H., Zhang, Z., Docherty, K. S., Zhang, H., Budisulistiorini, S. H., Rubitschun, C. L., Shaw, S. L., Knipping, E. M., Edgerton, E. S., and Kleindienst, T. E.: Isoprene epoxydiols as precursors to

secondary organic aerosol formation: acid-catalyzed reactive uptake studies with authentic compounds, Environ. Sci. Technol., 46, 250–258, doi:10.1021/es202554c, 2012.” (Lines 39–41)

4.) Page 2, Lines 41-42: The authors mean to say the following?

"Furthermore, the enhanced formation of SOA and organosulfates has been reported from the acid-catalyzed reactive uptake of epoxide compounds in ambient aerosols that are acidic enough to promote this multiphase chemistry."

The sentence referred to: “Furthermore, the enhanced formation of SOA, organic sulfates, and epoxide compounds has been reported in ambient environments with an abundance of acidic aerosol particles (Hawkins et al., 2010; Lin et al., 2012; Rengarajan et al., 2011; Zhang et al., 2012; Zhou et al., 2012)...”

Response: This statement proposed by the reviewer is more appropriate except the acid-catalyzed reactive uptake is not only limited to epoxide compounds. Therefore, we have revised the original sentence as follows:

“Furthermore, the enhanced formation of SOA and organic sulfates has been reported from the acid-catalyzed reactive uptake of VOC oxidation products in ambient aerosols that are acidic enough to promote this multiphase chemistry (Hawkins et al., 2010; Lin et al., 2012; Rengarajan et al., 2011; Zhang et al., 2012; Zhou et al., 2012)...” (Lines 45–48)

The studies you cite are fine, but you may want to report recent kinetics studies showing that this is feasible, such as work by Matthew Elrod's group (Oberlin college) as well as Gaston et al. (2014, ES&T) and Riedel et al. (2015, ES&T Lett).

Response: We have added the following statement and the relevant literatures in the revised manuscript:

“In contrast, recent kinetics studies have demonstrated that particle acidity strongly affects the reactive uptake of isoprene epoxydiols (Gaston et al., 2014; Riedel et al., 2015).” (Lines 44–45)

“Gaston, C. J., Riedel, T. P., Zhang, Z., Gold, A., Surratt, J. D., and Thornton, J. A.: Reactive uptake of an isoprene-derived epoxydiol to submicron aerosol particles, *Environ. Sci. Technol.*, 48, 11178–11186, doi:10.1021/es5034266, 2014.” (Lines 485–486)

“Riedel, T. P., Lin, Y., Budisulistiorini, S. H., Gaston, C. J., Thornton, J. A., Zhang, Z., Vizueté, W., Gold, A., and Surratt, J. D.: Heterogeneous reactions of isoprene-derived epoxides: reaction probabilities and molar secondary organic aerosol yield estimates, *Environ. Sci. Technol. Lett.*, 2, 38–42, doi:10.1021/ez500406f, 2015.” (Lines 618–620)

5.) Page 12, Line 368: Should "Noted" be changed to "It should be noted...."

The sentence referred to: “Noted that a small amount of $C_xH_yN_p^+$ and $C_xH_yO_zN_p^+$ fragments were also observed under low- NO_x conditions, where NO was not added (Figure 6b).”

Response: Yes, we agree with this correction. The original sentence has been revised to:

“It should be noted that a small amount of $C_xH_yN_p^+$ and $C_xH_yO_zN_p^+$ fragments were also observed under low- NO_x conditions, where NO was not added (Figure 6b).” (Lines 380–381)

The effect of particle acidity on secondary organic aerosol formation from α -pinene photooxidation under atmospherically relevant conditions

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Abstract. Secondary organic aerosol (SOA) formation from photooxidation of α -pinene has been investigated in a photochemical reaction chamber under varied inorganic seed particle acidity levels at moderate relative humidity. The effect of particle acidity on SOA yield and chemical composition was examined under high- and low- NO_x conditions. The SOA yield (4.2%–7.6%) increased nearly linearly with the increase in particle acidity under high- NO_x conditions. In contrast, the SOA yield (28.6%–36.3%) was substantially higher under low- NO_x conditions, but its dependency on particle acidity was insignificant. A relatively strong increase in SOA yield (up to 220%) was observed in the first hour of α -pinene photooxidation under high- NO_x conditions, suggesting that SOA formation was more effective for early α -pinene oxidation products in the presence of fresh acidic particles. The SOA yield decreased gradually with the increase in organic mass in the initial stage (approximately 0–1 hour) under high- NO_x conditions, which is likely due to the inaccessibility to the acidity over time with the coating of α -pinene SOA, assuming a slow particle-phase diffusion of organic molecules into the inorganic seeds. The formation of later-generation SOA was enhanced by particle acidity even under low- NO_x conditions when introducing acidic seed particles after α -pinene photooxidation, suggesting a different acidity effect exists for α -pinene SOA derived from later oxidation stages. This effect could be important in the atmosphere under conditions where α -pinene oxidation products in the gas-phase originating in forested areas (with low NO_x and SO_x) are transported to regions abundant in acidic aerosols such as power plant plumes or urban regions. The fraction of oxygen-containing organic fragments ($\text{C}_x\text{H}_y\text{O}_1^+$ 33–35% and $\text{C}_x\text{H}_y\text{O}_2^+$ 16–17%) in the total organics and the O/C ratio (0.52–0.56) of α -pinene SOA were lower under high- NO_x conditions than those under low- NO_x conditions (39–40%, 17–19%, and 0.61–0.64), suggesting that α -pinene SOA was less oxygenated in the studied high- NO_x conditions. The fraction of nitrogen-containing organic fragments ($\text{C}_x\text{H}_y\text{N}_z^+$ and $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$) in the total organics was enhanced with the increases in particle acidity under high- NO_x conditions, indicating that organic nitrates may be formed heterogeneously through a mechanism catalyzed by particle acidity or that acidic conditions facilitate the partitioning of gas phase organic nitrates into particle phase. The results of this study suggest that inorganic acidity has a significant role to play in determining various organic aerosol chemical properties such as mass yields, oxidation state, and organic nitrate content. The acidity effect being further dependent on the time scale of SOA formation is also an important parameter in the modeling of SOA.

1 Introduction

Secondary organic aerosols (SOA) formed by oxidation of biogenic and anthropogenic volatile organic compounds (VOC) comprise a substantial portion of submicron aerosol particles in the atmosphere (Kanakidou et al., 2005; Zhang et al., 2007a). Understanding the physical and chemical properties associated with SOA formation and transformation is important to adequately assess aerosol impacts on climate and human health (Hallquist et al., 2009). The effect of aerosol acidity on SOA formation is one of the scientific questions currently under open debate, as described below. Acid-catalyzed heterogeneous reactions such as hydration, hemiacetal/acetal formation, polymerization, and aldol condensation have been proposed to form SOA (Jang et al., 2002). The presence of acidic aerosol particles has been reported to enhance the reactive uptake of gas phase organic species and increase SOA yields due to acid-catalyzed reactions (i.e.g., Garland et al., 2006; Jang et al., 2004; Liggiio and Li, 2006; Lin et al., 2012; Northcross and Jang, 2007; Surratt et al., 2010; Xu et al., 2015a). However, other studies have suggested that those reactions may be thermodynamically or kinetically unfavorable and are possibly insignificant in the real atmosphere (Barsanti and Pankow, 2004; Casale et al., 2007; Kroll et al., 2005; Li et al., 2008). In contrast, recent kinetics studies have demonstrated that particle acidity strongly affects the reactive uptake of isoprene epoxydiols (Gaston et al., 2014; Riedel et al., 2015). Furthermore, the enhanced formation of SOA, and organic sulfates, and epoxide compounds has been reported from the acid-catalyzed reactive uptake of VOC oxidation products in ambient environments with an abundance of aerosols that are acidic aerosol particles enough to promote this multiphase chemistry (Hawkins et al., 2010; Lin et al., 2012; Rengarajan et al., 2011; Zhang et al., 2012; Zhou et al., 2012), which is contrary to other field studies showing no apparent evidence of acid-catalyzed SOA formation (Peltier et al., 2007; Takahama et al., 2006; Tanner et al., 2009; Zhang et al., 2007b). The dependence of SOA formation on aerosol acidity generally has not been incorporated in many atmospheric chemistry models thus far due to the large uncertainties associated with the quantification of acidity effects, with the exception of the acidity effect for SOA via isoprene epoxydiol uptake (Marais et al., 2016; Pye et al., 2013).

A number of laboratory studies have investigated the effect of particle acidity on SOA formation from oxidation of various precursor hydrocarbons such as isoprene, terpenes, toluene, m-xylene, and 1, 3-butadiene (e.g., Kristensen et al., 2014; Lewandowski et al., 2015; Ng et al., 2007a; Offenbergl et al., 2009; Song et al., 2013; Surratt et al., 2007b). α -Pinene is the most abundant biogenic monoterpene emitted from terrestrial vegetation (Guenther et al., 2012). The oxidation of α -pinene by hydroxyl radicals (OH), ozone (O₃), and nitrate radicals produces a variety of multifunctional organic compounds such as carboxylic acids, carbonyls, peroxides, ester dimers, epoxides, alcohols, and organic nitrates (Calogirou et al., 1999; Yasmeen et al., 2012; Zhang et al., 2015). Despite the efforts of previous laboratory studies under various experimental conditions, the effect of aerosol acidity on SOA formation from individual hydrocarbons remains unclear due to the complexity of this scientific question. In particular, the magnitude of the acidic effect on SOA yields for α -pinene has been found to vary significantly. For instance, a nearly 40% increase in organic carbon (OC) was observed for the ozonolysis of α -pinene in the presence of acidic seed particles without NO_x, and aerosol acidity played an important role in the formation

65 of high molecular weight organic molecules in particles (Iinuma et al., 2004). A linear increase of 0.04% in OC mass per
nmol $\text{H}^+ \text{m}^{-3}$ was reported from the photooxidation of α -pinene with NO_x , and this effect was independent of initial
hydrocarbon concentration or the generated organic mass (Offenberg et al., 2009). In contrast, Eddingsaas et al. (2012)
reported a relatively small increase of SOA yield (approximately 22%) for OH photooxidation of α -pinene under high- NO_x
70 photooxidation. Kristensen et al. (2014) similarly found that the increase of aerosol acidity has a negligible effect on SOA
formation from ozonolysis of α -pinene under low- NO_x conditions.

These inconsistent results reported previously are most likely attributed to the varied experimental parameters such as
particle acidity, initial hydrocarbon concentration, oxidant type and level, NO_x level, temperature, and relative humidity
(RH). Most previous studies were conducted with different acidity levels, and therefore a quantitative comparison of the
75 acidity effect among various studies is difficult. Laboratory studies were usually performed with relatively high loadings of
hydrocarbons (e.g., from tens of ppb to several ppm), which would result in higher yield and lower oxidation state of
laboratory SOA compared to ambient SOA (Ng et al., 2010; Odum Jay et al., 1996; Pfaffenberger et al., 2013; Shilling et al.,
2009). The oxidant used in laboratory studies is also possibly one of the important factors affecting SOA formation. For
example, a positive dependence of SOA yield on H_2O_2 level has been reported for the photooxidation of isoprene (Liu et al.,
80 2016). In addition, the presence of NO_x during α -pinene oxidation may change the reaction chemistry and lead to the
formation of relatively volatile oxidation products, and hence decrease α -pinene SOA yields (Eddingsaas et al., 2012; Ng et
al., 2007a). Moreover, temperature is an important factor in SOA formation; higher SOA yields may be obtained at lower
temperature (Saathoff et al., 2009; Takekawa et al., 2003). RH is another important factor, the decrease of which may lead to
an increase in α -pinene SOA yields (Jonsson et al., 2006); however, many previous studies have been performed at very low
85 RH (e.g., less than 10%) or even dry conditions. As a result of the above issues, it is highly important for laboratory studies
to investigate the acidity effect on SOA formation under more realistic conditions approaching those of the ambient
atmosphere. This would facilitate an accurate parameterization of the acidity effect for incorporation into air quality models.

This study aims to improve our current understanding of the effect of particle acidity on SOA formation from
photooxidation of α -pinene. Photochemical chamber experiments were performed under conditions with relatively low α -
90 pinene loadings and moderate RH, which are more representative of the ambient atmosphere. The yield of α -pinene SOA
was obtained at various particle acidity levels under high- and low- NO_x conditions. The dependence of SOA yield on particle
acidity and the time scale of the acidity effect are characterized and discussed. The effect of particle acidity on the chemical
composition of α -pinene SOA, the fragment distributions of bulk organics, and the oxidation state of organics are examined
based on the high-resolution analysis of organic aerosol mass spectra. The possible contribution of particle acidity to the
95 formation of particulate organic nitrates under high- NO_x conditions is also discussed. Finally, the potential significance of
the observed acidity effect in the ambient atmosphere is summarized.

2 Experimental methods

Photooxidation experiments were performed in a 2 m³ Teflon chamber (Welch Fluorocarbon) enclosed in an aluminum support (Liggio and Li, 2006; Liggio et al., 2005). Twelve black light lamps (model F32T8/350BL, Sylvania) were used as the irradiation source with intensity peaking at approximately 350 nm. The chamber was flushed by zero air with the lamps turned on for more than 20 hours before each experiment to avoid contamination from previous experiments. Hydrogen peroxide (H₂O₂) vapor was introduced into the chamber to produce OH radicals during the first 6 hours of flushing. Temperature and RH inside the chamber were monitored continually using a temperature and humidity probe (model HMP 60, Vaisala). Temperature was not controlled during the experiments, but it was relatively constant at 25 °C before experiments began and increased to a stable value (approximately 30–34 °C) after the lamps were turned on. RH was maintained manually by adding water vapors generated from a bubbler with zero air as a carrier gas (15 L min⁻¹). Other chamber inputs (e.g., H₂O₂ vapor, NO, seed particles, and α -pinene) were conducted after the RH reached approximately 60%. RH inside the chamber stabilized at approximately 29–43% after the lamps were turned on for about 1 hour due to the increase in temperature.

H₂O₂ vapor, as the source of OH radical, was introduced into chamber using a bubbler with a flow of zero air (0.09 L min⁻¹) passing through H₂O₂ aqueous solution (30 weight % in water, Sigma-Aldrich) for 1 hour. Ammonium sulfate (AS)/sulfuric acid (SA) solutions with varied NH₄/SO₄ molar ratios were used to provide various acidities in seed particles. A complete list of the composition of the seed particles and other initial conditions in all experiments is given in Table 1. The seed particles were generated by atomizing AS/SA aqueous solution using an aerosol generator (model 3706, TSI), dried in a silica gel diffusion dryer, and then size-selected at 150 nm in mobility diameter using a differential mobility analyzer (DMA, model 3081, TSI). Nitric oxide (NO) was added into the chamber from a compressed gas cylinder (9.1 ppm NO in nitrogen) in high-NO_x experiments, in contrast to low-NO_x experiments where NO was not added. A micro-syringe was used to inject approximately 0.25 μ L liquid α -pinene (99+%, Sigma-Aldrich) into the chamber through a stainless steel tube with a zero air at 3 L min⁻¹. After achieving the desired experimental conditions for a stable 30 min period, photooxidation reactions were initiated by turning on the lamps. The typical photooxidation time was 6 and 15 hours for high- and low-NO_x experiments, respectively.

Four experiments were also performed to investigate the effect of aerosol acidity on α -pinene oxidation products at different photooxidation stages (Exp. 9–12; Table 1). Photooxidation of α -pinene was conducted without seed particles in the reaction chamber for 2 and 4 hours under high- and low-NO_x conditions, respectively. This was followed by turning off the lamps and adding neutral/acidic seed particles into the chamber within 1 hour. The experiments continued for another 6 hours on the reactive uptake of the α -pinene oxidation products by the newly introduced seed particles in the dark.

The concentration of α -pinene in the chamber was measured in real-time using a proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS, Ionicon Analytik GmbH) (Hansel et al., 1999; Lindinger and Jordan, 1998). The mixing ratios of NO and O₃ were monitored using a NO analyzer (model 42i-Y, Thermo Scientific) and an O₃ monitor (model 202,

2B Technologies), respectively. The particle number size distribution was measured using a scanning mobility particle sizer (SMPS) consisting of a DMA (model 3081, TSI) and a condensation particle counter (model 3776, TSI). The non-refractory chemical composition of the submicron aerosol particles, including organics, sulfate, ammonium, nitrate, and chloride, was measured using a high resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS, Aerodyne Research) (DeCarlo et al., 2006). The AMS instrument was operated in a high-sensitivity mode (V-mode) with the data stored at 1 min intervals. The AMS data were processed using the standard ToF-AMS data analysis software (SQUIRREL v1.56D and PIKA v1.15D, <http://cires.colorado.edu/jimenez-group/ToFAMSResources/ToFSoftware/>). The mass concentrations of aerosol species were generated from the PIKA analysis of raw mass spectral data. A collection efficiency value of 0.7 was applied for the AMS data analysis based upon the comparison of the volume concentrations derived from AMS and SMPS measurements, assuming that particles are spherical and the densities of organics, sulfate, ammonium, and nitrate are 1.4, 1.77, 1.77, and 1.725 g cm⁻³, respectively. Note that aerosol particles were not dried upstream of the AMS and SMPS measurements, and thus particle water content might have contributed to the SMPS-derived volume concentrations. This was not taken into account for the AMS-derived volume concentration. The detection limits of organics, sulfate, nitrate, and ammonium, defined as 3 times the standard deviations of the mass concentrations of individual species (1-min average) in particle-free air, were 34, 4, 1, and 5 ng m⁻³, respectively.

SOA yield, which represents the aerosol formation potential of precursor hydrocarbon, was calculated from the ratio of generated SOA mass (ΔM_0) to the reacted α -pinene mass (ΔHC). The SOA yields and ΔM_0 presented in Table 1 correspond to the maximum values at the end of each experiment. Organic mass concentrations derived from AMS measurement were wall-loss corrected according to the decay of sulfate particles in the chamber, i.e., by multiplying the ratios of the initial sulfate concentrations to the instantaneously measured sulfate concentrations. This correction assumed that α -pinene oxidation products condensed on the sulfate particles instead of their self-nucleation. This assumption is appropriate given that less than 50 particles cm⁻³ were contributed by self-nucleation and that an obvious increase in organic mass concentration was not observed from the AMS measurement in the experiments without adding seed particles. The decay rate of particles coated with organics was assumed to be same as that of pure sulfate particles, although the later could be slightly higher due to the larger Brownian diffusion rate of smaller particles. The calculated SOA yield could have been affected by the wall loss of ~~semi-volatile~~-vapors at low α -pinene loadings, whereas this in particular for low- and semi-volatile gaseous species (Ehn et al., 2014); however, such an effect was not taken into account herein.

The initial seed composition in each experiment was predicted using the Extended Aerosol Inorganic Thermodynamic Model (E-AIM) II (<http://www.aim.env.uea.ac.uk/aim/aim.php>) (Clegg et al., 1998). The concentrations of inorganic sulfate, nitrate, and ammonium derived from the AMS measurement as well as the temperature and RH in the chamber were input parameters. The pH of aerosol particles was calculated by $-\log(\gamma \times [H^+])$ using the model outputs, where γ and $[H^+]$ are the activity coefficient of H⁺ and the molar concentration of dissociated H⁺ (mol L⁻¹) in the aqueous phase, respectively. OH concentration in each experiment was estimated from a linear fitting of the first order decay of gaseous α -pinene by OH radicals, i.e., the difference between the total α -pinene decay and the α -pinene consumed by O₃, as described by Liu et al.

165 (2015). The OH concentrations were calculated to be approximately $4.3\text{--}5.9 \times 10^6$ and $0.8\text{--}1.1 \times 10^6$ molecules cm^{-3} for experiments under high- and low- NO_x conditions, respectively. Nitrate radical (NO_3) generated from the reactions such as NO_2 with O_3 might also affect the α -pinene decay (and hence the estimated OH), whereas it was not taken into account here because NO_3 levels were likely to be small under the studied irradiation conditions.

170 3 Results and discussion

3.1 α -Pinene SOA formation under high- and low- NO_x conditions

An increase of α -pinene SOA mass concentration with the decay of α -pinene mixing ratio in high- and low- NO_x experiments using $(\text{NH}_4)_2\text{SO}_4$ seed particles (Exp. 1 and 5 in Table 1) is shown in Figure 1. Under the high- NO_x condition, the increase of α -pinene SOA mass was observed shortly after the irradiation started until the end of the experiment (Figure 175 1a). Gaseous α -pinene was mostly consumed within approximately 1.5 hours. NO (66 ppbv initially) was consumed in the first 30 min of the irradiation. The formation of O_3 was not suppressed over the experiment. O_3 increased to more than 200 ppb at the end of the experiments, and therefore ozonolysis reactions would have contributed to the formation of α -pinene SOA. A rough estimation shows that α -pinene consumed by ozonolysis accounted for in the range of 0–28% of the total α -pinene decay, as seen from the difference between the total α -pinene decay and OH consumed α -pinene in Figure 1a. Nitrate 180 radicals may also have been generated from NO_x reactions and have contributed to α -pinene SOA formation, whereas its direct measurement was not available in this study.

In contrast, under the low- NO_x condition, the increase of SOA mass concentration and the decay of α -pinene were relatively slower (Figure 1b). This is most likely due to the lower production of OH radicals from H_2O_2 photolysis under low- NO_x condition, that is, 1.1×10^6 molecules cm^{-3} compared to that of 5.3×10^6 molecules cm^{-3} under high- NO_x 185 conditions. A plateau of the generated SOA mass was observed after approximately 12 hours of irradiation, suggesting that SOA formation reached equilibrium after α -pinene was consumed completely, if the gas-particle partitioning was reversible (Grieshop et al., 2007). NO was less than 0.3 ppbv through the entire experiment. A slight increase of O_3 (up to 30 ppb) was also observed under low- NO_x conditions, which might have resulted from the photolysis of a small amount of NO_2 released from the chamber walls. Less than approximately 47% of α -pinene was consumed by ozonolysis.

190 The α -pinene SOA yield was 4.2% when using $(\text{NH}_4)_2\text{SO}_4$ seed particles under high- NO_x condition, which is a factor of 8.4 lower than that under low- NO_x condition (35.2%) (Table 1). The relatively lower SOA yield under higher NO_x levels is consistent with those reported previously for the photooxidation and ozonolysis of α -pinene (Eddingsaas et al., 2012; Ng et al., 2007a; Presto et al., 2005). Similar relationships are also observed in the photooxidation of isoprene and aromatic hydrocarbons such as benzene, toluene, and *m*-xylene (Kroll et al., 2006; Ng et al., 2007b). The dependence of α -pinene 195 SOA yield on NO_x level is possibly due to the different gas-phase chemical reactions of the intermediate organic peroxy radicals (RO_2) formed in the initial photooxidation stage. RO_2 reacted primarily with NO under high- NO_x conditions and

generated relatively more volatile products that reduced the overall SOA yield, whereas the reactions of RO₂ with other peroxy radicals (e.g., RO₂ and HO₂) were dominant under low-NO_x conditions (Kroll et al., 2006; Presto et al., 2005; Xu et al., 2014). Approximately 62–99% of RO₂ radicals reacted with NO over the entire experimental time (totally 6 hours) under high-NO_x conditions in this study, which was estimated based on the Master Chemical Mechanism constrained by the initial experimental conditions (S1 and Figure S1 in the Supplement). The observed difference in SOA yields might also be affected to some extent by other experimental conditions such as the initial α -pinene concentration, seed loading, and temperature, but NO_x level was most likely the primary cause, given that other factors did not vary as much as NO_x in these experiments (Table 1).

A comparison of SOA yields as a function of the generated SOA mass (ΔM_0) in this study and previous studies of α -pinene photooxidation is shown in Figure 2. The experimental parameters and SOA yields from previous studies are summarized in Table 2. SOA yields in these studies varied in the range of approximately 1.3–24% in the presence of NO_x, in contrast to those of 26–46% without NO_x. The SOA yields observed in our study are generally comparable to those reported from previous studies despite the different experimental parameters. The SOA yield under high-NO_x condition in our study is in particular closest to those with lower α -pinene level (Ng et al., 2007a; Odum et al., 1996) and at higher temperature (Takekawa et al., 2003). It has been established that low α -pinene level and high temperature can lead to relatively low SOA yields, which is possibly due to the changes of gas/particle partitioning thermodynamics in the reaction system (Odum et al., 1996; Pankow, 2007; Takekawa et al., 2003). The SOA yield under low-NO_x conditions here is similar to those reported by Eddingsaas et al. (2012) but lower than those reported by Ng et al. (2007a). The varied SOA yields among these studies most likely depend on different experimental conditions. Therefore, laboratory studies performed under conditions relevant to the atmosphere are important for an inter-comparison among studies and for ultimately using those results in air quality models.

3.2 Effect of particle acidity on α -pinene SOA yield

3.2.1 Dependence of SOA yield on particle acidity

The initial pH value of aerosol particles calculated from the E-AIM was in the range of –0.93 to –1.66 in the high- and low-NO_x experiments (see Table 1). An increase of the α -pinene SOA yield with an increase of particle acidity was observed under high-NO_x conditions. The final SOA yields were 5.6%, 6.6%, and 7.6% for acidic particles with the initial NH₄/SO₄ molar ratios of 1.0, 0.5, and 0.2, respectively (Table 1). This corresponds to 1.3, 1.6, and 1.8 times the SOA yield for neutral particles (i.e., 4.2%). Conversely, the final SOA yields for acidic particles varied from 28.6% to 36.3% under low-NO_x conditions, from which a systematic increase in SOA yield with particle acidity was not observed. Clearly, the presence of acidic particles promotes the formation of α -pinene SOA under high-NO_x conditions and NO_x is likely involved in the acid-catalyzed reactions during α -pinene photooxidation. The dependence of α -pinene SOA yield on particle acidity under only high-NO_x conditions in this study is similar to those reported by Eddingsaas et al. (2012), whereas they observed a smaller increase of SOA yield (approximately 22% compared to 30–80% here) when using acidic particles. The effect of particle

acidity on SOA formed from α -pinene has been reported to be much lower than that for isoprene, e.g., the former one was 8
230 times lower than the later one (Offenberg et al., 2009).

In addition to the effect of particle acidity, the α -pinene SOA yield was also possibly influenced by the liquid water
content in the particles. The initial water content in the seed particles estimated by the E-AIM was on average 5.2, 6.3, and
10.3 $\mu\text{g m}^{-3}$ for high- NO_x experiments with NH_4/SO_4 molar ratios of 1.0, 0.5, and 0.2, respectively. Therefore, more water
was present in the particles with higher acidity. The higher particle water content could prompt the partitioning of gas-phase
235 water-soluble organic species by providing a larger medium for their dissolution and therefore potentially increase the SOA
yield (Carlton and Turpin, 2013). However, there was no apparent increase in the SOA yield under low- NO_x conditions,
even though seed particles with similarly varied water content were used (Exp. 5–8; Table 1) and despite the fact that
products with higher O/C (hence higher solubility) were formed (section 3.3). This suggests that the particle water content
likely did not contribute substantially to the observed increase in α -pinene SOA yield with acidity under high- NO_x
240 conditions.

3.2.2 Time scale of acidity effect

SOA yield is found to be a strong function of the generated SOA mass (ΔM_0) (Odum et al., 1996). The time-dependent
SOA yield as a function of ΔM_0 for acidic and neutral particles under high- and low- NO_x conditions is shown in Figure 3.
245 Under high- NO_x conditions, the increase of SOA yield with particle acidity (black through green points in Figure 3a) was
much stronger in the first hour of photooxidation than in the later period, suggesting that the acidity effect was more
significant in the initial period of photooxidation in this reaction system. This is possibly due to fresh acidic particles being
more accessible for acid-catalyzed reactions by early α -pinene oxidation products in the initial stage. A slight decrease in the
SOA yield for acidic particles was also observed after the relatively higher SOA yields within the first 30 min. A possible
250 interpretation for such a decrease in yield is that acidic particles (i.e., the inorganic core) were gradually less accessible with
increased organic coating on acidic particles, ~~assuming~~. This assumes that a phase separation of particulate organic and
inorganic components occurred, from which a core-shell morphology is inferred (Drozd et al., 2013), and that the diffusion
of organic molecules into the inorganic ~~seed~~ score was considerably slowed. This process was indeed possible at the studied
final RH (approximately 29–43%), given that SOA could be in an amorphous solid or semisolid state with high viscosity at
255 low to moderate RH (e.g., $\leq 30\%$) (Renbaum-Wolff et al., 2013; Virtanen et al., 2010). This indicates that the acidity effect
is particularly important in the initial stages of α -pinene oxidation in the presence of acidic particles. It is expected that
further reactive uptake of α -pinene SOA to acidic particles might have been suppressed due to a phase separation, as has
been reported by other studies (Drozd et al., 2013; Lin et al., 2014; Riva et al., 2016). The SOA yields increased nearly
linearly with ΔM_0 after 2 hours of irradiation, suggesting that the growth of SOA mass continued after the complete
260 consumption of the α -pinene. This is possibly due to the further oxidation of early-generation products such as carbonyls,
hydrocarbonyls, and organic nitrates, and/or the continued partitioning of gas-phase oxidation products into particle-phase.
In contrast, the growth curves of SOA yields for acidic particles under low- NO_x conditions were quite similar to that for

neutral particles over the irradiation time (Figure 3b), which again suggests that acidity effect is insignificant under the studied low-NO_x conditions.

265 The acidity effect on α -pinene SOA yield was relatively strong in the first hour of irradiation under high-NO_x conditions, as illustrated above. This effect was characterized more quantitatively as a function of NH₄/SO₄ molar ratio, a proxy of particle acidity, in Figure 4. Here, the SOA yields at several specific ΔM_0 values from 0.7 to 1.9 $\mu\text{g m}^{-3}$ (within the first hour in Figure 3a) are used as it represents the strongest acidity effect observed. As seen in Figure 4, the SOA yield increased nearly linearly with the decrease in the NH₄/SO₄ molar ratio. A maximum increase of 220% in SOA yield was observed for the most acidic particles (i.e., NH₄/SO₄ molar ratio = 0.2) with the ΔM_0 of 0.7 $\mu\text{g m}^{-3}$ at the irradiation time of approximately 20 min compared to those for neutral particles (NH₄/SO₄ molar ratio = 2.0) (Figure 4). This increase is much higher than the increase in the final SOA yield with particle acidity (i.e., 80% at 6 hours) in the same experiments. Furthermore, the increase in the SOA yield gradually slowed with the increase in organic mass, which is evident by the decreased trend of the slope curve derived from the fitting of SOA yield with NH₄/SO₄ molar ratios (Figure 4b). This could be again explained, at least in part, by acidic particles being less accessible over time with the coating of α -pinene SOA. Another possible cause is the consumption of sulfate due to the formation of organic sulfates (Surratt et al., 2007a, 2008). However, we cannot identify organic sulfates clearly based upon the AMS measurement, since their fragmentation results mainly in inorganic sulfate fragments (Farmer et al., 2010).

280 3.2.3 Acidity effect on later-generation SOA

Due to organic coatings on acidic particles, the effect of particle acidity on SOA formation in a later experimental stage may be underestimated when introducing seed particles before α -pinene photooxidation, in particular under low-NO_x conditions with higher SOA yield. Figure 5 presents the growth curves of the generated organic aerosol mass for experiments with seed particles injected after 2 and 4 hours α -pinene photooxidation under high- and low-NO_x conditions, respectively. The organic aerosol mass was normalized by the reacted α -pinene concentration before adding seed particles. Aerosol particles from the nucleation of gas molecules were not significant in these experiments (less than 50 particles cm⁻³), and thus the oxidation products were likely present mainly in the gas phase prior to adding seed particles.

The generated organic aerosol mass increased immediately after adding seed particles for all experiments. This can be explained by the reactive uptake of the gas-phase α -pinene oxidation products formed in the early stages onto the acidic and ammonium sulfate seed particles. A higher increase in organic aerosol mass (up to 6 times) was observed for acidic particles than that for neutral particles in the first 2 hours under both high- and low-NO_x conditions (Figure 5). This suggests that the formation and/or partitioning of organic aerosols, possibly the mixture of early- and later-generation SOA (although their proportions are unknown based on the available data), were enhanced in the presence of acidic particles even under low-NO_x conditions, where no discernable acidity effect was observed previously (as seen in Figure 3b). It is postulated that this effect is apparent here since the acidic particles had not been coated previously with early-generation products of α -pinene photooxidation, which makes the acidic particles accessible to further acid-catalyzed chemistry. Eddingsaas et al. (2012) also

reported that α -pinene photooxidation products preferentially partition to highly acidic aerosols when introducing seed particles after OH oxidation under low-NO_x conditions. The results in Figure 5 also indicate that later products of α -pinene oxidation were more likely to be acid-catalyzed than the early products under low-NO_x conditions. Therefore, acidity effects may be different for α -pinene SOA products formed from multiple oxidation steps. A detailed analysis of those products at the molecular level is essential to fully understand this effect.

3.3 Chemical composition of SOA

The effect of particle acidity on the chemical composition of α -pinene SOA in high- and low-NO_x experiments is examined from the distribution of organic fragments in the high-resolution organic aerosol mass spectra- (see Figure S2 in the Supplement). The average fractions of organic fragment groups in the organic aerosol mass spectra for particles of different acidity are shown in Figure 6. C_xH_y⁺ fragments (accounted for 41–44% of total signal) dominated the organic aerosol mass spectra, followed by C_xH_yO₁⁺ (33–35%) and C_xH_yO₂⁺ (16–17%) fragments for experiments with varied particle acidity under high-NO_x conditions (Figure 6a). In contrast, C_xH_yO₁⁺ (39–40%) was the most dominant organic fragment, followed by C_xH_y⁺ (33–36%) and C_xH_yO₂⁺ (17–19%) fragments under low-NO_x conditions (Figure 6b). An increase in the fractions of oxygenated fragments (C_xH_yO₁⁺ and C_xH_yO₂⁺) and a decrease in the fraction of hydrocarbon fragments (C_xH_y⁺) were observed under low-NO_x conditions compared to those of high-NO_x conditions. Also, lower O/C ratios of α -pinene SOA were observed under high-NO_x conditions (0.52–0.56, averaged at the irradiation time of 1–6 hours) compared to those under low-NO_x conditions (0.61–0.64, averaged at the irradiation time of 2–12 hours). This indicates that less oxygenated α -pinene SOA was formed in the presence of high NO_x despite the fact that oxidants (i.e., OH and O₃) levels were higher during the high NO_x containing experiments (see Table 1 and Figure 1).

The dependence of chemical composition and oxidation state of α -pinene SOA on NO_x level is most likely associated with the different oxidation products from gas-phase chemistry of RO₂. For instance, peroxy nitrates and organic nitrates formed from the chemical reaction of RO₂ and NO_x are the dominant products under high-NO_x conditions, whereas organic peroxides and acids formed from RO₂ with HO₂ are dominant under low-NO_x conditions (Xia et al., 2008). Note that the observed variations in organic fragments in Figure 6 generally represent those over the whole photooxidation period in each experiment, since the individual mass spectrum of α -pinene SOA did not change significantly with irradiation time, as illustrated by the small standard deviations of individual fragment groups.

With the increase in particle acidity (i.e., NH₄/SO₄ molar ratio from 2.0 to 0.2) under high-NO_x conditions (Figure 6a), the fractions of major fragment ions (C_xH_y⁺ and C_xH_yO₁⁺) decreased gradually while C_xH_yO₂⁺ fractions increased; a slight increase in the O/C ratio from 0.52 to 0.56 was also observed. This suggests that more oxygenated SOA was possibly formed in the presence of acidic particles under high-NO_x conditions. A possible interpretation is that particle acidity enhances the formation of more oxygenated SOA in particles such as larger oligomers via acid-catalyzed reactions (Gao et al., 2004), and/or promotes the partitioning of those oxidation products into particle-phase (Healy et al., 2008), or particle acidity may also help to hydrolyze unsaturated organic molecules. Conversely, there is no systematic change in the chemical composition

330 of α -pinene SOA with particle acidity under low- NO_x conditions. Therefore, the effect of particle acidity on the chemical composition of α -pinene SOA may be important only under the studied high- NO_x conditions when introducing acidic seed particles before photooxidation, which is consistent with the acidity effect on the yield of α -pinene SOA (Sect. 3.2). It is likely that acidic particles coated rapidly by earlier-generation α -pinene SOA due to the higher SOA yield under low- NO_x conditions, or the reactions of RO_2 with HO_2 and RO_2 were dominated by termination products that were less affected by
335 | particle acidity. In addition, some oxidation products such as hydroperoxides might have reacted on the acidic particles and produced more volatile products (Liu et al., 2016), which may manifest as a decrease in the acidity effect (i.e., lower yield) for α -pinene SOA under low- NO_x conditions.

3.4 Acidity effect on organic nitrate formation

The formation of organic nitrates from α -pinene oxidation has been reported previously in the presence of NO_x (e.g.,
340 Atkinson et al., 2000; Albert et al., 2005). Nitrogen (N)-containing organic fragments ($\text{C}_x\text{H}_y\text{N}_p^+$ and $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$) accounted for less than 10% of total organic signal in our studied conditions. These fragments were most likely contributed by organic nitrates generated from the reactions of early α -pinene oxidation intermediate (RO_2) with NO and NO_2 . Organic nitrates likely account for an even higher fraction of the total organic aerosols, since their fragmentation would primarily contribute to inorganic nitrate fragments (NO^+ and NO_2^+) and other organic groups (Farmer et al., 2010). Assuming an average
345 molecular weight of organic nitrate molecules ranging from 200 to 300 g mol^{-1} , where 62 g mol^{-1} is attributed to the $-\text{ONO}_2$ group and the remaining from the organic mass (Boyd et al., 2015), the organic nitrate mass was estimated to be approximately 0.6–1.4 $\mu\text{g m}^{-3}$. This resulted in a contribution of 17.5–20.5% to total α -pinene SOA and an overall organic nitrate yield of 0.7–1.6% under high- NO_x conditions in this study. Organic nitrates yield has been reported to be in the range of approximately 1% up to more than 20% for α -pinene oxidation (Aschmann et al., 2002; Nozière et al., 1999; Rindelaub et
350 al., 2015).

Interestingly, both the fractions of $\text{C}_x\text{H}_y\text{N}_p^+$ and $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$ fragments increased gradually with the increase in particle acidity under high- NO_x conditions (Figure 6a), which is distinct from those without an apparent change under low- NO_x conditions (Figure 6b). The growth curves of the total N-containing organic fragments (sum of $\text{C}_x\text{H}_y\text{N}_x^+$ and $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$) for different acidic particles under high- NO_x conditions are shown in Figure 7a. The absolute mass concentrations of total N-
355 containing organic fragments were also enhanced with particle acidity over the irradiation period. These results indicate that organic nitrates were formed heterogeneously through a mechanism catalyzed by aerosol acidity or that acidic conditions facilitate the partitioning of gas phase nitrates into particle phase under high- NO_x conditions. One possible reaction is the acid-catalyzed formation of sulfated organic nitrates through α -pinene oxidation products such as nitroxyl alcohols and carbonyls reacting with sulfuric acid (Surratt et al., 2008). Further investigations on the individual particle phase organic
360 nitrate species at a molecular level combined with gas-particle kinetics are required to elucidate the detailed reaction mechanisms. Moreover, it has been demonstrated that acid-catalyzed hydrolysis is an important removal process for organic nitrates in the particle phase, from which organic nitrates can be converted to alcohols and nitric acid (Day et al., 2010; Hu et

al., 2011; Liu et al., 2012; Rindelaub et al., 2015). This process would also enhance the partitioning of gaseous organic nitrates into the particle phase due to the perturbation in gas/particle partitioning, and therefore decrease the organic nitrate yields both in the gas and particle phases (Rindelaub et al., 2015). The observed increase in N-containing organic fragments with particle acidity under high-NO_x conditions suggests that the production of organic nitrates generally exceeded their removal rates in this reaction system.

The time-dependent mass concentrations of NO⁺ and NO₂⁺ fragments for various acidic particles under high-NO conditions are shown in Figure 7b. The mass concentrations of the NO⁺ fragment for acidic particles were higher than those of neutral particles, whereas no obvious difference in the NO₂⁺ fragment was observed for particles with varied acidity. Therefore, the enhanced organic nitrates by particle acidity might contribute mainly to the increase in the NO⁺ fragment. Large relative contribution of organic nitrates to the nominal inorganic nitrate fragments is demonstrated by a higher NO⁺/NO₂⁺ ratio than those of pure ammonium nitrate (Bae et al., 2007; Boyd et al., 2015; Farmer et al., 2010; Fry et al., 2009; Xu et al., 2015b). The average NO⁺/NO₂⁺ ratio was 9.13 ± 4.24, 9.28 ± 5.19, 9.31 ± 4.27, and 10.44 ± 5.48 for particles with initial NH₄/SO₄ molar ratio of 2.0, 1.0, 0.5, and 0.2, respectively. These values are significantly higher than 2.6 ± 0.2 from the current AMS measurement of pure ammonium nitrate, but close to that of 11 ± 8 reported for NO₃ oxidation of α-pinene, from which organic nitrates were likely the dominant aerosol component (Bruns et al., 2010). The increase in NO⁺/NO₂⁺ ratio with particle acidity suggests that the composition of organic nitrate species might be different under various acidic conditions, which is possibly due to the varied effect of particle acidity on the formation and/or partitioning of different organic nitrate species.

NotedIt should be noted that a small amount of C_xH_yN_p⁺ and C_xH_yO_zN_p⁺ fragments were also observed under low-NO_x conditions, where NO was not added (Figure 6b). This may be contributed by the formation of minor amounts of organic nitrates from the reactions of NO₂ released from the chamber walls with α-pinene oxidation products. The average NO⁺/NO₂⁺ ratio was in the range of 6.92–7.91 for particles with different acidities under low-NO_x conditions, which indicates that some organic nitrate species different from those under high-NO_x conditions might be formed. No apparent changes are observed in the mass fractions of C_xH_yN_p⁺ and C_xH_yO_zN_p⁺ fragments with particle acidity under low-NO_x conditions, suggesting that acid-catalyzed formation and partitioning of those organic nitrate species were possibly insignificant.

4 Implications

This study investigated the effect of particle acidity on the yield and chemical composition of α-pinene SOA from photooxidation in a photochemical reaction chamber. A nearly linear increase of α-pinene SOA yield with the increase in particle acidity was observed under high-NO_x conditions, which is contrary to the insignificant acidity effect under low-NO_x conditions. The potential mechanisms leading to the different acidity effects between high- and low-NO_x conditions warrant further investigation. The acidity effect was relatively strong in the early photooxidation stages under high-NO_x conditions, and this effect decreased gradually with the growth of SOA mass. This may be explained by a reduced accessibility of the

SOA partitioning species to the acidic particles for acid-catalyzed chemistry, possibly as a result of the SOA coating. Given that the α -pinene loading used in this study was low and the generated organic aerosol mass was relevant to ambient levels (e.g., the final ratio of organic/sulfate was 0.6–0.8 and 1.7–2.8 under high- and low-NO_x conditions, respectively), similar process may also occur in the atmosphere. Consequently, an ambient acidity effect is likely stronger for newly formed particles and/or freshly formed sulfate coating. Therefore, the time scale of SOA formation with respect to acidity effects is expected to be an important factor for field studies measuring acidity effect in the atmosphere.

More oxygenated SOA was formed with the increase of particle acidity under high-NO_x conditions. Since aerosol acidity could affect the oxidation state of aerosol particles and alter their chemical composition and other properties as demonstrated here, this may be an important process in the atmosphere and deserve further investigation. The formation of SOA from later-generation gas phase products was enhanced by particle acidity even under low-NO_x conditions when introducing acidic seed particles after α -pinene photooxidation. This suggests that the overall acidity effect on the formation of SOA could be underestimated, and that more systematic studies are necessary to evaluate the acidity effect on SOA generated from multiple oxidation steps. This effect could also be important in the atmosphere under conditions where α -pinene oxidation products in the gas-phase originating in forested areas (with low NO_x and SO_x) are transported to regions abundant in acidic aerosols such as power plant plumes or urban regions. Organic nitrates in these experiments may be formed heterogeneously through a mechanism catalyzed by particle acidity and/or the acidic conditions facilitate the partitioning of gas phase nitrates into the particle phase under high-NO_x conditions. This implies that aerosol acidity could also be of importance in the atmosphere by altering the deposition patterns and rates of gas phase NO_x via its conversion to particle nitrates with differing atmospheric lifetimes.

Despite the initial pH value of aerosol particles investigated in this study (–0.93 to –1.72) being in the higher acidity range relative to that generally observed for ambient aerosols, pH values less than –2.0 have been reported for atmospheric aerosol particles and haze droplets (Herrmann et al., 2015). It is therefore expected that the effect of particle acidity observed in this study is relevant to the ambient atmosphere, especially in regions enriched with acidic aerosols, and possibly during initial particle growth via sulfuric acid. Moreover, we have studied the acidity effect under more realistic RH conditions. While RH is an important factor affecting the concentrations of [H⁺], the kinetics of hydrolysis reactions, and the physical properties of SOA such as viscosity, more investigation over a broader RH range are essential to understand the acidity effect in the real atmosphere. Finally, further studies on SOA formation from various other hydrocarbons under conditions near ambient atmospheric levels will be valuable in understanding the complex physical and chemical interactions facilitated by aerosol acidity and evaluating the acidity effect more accurately, and to ultimately incorporate such effects into regional air quality model for improved SOA prediction.

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Tables

Table 1. Experimental conditions and SOA yields from OH-initiated photooxidation of α -pinene under high- and low-NO_x conditions.

Exp.	NH ₄ /SO ₄ ratio ^a	Initial seed composition, ^b molality (mole kg ⁻¹)	Aerosol pH ^c	Temp. ^d (°C)	RH ^e (%)	Seed ($\mu\text{g m}^{-3}$)	NO (ppb)	α -pinene (ppb)	ΔHC ($\mu\text{g m}^{-3}$)	ΔM_0 ($\mu\text{g m}^{-3}$)	Yield (%)
High-NO_x conditions											
1	2	(NH ₄) ₂ SO ₄ (no liquid phase)		24–31	47–29	4.4	66	15.9	84.2	3.5	4.2±0.1
2	1	H ⁺ =3.2, NH ₄ ⁺ =15.3, HSO ₄ ⁻ =11.2, SO ₄ ²⁻ =3.7	-1.31	23–30	58–34	8.4	69	17.6	93.4	5.2	5.6±0.1
3	0.5	H ⁺ =5.0, NH ₄ ⁺ =7.0, HSO ₄ ⁻ =7.5, SO ₄ ²⁻ =2.3	-1.50	24–30	61–38	6.3	68	13.6	71.8	4.7	6.6±0.1
4	0.2	H ⁺ =7.2, NH ₄ ⁺ =2.7, HSO ₄ ⁻ =6.2, SO ₄ ²⁻ =1.9	-1.66	26–34	58–33	7.9	72	17.0	89.9	6.8	7.6±0.2
Low-NO_x conditions											
5	2	(NH ₄) ₂ SO ₄ (no liquid phase)		25–32	67–43	12.6	<0.3	19.6	96.7	34.1	35.2±1.1
6	1	H ⁺ =1.9, NH ₄ ⁺ =14.8, HSO ₄ ⁻ =8.5, SO ₄ ²⁻ =4.1	-0.93	25–32	64–37	12.6	<0.3	17.4	79.1	22.6	28.6±1.5
7	0.5	H ⁺ =3.2, NH ₄ ⁺ =10.6, HSO ₄ ⁻ =8.0, SO ₄ ²⁻ =2.9	-1.22	26–33	64–38	11.9	<0.3	19.3	92.6	33.7	36.3±1.5
8	0.2	H ⁺ =5.3, NH ₄ ⁺ =4.1, HSO ₄ ⁻ =5.6, SO ₄ ²⁻ =1.9	-1.35	24–33	66–36	11.4	<0.3	19.5	88.6	28.4	32.0±1.9
Adding seeds after photooxidation											
9	2	(NH ₄) ₂ SO ₄ (no liquid phase)		23–31	57–34	9.7	82	20.4			
10	0.5	H ⁺ =5.9, NH ₄ ⁺ =7.0, HSO ₄ ⁻ =8.4, SO ₄ ²⁻ =2.3	-1.72	24–31	56–33	12.2	72	18.5			
11	2	(NH ₄) ₂ SO ₄ (no liquid phase)		25–33	68–42	7.4	<0.3	16.1			
12	0.5	H ⁺ =4.9, NH ₄ ⁺ =9.6, HSO ₄ ⁻ =9.3, SO ₄ ²⁻ =2.6	-1.64	25–33	57–33	11.4	<0.3	17.3			

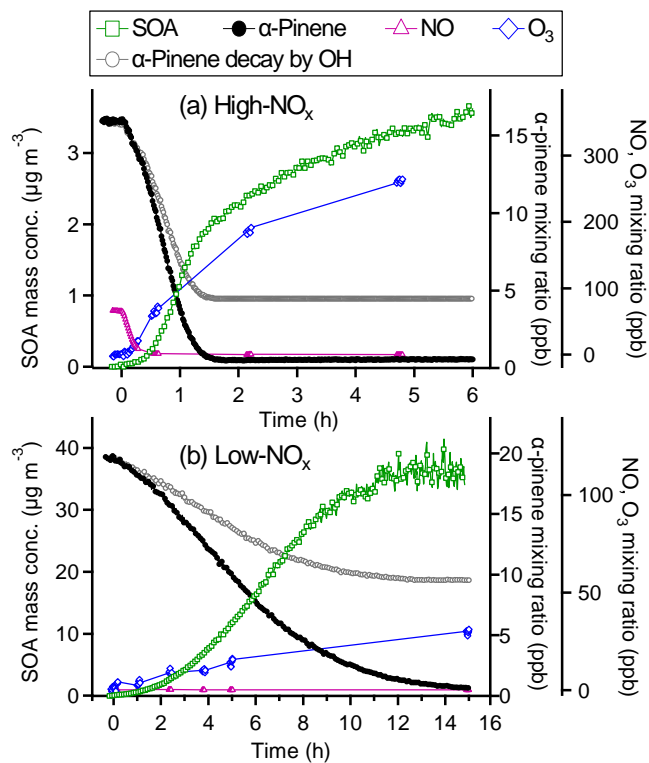
700 ^a NH₄/SO₄ molar ratios of ammonium sulfate/sulfuric acid aqueous solution used for atomizing seed particles. ^b Initial seed composition was estimated using the E-AIM II. ^c Aerosol pH was calculated with the E-AIM output. ^d Initial and final temperature inside the chamber. ^e Initial and final RH inside the chamber.

Table 2. Comparison of experimental parameters and SOA yields reported in literature for the photooxidation of α -pinene.

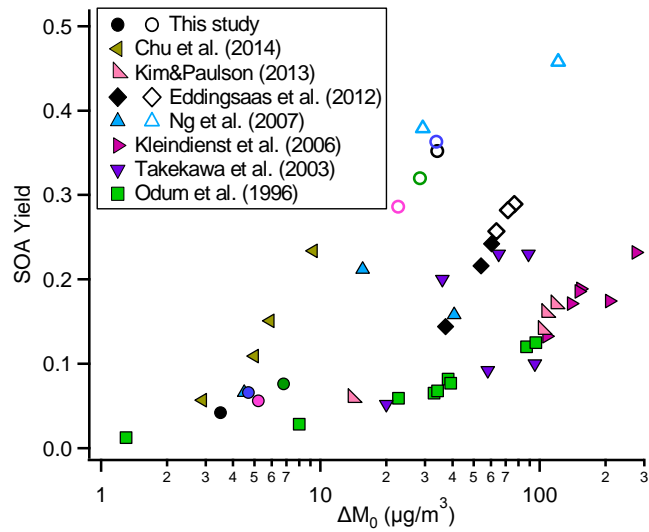
Reference	Temp. (°C)	RH (%)	Oxidant	Seed	NO _x (ppb)	α -pinene (ppb)	Δ HC ($\mu\text{g m}^{-3}$)	Δ M ₀ ($\mu\text{g m}^{-3}$)	SOA Yield (%)
Chu et al. (2014)	28	12, 50	HONO	AS	n.a.	8.1, 11.7	n.a.	5.9, 9.3	15.1, 23.4
	28	12,50	HONO	FeSO ₄	n.a.	9.7, 10.0	n.a.	5.0, 2.9	10.9, 5.7
Kim and Paulson (2013)	33–42 ^a	15–25 ^a	propene	no seed	47–230	143–153	n.a.	9–118	5.9–17
Eddingsaas et al. (2012)	20–25	<10	H ₂ O ₂	AS	n.a.	45.0–48.5	247–265	63.5–76.6	25.7–28.9
	20–23	<10	HONO, CH ₃ ONO	AS	~800	44.9–52.4	249–258	37.2–60.3	14.4–24.2
Ng et al. (2007a)	23–25	5.3–6.4	H ₂ O ₂	AS	0,1	n.a.	76.7, 264.1	29.3, 121.3	37.9–45.8
	25–26	3.3–3.7	H ₂ O ₂ +NO, HONO	AS	198–968	n.a.	69.8–259.1	4.5–40.8	6.6–21.2
Kleindienst et al. (2006)	26.3	29	NO _x	no seed	242, 543	2550	1190, 815	130, 67.3 ^b	10.9, 8.3 ^c
	26.3	29	NO _x	sulfate	242, 543	2550	1190, 815	87–172 ^b	10.7–14.5 ^c
Takekawa et al. (2003)	10	~60	propene	Na ₂ SO ₄	30–53	55–100	260–540	36–89	20–23
	30	~60	propene	Na ₂ SO ₄	54–102	93–196	500–1000	20–95	5.2–10
Odum et al. (1996)	35–40	~10	propene	AS	300	~19–143	104–769	1.3–96.0	1.25–12.5

^a Final temperature and RH were presented. ^b OC mass was reported. ^c SOC yield was reported.

Figures



710 **Figure 1.** Time series of the mass concentrations of generated SOA and the mixing ratios of NO, O_3 , total α -pinene decay, and OH consumed α -pinene in (a) high- and (b) low- NO_x experiments using ammonium sulfate as seed particles. Time = 0 hour is defined as α -pinene photooxidation initiated when lamps were turned on. The presented SOA mass concentrations have been corrected for particle wall loss according to the decay of sulfate mass.



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Figure 2. Comparison of final α -pinene SOA yields as a function of organic mass concentration (ΔM_0) under high- and low- NO_x conditions in this study with those reported **previously-in literature**. The solid and open symbols represent the SOA yields under high- and low- NO_x conditions, respectively. The black, pink, blue, and green cycles represent the SOA yield for experiments in this study with NH_4/SO_4 molar ratios of 2.0, 1.0, 0.5, and 0.2, respectively. A factor of 1.6 was used to convert SOC yield and OC mass concentration to SOA yield and OA mass concentration in Kleindienst et al. (2006).

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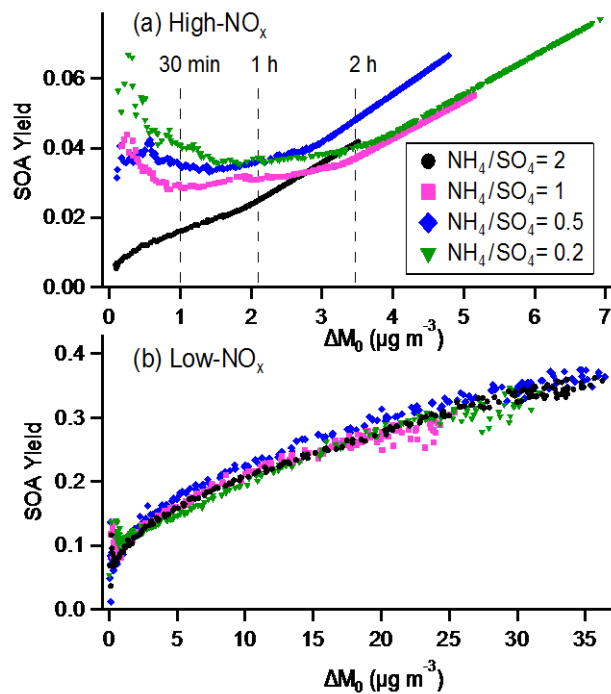
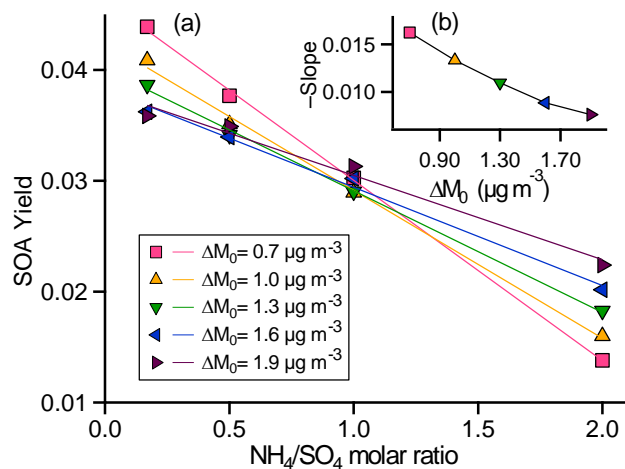
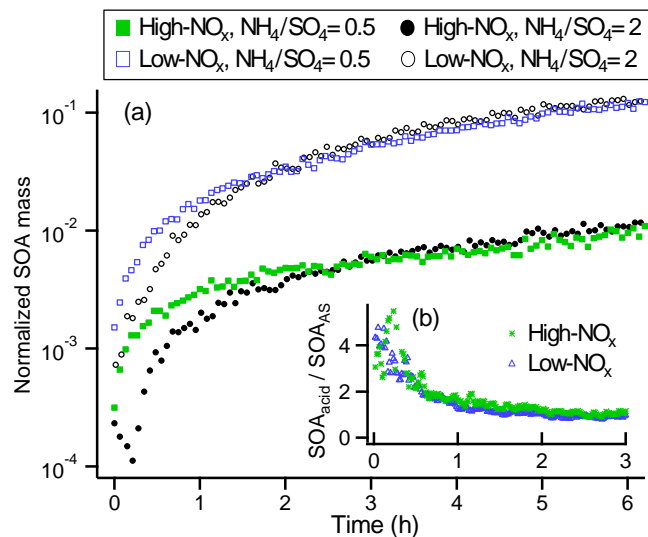


Figure 3. SOA yields as a function of organic mass concentrations for experiments using seed particles with varied acidity levels under (a) high- and (b) low- NO_x conditions. The dashed lines in (a) represent the irradiation time at approximately 30 min, 1 hour, and 2 hours, respectively.

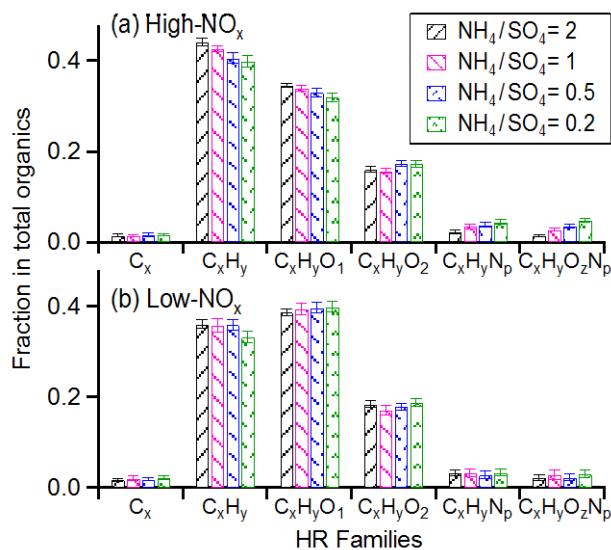
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730 **Figure 4. (a) SOA yield versus NH₄/SO₄ molar ratio in the initial period of photooxidation (approximately 0–1 hours) under high-NO_x conditions. The colored lines represent the linear fitting of the markers. The SOA yields at specific ΔM₀ values were retrieved from the plotting of SOA yields versus ΔM₀ in Figure 3a. (b) The negative slope derived from the fitting of SOA yields with NH₄/SO₄ molar ratios in (a) decreased with ΔM₀.**

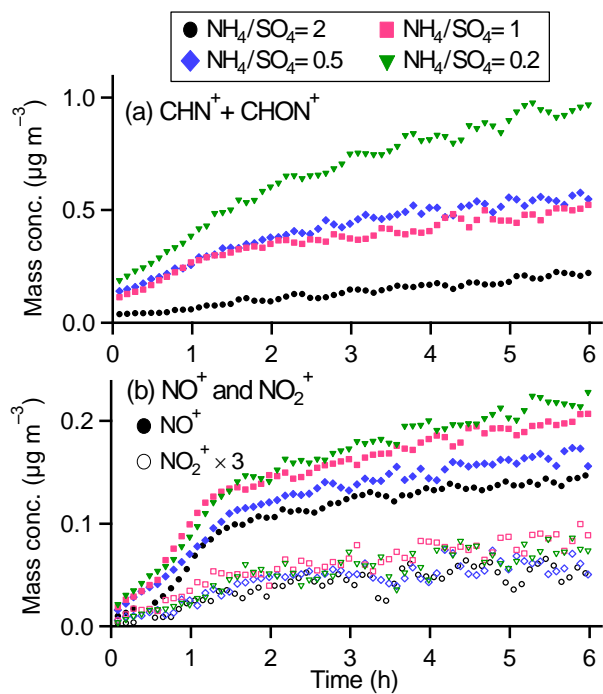


735 **Figure 5. (a) The increase of SOA mass with time for experiments injecting ammonium sulfate and acidic seed particles after α -pinene photooxidation for 2 and 4 hours under high- and low- NO_x conditions, respectively (Exp. 9–12 in Table 1). Time= 0 hour represents the beginning of reactive uptake of oxidation products after seed particles were added. The SOA mass was normalized by the reacted α -pinene concentration before adding seed particles. (b) The ratio of SOA mass for acidic particles to that of ammonium sulfate particles.**



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Figure 6. The mass fractions of organic fragment groups in total organic aerosols under (a) high- and (b) low-NO_x conditions. The organic mass spectra were averaged for the irradiation times of 1–6 and 2–12 hours under high- and low-NO_x conditions, respectively. The bars represent the standard deviations ($\pm 1\sigma$) of the mean values for individual fragment groups.



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Figure 7. The temporal variations of (a) total N-containing organic fragments (the sum of $\text{C}_x\text{H}_y\text{N}_z^+$ and $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$) and (b) NO^+ and NO_2^+ fragments for experiments using ammonium sulfate and acidic particles under high- NO_x conditions.

S1 High-NO_x regime assessment

The Master Chemical Mechanism (MCM v3.3.1, <http://mcm.leeds.ac.uk/MCMv3.3.1/home.htm>) was incorporated into a box model to assess the NO_x regime for the gas-phase reactions of α -pinene photooxidation under high-NO_x conditions. The box model was constrained with the initial experimental conditions including temperature, pressure, and the concentrations of α -pinene, NO, water vapor, and H₂O₂ for the individual chamber experiments in this study. The photooxidation reaction of α -pinene was simulated for 6 hours with the box model. The output of the box model was the time series of the concentrations of α -pinene, NO, O₃, HO₂, and organic peroxy radicals (RO₂) (molecule cm⁻³) from each time step with a 1-min resolution. The fraction of RO₂ radicals reacted with NO compared to the total reacted RO₂ radicals (with NO, HO₂, and RO₂) was calculated by

$$\frac{k_{\text{NO}}[\text{NO}]}{k_{\text{NO}}[\text{NO}] + k_{\text{HO}_2}[\text{HO}_2] + k_{\text{RO}_2}[\text{RO}_2]}$$

where k_{NO} , k_{HO_2} , and k_{RO_2} are the reaction rates of RO₂ + NO, RO₂ + HO₂ and RO₂ + RO₂, respectively and [NO], [HO₂], and [RO₂] are the concentration of NO, HO₂, and RO₂, respectively. The results from the box model are presented in Figure S1. At the start of the simulations, more than 99% of the RO₂ radicals were reacting with NO; while by the end of the experiments (after 6 hours), at least 62% of the RO₂ radicals continued to react with NO (Figure S1a). The time series for α -pinene, NO, and O₃ from the measurements were reasonably well captured by the box model (Figure S1b, c, and d).

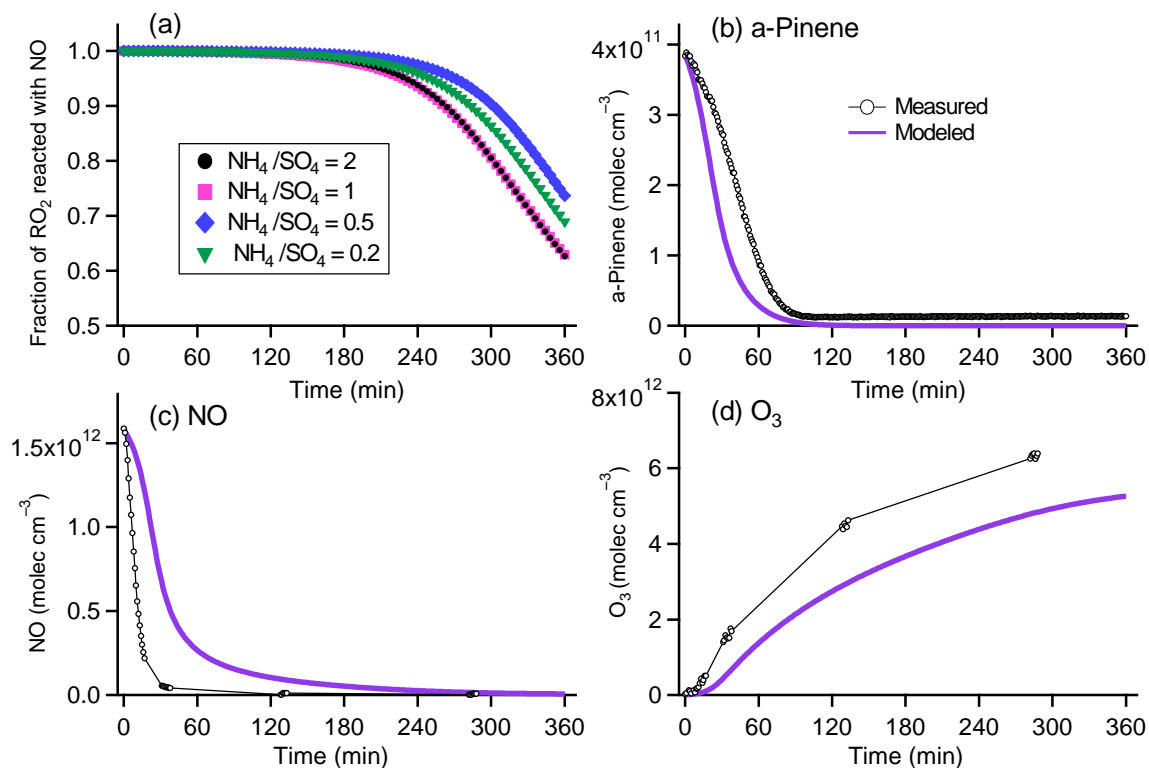


Figure S1. (a) Fraction of RO₂ reacted with NO compared to the total reacted RO₂ radicals for high-NO_x experiments with ammonium sulfate and acidic seed particles. The measured and the modeled time series of the concentrations of (b) *α*-pinene, (c) NO, and (d) O₃ for the high-NO_x experiment with ammonium sulfate particles (NH₄/SO₄ = 2). The variations in time for each species in all experiments with acidic particles under high-NO_x conditions are similar to (b), (c), and (d).

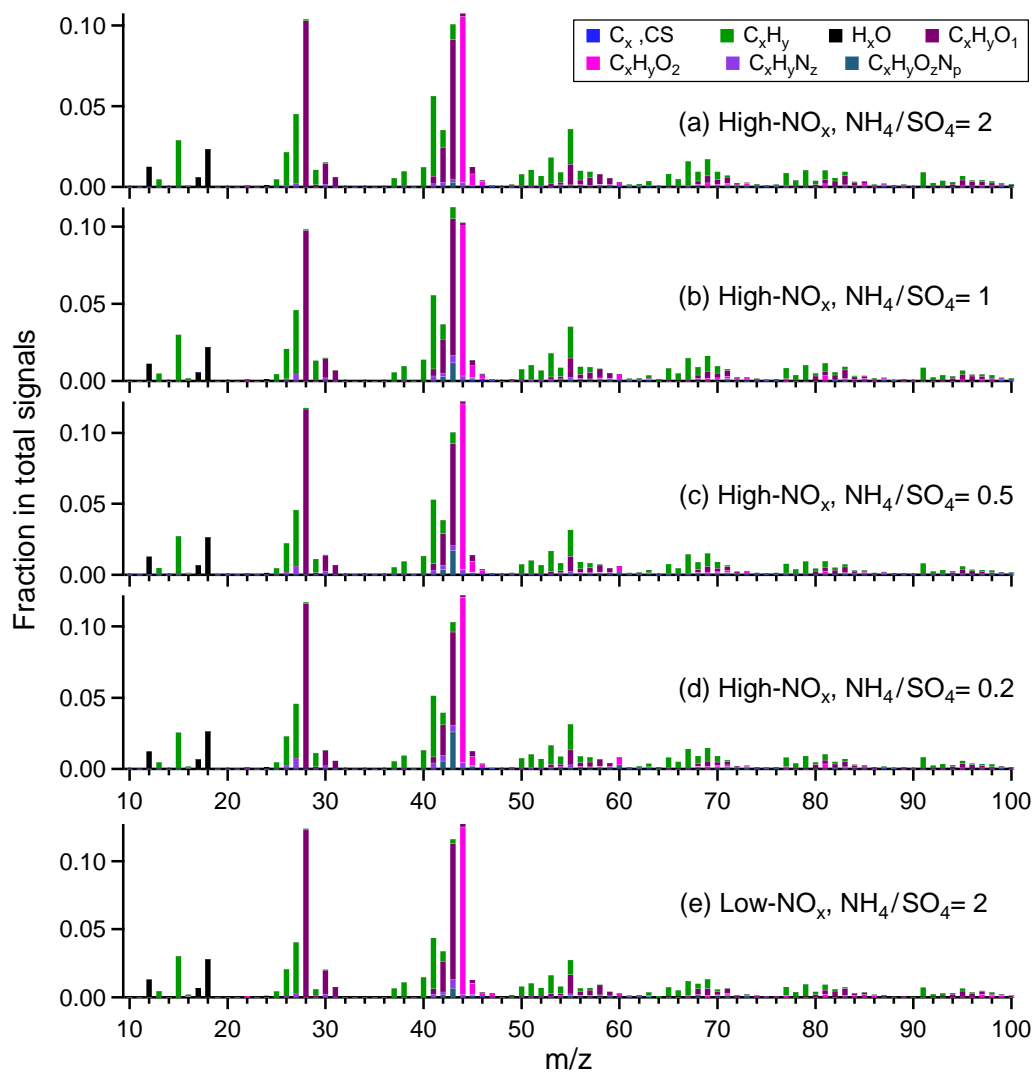


Figure S2. High-resolution mass spectra of α -pinene SOA under (a–d) high- and (e) low- NO_x conditions. The mass spectra were averaged on the irradiation times of 1–5 h and 2–12 h under high- and low- NO conditions, respectively. The mass spectra of α -pinene SOA under low- NO_x conditions for acidic particles, which are not presented here, resemble that of ammonium sulfate particles in (e).