

Response to referee #2: “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.)

The authors performed laboratory chamber experiments to study the effect of particle acidity on α -pinene SOA. Firstly, the authors found that the particle acidity has small effect on α -pinene SOA yield under low-NO_x conditions, but has large effects on α -pinene SOA yield under high-NO_x conditions. This has been shown in Eddingsaas et al. (2012a). Secondly, the authors showed that α -pinene SOA formation under low-NO_x conditions is influenced if the particle seed is injected after α -pinene photooxidation. This has also been shown in Eddingsaas et al. (2012a). Thirdly, the authors observed that the fraction of $C_xH_yN_z^+$ and $C_xH_yO_zN_p^+$ fragments in total organics increases with particle acidity, which is the only new finding in the manuscript. Considering the lack of novel findings in the manuscript, I would not recommend this manuscript for publication in its current state.

Response: We thank reviewer #2 for the comments on our manuscript. The reviewer has proposed some relevant points that could improve the quality of this paper. However, it seems that the reviewer has missed the main concept of our study on some points, as will be expanded upon further below. Regardless, the reviewer’s conclusion that this study lacks novelty is inaccurate and it is further

inappropriate to make such a conclusion by simply comparing with Eddingsaas et al. (2012a). However, we agree that perhaps we could have improved the description in the paper of how this current study is different from Eddingsaas et al. (2012a), and specifically what aspects are novel. We assumed that the novelty of the study's results would be apparent, however we admit that additional clarity is warranted. Our study is unique as it investigates the effect of aerosol acidity under conditions more relevant to the ambient atmosphere. The originality and the differences of our paper compared to Eddingsaas et al. (2012a) have been summarized in the response to major comment #1. Clearly there are enough differences and novelty to warrant publication. Moreover, a single study is generally far from enough to demonstrate a scientific fact, especially since some of the current results contradict those of Eddingsaas et al. (2012a). We have addressed all the issues noted by the reviewer and have made the relevant changes in the manuscript.

Major comments:

1.1 This manuscript does not represent a substantial contribution to scientific progress, because most of the findings have been shown in Eddingsaas et al. (2012a). The authors should try to differentiate this study from Eddingsaas et al. (2012a).

Response: We strongly disagree with this viewpoint, although as noted above we could have made the differences more apparent. Our study does not simply replicate or follow the work of Eddingsaas et al. (2012a). Our study was originally designed to investigate the effect of particle acidity on α -pinene SOA formation under relevant ambient conditions as opposed to Eddingsaas et al. Furthermore, there are a number of other substantial differences between our study and Eddingsaas et al. in terms of studied conditions and research focus. The difference in experimental conditions between the two studies is summarized in the table below. The modest relative humidity and the lower initial concentrations of

seed particles and α -pinene applied in our study are more relevant to the atmosphere compared to Eddingsaas et al. (2012a). In fact, one could argue that the experiments of Eddingsaas et al. (2012a) were conducted under conditions that were entirely irrelevant to the atmosphere, as NO_x levels of 800 ppb are never encountered and RH of $<10\%$ are similarly rare.

	RH (%)	Seed size (nm)	Seed volume ($\mu\text{m}^3 \text{cm}^{-3}$)	α -pinene (ppb)	High- NO_x level (ppb)
Eddingsaas et al. (2012a)	< 10	60	$\sim 10\text{--}15$	19.8–52.4	800
This study	33–67	150	$\sim 2.5\text{--}7.1$	13.6–20.4	66–82

Regarding the research focus, we investigate the effect of particle acidity at four acidic levels; we observed that the acidity effect was stronger in the initial photooxidation period under high- NO_x conditions; we reported the time scale of the acidity effect, the high-resolution organic fragment distributions, the oxidation state of α -pinene SOA in the different experiments, and the potential formation of organic nitrates based on the AMS measurements. In contrast, there is little or no discussion on these topics by Eddingsaas et al. (2012a). In order to highlight the novelty of our study, an explicit research objective has been added in the revised manuscript:

“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 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.” (Lines 83–89)

1.2. For example, while the RH was below 10% in Eddingsaas et al. (2012a), the experiments were conducted under humid conditions in this study. Thus, discussions on dry vs. humid could be added.

Response: It is true that RH is an important factor in the formation of α -pinene SOA. However, given that we did not conduct experiments under dry conditions, a direct comparison between the dry and humid conditions are not available from this study. We could roughly compare our results with those from previous studies under dry conditions, but other experimental conditions such as temperature and hydrocarbon loading are generally different as well. Therefore, rather than to discuss the dry and humid condition itself, we have added the following statement to indicate the importance of RH in SOA chamber studies:

“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.” (Lines 403–406)

1.3. In addition, the authors should provide more insights into why the effects of acidic seed are different between low-NO_x and high-NO_x conditions.

Response: The acidity effect has been discussed mostly in section 3.2 of the manuscript. The different effects of particle acidity were most likely associated to the distinct reaction mechanisms between high- and low-NO_x conditions, which resulted in the different chemical composition of α -pinene SOA (as seen in Figure 6). It was possible that acid-catalyzed heterogeneous reactions occurred under high-NO_x but not low-NO_x conditions. However, given that the bulk organic aerosol mass was measured by the

AMS (with very strong fragmentation), it is a challenge to provide detailed reaction mechanisms from this study. Therefore, we have proposed this topic to be an open question as follows:

“The potential mechanisms leading to the different acidity effects between high- and low- NO_x conditions warrant further investigation.” (Lines 379–380)

2. The authors observed that the mass fraction of $\text{C}_x\text{H}_y\text{N}_z^+$ and $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$ in total OA increases with particle acidity under high- NO_x conditions. However, the discussions on this observation are highly speculative.

(1) In order to explain this observation, the authors propose “organic nitrates may be formed heterogeneously through a mechanism catalyzed by particle acidity”. line 191-192, the authors suggest that particle acidity can facilitate the gas phase RO_2 and NO_x reaction and organic nitrate formation. This mechanism is highly speculative. The authors need to provide more evidence and cite related reference to support the proposed mechanism.

The sentence referred to:

- a. “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.”
- b. “Clearly, NO_x is most likely involved in the acid-catalyzed reactions during α -pinene photooxidation, such as the formation of organic nitrates from RO_2 reacting with NO_x facilitated by particle acidity (as discussed in Sect. 3.4).”

Response: The acid-catalyzed formation of organic nitrates could indeed occur, although we agree that is rarely reported in literature. We did not intend to say that acidity can facilitate the $\text{RO}_2 + \text{NO}_x$ reactions in the gas phase, as the reviewer states. Rather, we are saying that the acidity can enhance the

partitioning into the particle phase and there may also be particle phase reactions which are enhanced by acidity leading to nitrates. As there is no detailed information on the exact form of the organic molecules here, it is not possible to provide a mechanism from the available data of this study. However, one example is the formation of sulfated organic nitrates through the further reactions of sulfuric acid with α -pinene oxidation products of nitroxyl alcohols and carbonyls, as proposed by Surratt et al. (2008). We have revised the original sentences as follows (a and b) and also have added a statement (c) for the possible mechanisms:

a. "..., 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.*" (Lines 23–25)

b. "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." (Lines 217–219)

c. "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 nitrate species at a molecular level combined with gas-particle kinetics are required to elucidate the detailed reaction mechanisms." (Lines 344–348)

Surratt, J. D., Gómez-González, Y., Chan, A. W. H., Vermeylen, R., Shahgholi, M., Kleindienst, T. E., Edney, E. O., Offenberg, J. H., Lewandowski, M., Jaoui, M., Maenhaut, W., Claeys, M., Flagan, R. C., and Seinfeld, J. H.: Organosulfate Formation in Biogenic Secondary Organic Aerosol, J. Phys. Chem. A, 112(36), 8345–8378, doi:10.1021/jp802310p, 2008.

(2) line 322-323. The change in $\text{NO}^+/\text{NO}_2^+$ ratio is a reflection of the change in organic nitrate composition, instead of organic nitrate amount. The increasing in $\text{NO}^+/\text{NO}_2^+$ ratio with particle acidity likely suggests that particle acidity has different effects on the partition of different organic nitrate species. This is one possible explanation for the observation that the mass fraction of organic nitrates increases with particle acidity under high- NO_x conditions.

The sentence referred: “An increasing $\text{NO}^+/\text{NO}_2^+$ ratio again suggests that organic nitrates were enhanced with the increase in particle acidity under high- NO_x conditions.”

Response: We agree that the composition of organic nitrate species might be different under various acidic conditions and particle acidity could have different effects on the partitioning of different organic nitrate species. The original sentence has been revised to:

“The increase in $\text{NO}^+/\text{NO}_2^+$ 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.” (Lines 364–367)

(3) As shown in figure 6b, the mass fractions of $\text{C}_x\text{H}_y\text{N}_z^+$ and $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$ under low- NO_x conditions are similar to that under high- NO_x conditions. How are organic nitrates formed under low- NO_x conditions? Why are the mass fractions of $\text{C}_x\text{H}_y\text{N}_z^+$ and $\text{C}_x\text{H}_y\text{O}_z\text{N}_p^+$ under low- NO_x conditions not affected by particle acidity?

Response: A possible explanation is that a small amount of NO_2 released from the chamber walls was involved in the α -pinene photooxidation under low- NO_x conditions. The average $\text{NO}^+/\text{NO}_2^+$ ratio was in the range of 6.92–7.91 for particles with different acidities under low- NO_x conditions, compared to

those of 9.13–10.44 under high-NO_x conditions. This possibly suggests that different organic nitrate species were formed under high- and low-NO_x conditions, and that the particle acidity had different effects on the formation and partitioning of those organic nitrate species. We have added the following statement in the revised manuscript:

“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.” (368–374)

(4) line 296. The organic nitrate yield reported in this study is misleading. It is because the fragmentation of organic nitrate in AMS give rise to C_xH_yO_z⁺, which accounts for a large mass fraction in organic nitrate but not included in the yield calculation in this study. The authors could estimate the organic nitrate yield based on the concentration of the sum of NO⁺ + NO₂⁺ and assumed molecular weight of organic nitrate (A.W.Rollins, 2012; Boyd et al., 2015; Xu et al., 2015a).

Response: We agree that the original method for the calculation of SOA yield is not appropriate. We have estimated the organic nitrates mass and yield using the method suggested by the reviewer and have added the following details in the revised manuscript:

“Assuming an average molecular weight of organic nitrate molecules ranging from 200 to 300 g mol⁻¹, where 62 g mol⁻¹ is attributed to the -ONO₂ 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 μg 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.” (Lines 331–335)

Also, are NO⁺ and NO₂⁺ included in the SOA yield and O:C calculation?

Response: As NO⁺ and NO₂⁺ were considered to be the fragments from organic nitrates in this study, we have included them in the SOA yield and O/C ratio calculation. The mass concentrations of NO⁺ and NO₂⁺ fragments were generally small and the sum of them was in the range of 0–0.3 μg m⁻³. Therefore, the SOA yield and O/C ratio reported in the revised manuscript only changed very slightly compared to the original values, and these changes did not affect the conclusions in this study.

3. Many results are confusing.

(1) Figure 3: the SOA yield curves under both conditions are not typical and problematic (Griffin et al., 1999). Under low-NO_x conditions, why would SOA yield decrease with delta_Mo at the beginning of the experiments? Under high-NO_x conditions, what causes the SOA yield decrease within the first 30min? If one looks at the figure 1, the yield curve is expected to be monotonic. Is the weird yield curve caused by the SOA wall loss correction? What does the sulfate concentration (measured by AMS) look like over the course of the experiments? Does the sulfate concentration (measured by AMS) change once organics are formed?

Response: We do not regard the results in Figure 3 as problematic. The main difference in Griffin et al. (1999) compared to our study is that they investigated the SOA yield from ozonolysis of α -pinene without the consideration of an acidity effect. We attribute the gradual decrease in the first 30 minutes to the acidity effect, and more specifically, the decrease in the availability of the acidic phase as organics were formed. This is discussed in the manuscript as follows:

“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 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 that the diffusion of organic molecules into the inorganic seeds 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 low to moderate RH (e.g., $\leq 30\%$) (Renbaum-Wolff et al., 2013; Virtanen et al., 2010).” (Lines 241–247)

Also, Figure 3 in our study presents the time series of instantaneous SOA yields vs. ΔM_0 for individual experiments, in contrast to the final SOA yield presented in Griffin et al. (1999). The mass concentration of sulfate decreased smoothly over the experiment period due to particle loss on the chamber wall. There was no significant unexpected change in sulfate concentration once organic mass was formed. The calculated α -pinene SOA yield (i.e., the ratio of $\Delta M_0/\Delta HC$) can be affected by both ΔM_0 and ΔHC . The ΔM_0 in individual experiments increased constantly as seen in Figure 1. The high yields at the very beginning are caused mainly by the very low ΔHC . These data points were acquired by the PTR-MS when α -pinene concentration was high at the very beginning, whereas the calculated ΔHC was too low and within the α -pinene detection limit. Therefore, we have removed the initial data points with extremely low ΔHC in Figure 3.

(2) Figure 4: This figure is confusing. Firstly, following the same ΔM_0 , the authors are comparing the SOA yield under different NH_4/SO_4 ratio. The trend shown in figure 4 does not hold if the authors add data points when $\Delta M_0 = \sim 0.25 \text{ } \mu\text{g}/\text{m}^3$ (where SOA yield peaks for $\text{NH}_4/\text{SO}_4 = 0.2$). Secondly, many data points are obtained from the period when SOA yield decreases with ΔM_0 , the reason for which is not clear yet.

Response: We agree that the data points in the initial period for the experiment with $\text{NH}_4/\text{SO}_4 = 0.5$ was not in line with the other three experiments ($\text{NH}_4/\text{SO}_4 = 2, 1, \text{ and } 0.2$) when making similar plots for $\Delta M_0 = \sim 0.25 \text{ } \mu\text{g}/\text{m}^3$ in Figure 4a. However, as these are experimental results, it should be acceptable if any of the experiments did not perfectly match the trend. There could be some uncertainty in the SOA yield for the experiment with $\text{NH}_4/\text{SO}_4 = 0.5$ at the very beginning. We therefore have used the ΔM_0 values above $0.7 \text{ } \mu\text{g}/\text{m}^3$ for plotting in Figure 4. As SOA yield depended both on ΔM_0 and ΔHC , a decrease of yield indicates a lower aerosol formation potential, which was possibly due to the reduced acidity effect caused by inaccessibility to the acidic medium as organics were formed. That is in fact the point of choosing the first hour to demonstrate that the acidic effect on the yield does indeed change with organic mass increases. We have provided the reason for the decrease of SOA yield 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, assuming that the diffusion of organic molecules into the inorganic seeds 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 low to moderate RH (e.g., $\leq 30\%$) (Renbaum-Wolff et al., 2013; Virtanen et al., 2010).” (Lines 242–247)

(3) *Figure 5: Firstly, the y-axis scale is misleading. Although it seems that SOA yield increases a lot once injecting seed, the actual enhancement is only on the order of 0.01, which is within measurement uncertainty.*

Response: We agree that using “SOA yield” as the label of y-axis is not appropriate here, as this is different from the general definition of SOA yield. The main point of Figure 5 is to show the increase in organic aerosol mass for experiments with acidic particles (high- and low- NO_x) compared to those with ammonium sulfate particles. We have changed the “SOA yield” to “Normalized SOA mass” and also added an additional graph in the revised Figure 5 to show the increased organic aerosol mass for the acidic particles compared to the ammonium sulfate particles. The increase in organic aerosol mass was up to 6 times higher for acidic particles than those of ammonium sulfate particles at the initial stages, as presented in Figure 5b below.

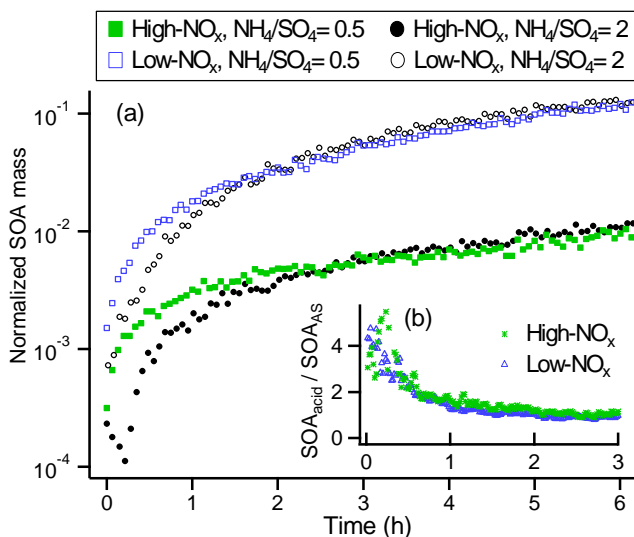


Figure 5. (a) The increase of SOA mass with time for experiments with injecting neutral and acidic seed particles after α -pinene photooxidation for 2 and 4 hours under high- and low- NO_x conditions, respectively (Exp. 9–12 in Table 1). Time= 0 hour represents the beginning of reactive uptake of

oxidation products after seed particles 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.

Secondly, is there organics associated with sulfate seed in the atomizing solution? Based on some tests in our lab, the injection of sulfate would introduce organics, which comes from the atomizing solution, even if HPLC-grade DI water is used to make solution. Actually, the organics associated with sulfate seed may explain the immediate OA increase after adding seed particles (line 239).

The sentence referred: “Organic aerosol mass increased immediately after adding seed particles for all experiments.

Response: The reviewer is correct in terms of the potential organic contamination during the atomization procedure. We also have noticed that the organic concentration was increased slightly when adding acidic seed particles. However, the organics associated with sulfate seed is not a concern here, as we are discussing the generated organic aerosol mass (ΔM_0), which was obtained by subtracting the initial organic mass from the total organic mass measured in real-time. We have clarified the meaning of the original sentence:

“The *generated* organic aerosol mass increased immediately after adding seed particles for all experiments.” (Line 277)

Thirdly, how is the increase of SOA yields calculated? What’s the reference?

Response: We calculated the SOA yields for the four experiments in Figure 5 using the ratios of $\Delta M_0/\Delta HC$ in the original manuscript. However, as described in the response to the first question, we

believe that it is not appropriate to use “SOA yield” as the label of the y-axis in Figure 5. Therefore, the “SOA yield” has been replaced by the “Normalized SOA mass”.

Fourthly, the results are not consistent with Eddingsaas et al. (2012a) (figure 7), who showed that AS particles have no effect on for both low and high NO_x conditions.

Response: It is not clear why there was no additional SOA was formed after introducing ammonium sulfate particles in Eddingsaas et al. (2012a). In contrast, the increase of particulate organic aerosol mass in our study can be explained by the reactive uptake of the gas-phase α -pinene oxidation products formed in the early stage by the acidic and ammonium sulfate seed particles. The point here is that the increase of particulate organic aerosol mass was stronger for acidic particles than for ammonium sulfate particles. The results of our study are also not necessary to be consistent with those of Eddingsaas et al. (2012a), considering the different initial conditions. We have added this statement in the revised manuscript:

“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.” (Lines 277–279)

Minor comments:

1. Table 1: (1) Since both H^+ and LWC are modeled by E-AIM in the study, I suggest the authors to replace NH_4/SO_4 by particle pH, because NH_4/SO_4 or ion balance is not a good proxy for particle pH (Guo et al., 2015; Hennigan et al., 2015). (2) Are the $[NH_4]$ and $[SO_4]$ input for E-AIM obtained from aqueous solution or AMS measurements? The latter should be used, because the NH_3/NH_4^+ partitioning would cause the real $[NH_4]/[SO_4]$ ratio different from that in aqueous solution.

Response: We have added the aerosol pH value calculated from the E-AIM II in Table 1, as presented below. The mass concentrations of NH_4^+ and SO_4^{2-} measured by the AMS have been used as inputs in the E-AIM. The initial seed composition also has been updated accordingly. We still kept the initial NH_4/SO_4 molar ratios in Table 1, because they are important references for making ammonium sulfate/sulfuric acid aqueous solution.

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	$(\text{NH}_4)_2\text{SO}_4$ (no liquid phase)		24–31	47–29	4.4	66	15.9	84.2	3.5	4.2±0.1
2	1	$\text{H}^+=3.2$, $\text{NH}_4^+=15.3$, $\text{HSO}_4^-=11.2$, $\text{SO}_4^{2-}=3.7$	-1.31	23–30	58–34	8.4	69	17.6	93.4	5.2	5.6±0.1
3	0.5	$\text{H}^+=5.0$, $\text{NH}_4^+=7.0$, $\text{HSO}_4^-=7.5$, $\text{SO}_4^{2-}=2.3$	-1.50	24–30	61–38	6.3	68	13.6	71.8	4.7	6.6±0.1
4	0.2	$\text{H}^+=7.2$, $\text{NH}_4^+=2.7$, $\text{HSO}_4^-=6.2$, $\text{SO}_4^{2-}=1.9$	-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	$(\text{NH}_4)_2\text{SO}_4$ (no liquid phase)		25–32	67–43	12.6	<0.3	19.6	96.7	34.1	35.2±1.1
6	1	$\text{H}^+=1.9$, $\text{NH}_4^+=14.8$, $\text{HSO}_4^-=8.5$, $\text{SO}_4^{2-}=4.1$	-0.93	25–32	64–37	12.6	<0.3	17.4	79.1	22.6	28.6±1.5
7	0.5	$\text{H}^+=3.2$, $\text{NH}_4^+=10.6$, $\text{HSO}_4^-=8.0$, $\text{SO}_4^{2-}=2.9$	-1.22	26–33	64–38	11.9	<0.3	19.3	92.6	33.7	36.3±1.5
8	0.2	$\text{H}^+=5.3$, $\text{NH}_4^+=4.1$, $\text{HSO}_4^-=5.6$, $\text{SO}_4^{2-}=1.9$	-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	$(\text{NH}_4)_2\text{SO}_4$ (no liquid phase)		23–31	57–34	9.7	82	20.4			
10	0.5	$\text{H}^+=5.9$, $\text{NH}_4^+=7.0$, $\text{HSO}_4^-=8.4$, $\text{SO}_4^{2-}=2.3$	-1.72	24–31	56–33	12.2	72	18.5			
11	2	$(\text{NH}_4)_2\text{SO}_4$ (no liquid phase)		25–33	68–42	7.4	<0.3	16.1			
12	0.5	$\text{H}^+=4.9$, $\text{NH}_4^+=9.6$, $\text{HSO}_4^-=9.3$, $\text{SO}_4^{2-}=2.6$	-1.64	25–33	57–33	11.4	<0.3	17.3			

^a NH_4/SO_4 molar ratios of ammonium sulfate/sulfuric acid aqueous solution used for atomizing seed particles. ^bInitial seed composition was estimated using the E-AIM II. ^cAerosol pH was calculated with the E-AIM output. ^dInitial and final temperature inside the chamber. ^eInitial and final RH inside the chamber.

2. Figure 1: (1) The legend “OH consumed α -pinene” is confusing because cumulative α -pinene consumed by OH should increase with time instead of decreasing as shown in the figure. I suggest to change the y-axis to “ $\Delta\alpha$ -pinene consumed by OH”. (2) Is SOA mass concentration shown in this figure corrected for wall loss?

Response: (1) As the y-axis is scaled both for total α -pinene concentration and α -pinene consumed by OH, it is not appropriate to change the y-axis to “ $\Delta\alpha$ -pinene consumed by OH”. Therefore, in order to avoid confusion, we have changed the “OH consumed α -pinene” to “ α -Pinene decay by OH” in the legend of Figure 1.

(2) The SOA mass concentrations were corrected for particle wall loss using the method described in the manuscript. We have added the following statement in the caption of Figure 1: “The presented SOA mass concentrations have been corrected for particle wall loss according to the decay of sulfate mass.”

(Lines 664–665)

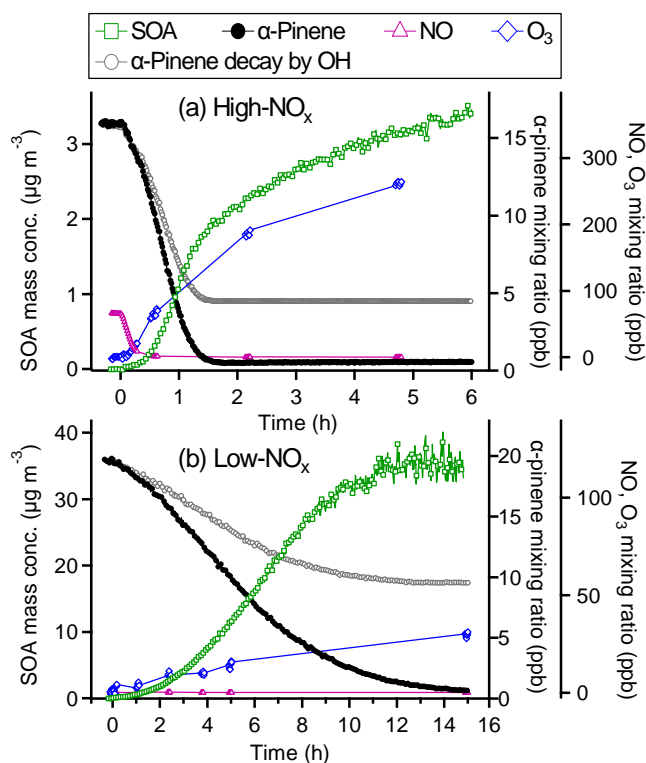


Figure 1. Time series of the mass concentrations of generated SOA and the mixing ratios of NO, O_3 , total α -pinene decay, and OH consumed α -pinene in (a) high- and (b) low- NO_x experiments using ammonium sulfate as seed particles. Time = 0 hour is defined as α -pinene photooxidation initiated when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

3. line 15. The core-shell model contradicts with literature. For example, Renbaum-Wolff et al. (2013) measured the viscosity of α -pinene SOA and calculated that the mixing time is on the order of 10-100s under 40-50% RH.

The sentence referred to: “The SOA yield decreased gradually with the increase in organic mass under high-NO_x conditions, which is likely due to the inaccessibility of the acidity over time with the coating of α -pinene SOA.”

Response: The reviewer’s comment is not accurate in this case. According to Figure 2 in Renbaum-Wolff et al. (2013), the viscosity of α -pinene SOA varied up to 5 orders of magnitude at 40–50% RH, and the mixing time due to bulk diffusion was in the range of several seconds to 2×10^4 seconds (i.e., approximately 5.6 hours). As a result, the proposed core-shell model in this study is reasonable at the studied final RH of approximately 29–43%. Nevertheless, this assumption is based on the upper limit of the estimated viscosity. We have revised the original sentence to:

“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.**” (Lines 14–17)

4. line 18-20. The authors found that the SOA is more oxidized under low-NO_x conditions than high-NO_x conditions. However, Chhabra et al. (2011) figure 2c showed that the O:C of α -pinene SOA under low-NO_x (using H₂O₂) and high-NO_x conditions (using CH₃ONO) are similar.

The sentence referred to: “The fraction of oxygen-containing organic fragments (C_xH_yO₁⁺ 33–35% and C_xH_yO₂⁺ 16–17%) in the total organics and the O/C ratio (0.49–0.54) of α -pinene SOA were lower

under high-NO_x conditions than those under low-NO_x conditions (39–40%, 17–19%, and 0.60–0.62), suggesting that α -pinene SOA was less oxygenated in the studied high-NO_x conditions.”

Response: The different results between the two studies are most likely due to the distinct experimental conditions. Chhabra et al. (2011) performed their α -pinene photooxidation experiments at lower RHs (4.2% and 4.9%), higher initial α -pinene concentrations (46 and 47 ppb), and generated higher α -pinene SOA loadings (63.9 and 53.7 $\mu\text{g m}^{-3}$), and eventually they obtained lower O/C ratios of 0.40 and 0.42 under low- and high-NO_x conditions, respectively. In contrast, the higher O/C ratios observed in our study (0.52–0.56 and 0.61–0.64 under high and low-NO_x conditions, respectively) suggest that α -pinene SOA was more oxygenated, which is most likely associated to the lower initial α -pinene concentrations used in our reaction system (approximately 14–20 ppb). This is consistent with the following statement in our manuscript:

“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).” (Lines 70–73)

5. line 35. It should be “enhance the reactive uptake of gas phase organics”, instead of “particle phase”.

The sentence referred to: “The presence of acidic aerosol particles has been shown to enhance the reactive uptake of particle phase organics and increase SOA yields due to acid-catalyzed reactions (i.e., Garland et al., 2006; Jang et al., 2004; Liggió and Li, 2006; Northcross and Jang, 2007).”

Response: The “particle phase organics” has been changed to “gas phase organic species” in the revised manuscript.

6. line 37. Cite Surratt et al. (2010) and Xu et al. (2015a), who showed the effect of sulfate on the reactive uptake of IEPOX.

Response: The two references have been cited as below and also listed in the References.

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

(Lines 37–39)

7. line 43. It is not accurate to state that atmospheric chemistry models do not consider the dependence of SOA formation on aerosol acidity. Large efforts have been devoted to consider the effect of particle acidity for SOA through IEPOX uptake (Marais et al., 2016; McNeill et al., 2012; Pye et al., 2013). Please rephrase this sentence.

The sentence referred to: “The dependence of SOA formation on aerosol acidity has not been considered in most atmospheric chemistry models thus far due to the large uncertainties associated with its quantification.”

Response: The original sentence has been reworded to:

“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).” (Lines 45–48)

8. line 50-52 and line 63-66. I don't agree with the authors that “large discrepancies among experiments remain with respect to the effects of aerosol acidity on SOA formation”. The seemingly “contradictory” observations among studies listed in the manuscript are just due to the difference in experimental conditions. For example, the effects of particle acidity on α -pinene SOA formation are different for low-NO_x and high-NO_x conditions. Thus, the previous studies cited in the manuscript only show the complexity of this scientific question, instead of the discrepancy.

The sentence referred to:

- a. “Despite the efforts of previous laboratory studies, large discrepancies among experiments remain with respect to the effect of aerosol acidity on SOA formation from individual hydrocarbons.”
- b. “The large discrepancy regarding the previously reported acidity effect on α -pinene SOA is 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).”

Response: The “discrepancies” in the above two sentences are actually more close to “dissimilarities”, instead of “contradictory”. We agree that different results in previous studies show the complexity of this scientific question. To clarify these points, we have revised the original sentences to:

- a. “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.” (Lines 55–57)

b. “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).” (Lines 67–69)

9. line 124. The collection efficiency of AMS. Was a dryer deployed upstream of AMS and SMPS? If not, considering the high RH in this study, the particle water could affect the comparison between AMS and SMPS.

The sentence referred to: “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.”

Response: We did not use a dryer upstream of AMS and SMPS during the experiments. As a result, the particle volume concentrations derived from the SMPS could have a contribution by aerosol water, whereas those derived from the AMS does not include water. This is an uncertainty for the collection efficiency estimation. We have added the following statement to demonstrate this uncertainty in the revised manuscript:

“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.” (Lines 134–136)

10. line 133-134. How do the authors estimate the concentration of organics from self-nucleation? Is the particle size distribution bimodal? Please show the particle size distribution measured by SMPS.

The sentence referred to: “This assumption is appropriate given that organics contributed by self-nucleation was estimated to be less than $0.1 \mu\text{g cm}^{-3}$ in the studied system.”

Response: This is same as minor comment #4 from reviewer #1. This estimation is based on the particle number concentration measured by the CPC and the organic mass concentration measured by the AMS, not obtained from the particle size distribution measured by SMPS. We observed less than 50 cm^{-3} particles contributed by self-nucleation and also no obvious increase in organic mass concentration by the AMS measurement in the experiments without adding seed particles. We therefore estimated a maximum concentration of $0.1 \mu\text{g cm}^{-3}$ for self-nucleated organic aerosols by using a particle number concentration of 50 cm^{-3} and a particle diameter of 70 nm. However, this estimation may have some uncertainties in terms of the particle size. We have therefore replaced the estimated value with the observed experimental results as follows:

“This assumption is appropriate given that less than $50 \text{ particles cm}^{-3}$ 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.” (Lines 144–146)

11. line 166-167. The lower SOA yield under high- NO_x conditions is due to RO_2 reacts with NO and likely undergo fragmentation to produce volatile species, not due to the formation of organic nitrates. According to group contribution method by Pankow and Asher (2008), the reduction in vapor pressure by adding of one nitrate functional group is similar to that of adding one hydroxyl group.

The sentence referred to: “ RO_2 reacted primarily with NO and NO_2 under high- NO_x conditions, which would result in the formation of relatively volatile species such as organic nitrates and reduce the overall SOA yield; ...”

Response: We agree that using organic nitrates as an example here is inappropriate, as some organic nitrates are less- or non-volatile. The original sentence has been reworded to:

“RO₂ reacted primarily with NO under high-NO_x conditions and generated relatively more volatile products that reduced the overall SOA yield, ...” (Lines 189–190)

12. line 246-247. Eddingsaas et al. (2012a) is not properly cited. Section 3.3 in Eddingsaas et al. (2012a) stated that “Under high-NO₂ conditions, no additional SOA is formed after the addition of either neutral or acidic seed particles in the dark”. Thus, the finding in this study is not consistent with Eddingsaas et al. (2012a).

The sentence referred to: “Eddingsaas et al. (2012) similarly reported that α -pinene photooxidation products preferentially partition to highly acidic aerosols when introducing seed particles after OH oxidation under both low-NO_x and high-NO₂ conditions.”

Response: We agree that this effect was not observed under high-NO₂ conditions by Eddingsaas et al. (2012a). The original sentence has been rephrased to:

“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.” (Lines 285–287)

13. line 249-250. The authors propose that the early generation products don't participate in acid catalysis. This is not consistent with Eddingsaas et al. (2012a) (figure 8), who showed that the first generation products can partition to acidic particles.

The sentence referred to: “The results of Figure 5 also indicate that early α -pinene oxidation products under low-NO_x condition did not participate in acid catalysis, whereas the later products did.”

Response: This conclusion is not in conflict with Eddingsaas et al. (2012a). Indeed, the increase of organic mass was only observed when introduced seed particles after photooxidation under low-NO_x conditions. We therefore concluded that early α -pinene oxidation products under low-NO_x condition did not participate in acid catalysis. Note that here the “early α -pinene oxidation products” in our study are not necessarily the “first generation products”. Figure 8 in Eddingsaas et al. (2012a) presents the time series of CIMS traces in experiments with adding seed particles after 4-hour α -pinene photooxidation under low-NO_x condition, where the products are similar to “the later products” defined in our study. We have rephrased the original sentence to make it more clear:

“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.” (Lines 287–288)

14. line 267-270. The authors need to cite previous studies which discussed the gas phase products from α -pinene oxidation. Especially, Eddingsaas et al. (2012b) showed that pinonaldehyde is important intermediate under both low and high-NO_x conditions.

The sentence referred to: “The dependence of chemical composition and oxidation state of α -pinene SOA on NO_x level is most likely associated with the 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).”

Response: We intended to address the different final oxidation products from the gas-phase chemistry of RO₂ rather than to refer to the detailed gas-phase chemistry here. Therefore, we have rephrased the first sentence slightly as follows:

“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 RO_2 .” (Lines 305–306)

15. line 270-272. Xu et al. (2014) is not properly cited. Instead of showing that isoprene SOA is more oxidized under low- NO_x conditions, Xu et al. (2014) showed that the oxidation state of isoprene SOA shows a non-linear dependence on NO_x level.

The sentence referred to: “SOA formed from photooxidation of isoprene has also been reported to become more oxidized under low- NO_x conditions, which is contrary to those under high- NO_x conditions (Xu et al., 2014).”

Response: As stated by Xu et al. (2014), “SOA becomes less volatile and more oxidized as oxidation progresses in HO_2 -dominant experiments, while the volatility of SOA in mixed experiments does not change substantially over time”. Therefore, this sentence itself is correct, but it was not appropriate to be cited here and also it distracted our major focus on α -pinene. We have removed this sentence in the manuscript.

16. line 318. Please cite Boyd et al. (2015) and Xu et al. (2015b).

Response: These two references have been cited as follows and also listed in the section of References: “Large relative contribution of organic nitrates to the nominal inorganic nitrate fragments is demonstrated by a higher $\text{NO}^+/\text{NO}_2^+$ 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).” (Lines 359–361)

17. line 331. What's the Org/SO₄ ratio in this study? Is it atmospherically relevant?

The sentence referred to: “Given that the α -pinene loading used in this study was low, similar phenomenon may also occur in the atmosphere.”

Response: The final ratio of organics to sulfate at the end of each experiment was in the range of 0.6–0.8 and 1.7–2.8 under high- and low-NO_x conditions, respectively. These are relevant to atmospheric levels. We have added this information to the original sentence as follows:

“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.” (Lines 382–385)

18. line 342. The authors have already ruled out the mechanism “acidic seed facilitates the partitioning of gas phase organic nitrate” (line 308-310). Please rephrase this sentence.

The sentence referred to:

- a. “This is inconsistent with the observed increase in organic nitrate fragments with increasing acidity. Therefore, acid-catalyzed formation of organic nitrates also very likely contributed to the observed enhancement of N-containing organic fragments with particle acidity.”
- b. “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.”

Response: We did not rule out the partitioning mechanism from the original line 308–310. We meant that the partitioning mechanism cannot solely explain the enhanced N-containing organic fragments. We have added the following explanations to clarify the meaning:

“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.” (Lines 348–354)

19. line 495. The author list of this citation is wrong.

Response: The author list of this citation was correct. Please find the entire author lists from the original line 494.

“Shilling, J. E., Chen, Q., King, S. M., Rosenoern, T., Kroll, J. H., Worsnop, D. R., DeCarlo, P. F., Aiken, a. C., Sueper, D., Jimenez, J. L. and Martin, S. T.: Loading-dependent elemental composition of α -pinene SOA particles, *Atmos. Chem. Phys.*, 9, 771–782, doi:10.5194/acp-9-771-2009, 2009.” (Lines 583–585)