

Review of “The effect of particle acidity on secondary organic aerosol formation from  $\alpha$ -pinene photooxidation under atmospherically relevant conditions” by Han et al.

The authors performed laboratory chamber experiments to study the effect of particle acidity on  $\alpha$ -pinene SOA. Firstly, the authors found that the particle acidity has small effect on  $\alpha$ -pinene SOA yield under low-NO<sub>x</sub> conditions, but has large effects on  $\alpha$ -pinene SOA yield under high-NO<sub>x</sub> conditions. This has been shown in Eddingsaas et al. (2012a). Secondly, the authors showed that  $\alpha$ -pinene SOA formation under low-NO<sub>x</sub> conditions is influenced if the particle seed is injected after  $\alpha$ -pinene photooxidation. This has also been shown in Eddingsaas et al. (2012a). Thirdly, the authors observed that the fraction of C<sub>x</sub>H<sub>y</sub>N<sub>z</sub><sup>+</sup> and C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>N<sub>p</sub><sup>+</sup> 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.

Major comments:

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). 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. In addition, the authors should provide more insights into why the effects of acidic seed are different between low-NO<sub>x</sub> and high-NO<sub>x</sub> conditions.

2. The authors observed that the mass fraction of C<sub>x</sub>H<sub>y</sub>N<sub>z</sub><sup>+</sup> and C<sub>x</sub>H<sub>y</sub>O<sub>z</sub>N<sub>p</sub><sup>+</sup> in total OA increases with particle acidity under high-NO<sub>x</sub> 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<sub>2</sub> and NO<sub>x</sub> 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.

(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- $\text{NO}_x$  conditions.

(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- $\text{NO}_x$  conditions are similar to that under high- $\text{NO}_x$  conditions. How are organic nitrates formed under low- $\text{NO}_x$  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- $\text{NO}_x$  conditions not affected by particle acidity?

(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  $\text{C}_x\text{H}_y\text{O}_z^+$ , 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  $\text{NO}^+ + \text{NO}_2^+$  and assumed molecular weight of organic nitrate (A.W.Rollins, 2012; Boyd et al., 2015; Xu et al., 2015a). Also, are  $\text{NO}^+$  and  $\text{NO}_2^+$  included in the SOA yield and O:C calculation?

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- $\text{NO}_x$  conditions, why would SOA yield decrease with  $\Delta\text{Mo}$  at the beginning of the experiments? Under high- $\text{NO}_x$  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?

(2) Figure 4: This figure is confusing. Firstly, following the same  $\Delta\text{Mo}$ , the authors are comparing the SOA yield under different  $\text{NH}_4/\text{SO}_4$  ratio. The trend shown in figure 4 does not hold if the authors add data points when  $\Delta\text{Mo} = \sim 0.25 \text{ ug/m}^3$  (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  $\Delta\text{Mo}$ , the reason for which is not clear yet.

(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. Secondly, are 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). Thirdly, how is the increase of SOA yields calculated? What's the reference? 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  $\text{NO}_x$  conditions.

Minor comments:

1. Table 1: (1) Since both  $\text{H}^+$  and LWC are modeled by E-AIM in the study, I suggest the authors to replace  $\text{NH}_4/\text{SO}_4$  by particle pH, because  $\text{NH}_4/\text{SO}_4$  or ion balance is not a good proxy for particle pH (Guo et al., 2015; Hennigan et al., 2015). (2) Are the  $[\text{NH}_4]$  and  $[\text{SO}_4]$  input for E-AIM obtained from aqueous solution or AMS measurements? The latter should be used, because the  $\text{NH}_3/\text{NH}_4^+$  partitioning would cause the real  $[\text{NH}_4]/[\text{SO}_4]$  ratio different from that in aqueous solution.
2. Figure 1: (1) The legend "OH consumed a-pinene" is confusing because cumulative a-pinene consumed by OH should increase with time instead of decreasing as shown in the figure. I suggest to change the y-axis to " $\Delta$ a-pinene consumed by OH". (2) Is SOA mass concentration shown in this figure corrected for wall loss?
3. line 15. The core-shell model contradicts with literature. For example, Renbaum-Wolff et al. (2013) measured the viscosity of a-pinene SOA and calculated that the mixing time is on the order of 10-100s under 40-50% RH.
4. line 18-20. The authors found that the SOA is more oxidized under low- $\text{NO}_x$  conditions than high- $\text{NO}_x$  conditions. However, Chhabra et al. (2011) figure 2c showed that the O:C of a-pinene SOA under low- $\text{NO}_x$  (using  $\text{H}_2\text{O}_2$ ) and high- $\text{NO}_x$  conditions (using  $\text{CH}_3\text{ONO}$ ) are similar.

5. line 35. It should be “enhance the reactive uptake of gas phase organics”, instead of “particle phase”.
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.
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.
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  $\alpha$ -pinene SOA formation are different for low-NO<sub>x</sub> and high-NO<sub>x</sub> conditions. Thus, the previous studies cited in the manuscript only show the complexity of this scientific question, instead of the discrepancy.
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.
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.
11. line 166-167. The lower SOA yield under high-NO<sub>x</sub> conditions is due to RO<sub>2</sub> 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.
12. line 246-247. Eddingsaas et al. (2012a) is not properly cited. Section 3.3 in Eddingsaas et al. (2012a) stated that “Under high-NO<sub>2</sub> 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).

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.
14. line 267-270. The authors need to cite previous studies which discussed the gas phase products from  $\alpha$ -pinene oxidation. Especially, Eddingsaas et al. (2012b) showed that pinonaldehyde is important intermediate under both low and high-NO<sub>x</sub> conditions.
15. line 270-272. Xu et al. (2014) is not properly cited. Instead of showing that isoprene SOA is more oxidized under low-NO<sub>x</sub> conditions, Xu et al. (2014) showed that the oxidation state of isoprene SOA shows a non-linear dependence on NO<sub>x</sub> level.
16. line 318. Please cite Boyd et al. (2015) and Xu et al. (2015b).
17. line 331. What's the Org/SO<sub>4</sub> ratio in this study? Is it atmospherically relevant?
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.
19. line 495. The author list of this citation is wrong.

## References

A.W.Rollins: Evidence for NO<sub>x</sub> Control over Nighttime SOA Formation, *science*, 337, 2012.

Boyd, C. M., Sanchez, J., Xu, L., Eugene, A. J., Nah, T., Tuet, W. Y., Guzman, M. I., and Ng, N. L.: Secondary organic aerosol formation from the  $\beta$ -pinene+NO<sub>3</sub> system: effect of humidity and peroxy radical fate, *Atmos. Chem. Phys.*, 15, 7497-7522, 10.5194/acp-15-7497-2015, 2015.

Chhabra, P. S., Ng, N. L., Canagaratna, M. R., Corrigan, A. L., Russell, L. M., Worsnop, D. R., Flagan, R. C., and Seinfeld, J. H.: Elemental composition and oxidation of chamber organic aerosol, *Atmos Chem Phys*, 11, 8827-8845, DOI 10.5194/acp-11-8827-2011, 2011.

Eddingsaas, N. C., Loza, C. L., Yee, L. D., Chan, M., Schilling, K. A., Chhabra, P. S., Seinfeld, J. H., and Wennberg, P. O.:  $\alpha$ -pinene photooxidation under controlled chemical conditions &ndash; Part 2: SOA yield and composition in low- and high-NO<sub>x</sub> environments, *Atmos. Chem. Phys.*, 12, 7413-7427, 10.5194/acp-12-7413-2012, 2012a.

Eddingsaas, N. C., Loza, C. L., Yee, L. D., Seinfeld, J. H., and Wennberg, P. O.:  $\alpha$ -pinene photooxidation under controlled chemical conditions – Part 1: Gas-phase composition in low- and

high-NO<sub>x</sub> environments, *Atmos. Chem. Phys.*, 12, 6489-6504, 10.5194/acp-12-6489-2012, 2012b.

Griffin, R. J., Cocker, D. R., Flagan, R. C., and Seinfeld, J. H.: Organic aerosol formation from the oxidation of biogenic hydrocarbons, *J Geophys Res-Atmos*, 104, 3555-3567, Doi 10.1029/1998jd100049, 1999.

Guo, H., Xu, L., Bougiatioti, A., Cerully, K. M., Capps, S. L., Hite Jr, J. R., Carlton, A. G., Lee, S. H., Bergin, M. H., Ng, N. L., Nenes, A., and Weber, R. J.: Fine-particle water and pH in the southeastern United States, *Atmos. Chem. Phys.*, 15, 5211-5228, 10.5194/acp-15-5211-2015, 2015.

Hennigan, C. J., Izumi, J., Sullivan, A. P., Weber, R. J., and Nenes, A.: A critical evaluation of proxy methods used to estimate the acidity of atmospheric particles, *Atmos. Chem. Phys.*, 15, 2775-2790, 10.5194/acp-15-2775-2015, 2015.

Marais, E. A., Jacob, D. J., Jimenez, J. L., Campuzano-Jost, P., Day, D. A., Hu, W., Krechmer, J., Zhu, L., Kim, P. S., Miller, C. C., Fisher, J. A., Travis, K., Yu, K., Hanisco, T. F., Wolfe, G. M., Arkinson, H. L., Pye, H. O. T., Froyd, K. D., Liao, J., and McNeill, V. F.: Aqueous-phase mechanism for secondary organic aerosol formation from isoprene: application to the southeast United States and co-benefit of SO<sub>2</sub> emission controls, *Atmos. Chem. Phys.*, 16, 1603-1618, 10.5194/acp-16-1603-2016, 2016.

McNeill, V. F., Woo, J. L., Kim, D. D., Schwier, A. N., Wannell, N. J., Sumner, A. J., and Barakat, J. M.: Aqueous-Phase Secondary Organic Aerosol and Organosulfate Formation in Atmospheric Aerosols: A Modeling Study, *Environ Sci Technol*, 46, 8075-8081, 10.1021/es3002986, 2012.

Pankow, J. F., and Asher, W. E.: SIMPOL.1: a simple group contribution method for predicting vapor pressures and enthalpies of vaporization of multifunctional organic compounds, *Atmos Chem Phys*, 8, 2773-2796, 2008.

Pye, Pinder, R. W., Piletic, I. R., Xie, Y., Capps, S. L., Lin, Y. H., Surratt, J. D., Zhang, Z. F., Gold, A., Luecken, D. J., Hutzell, W. T., Jaoui, M., Offenberg, J. H., Kleindienst, T. E., Lewandowski, M., and Edney, E. O.: Epoxide Pathways Improve Model Predictions of Isoprene Markers and Reveal Key Role of Acidity in Aerosol Formation, *Environ Sci Technol*, 47, 11056-11064, Doi 10.1021/Es402106h, 2013.

Renbaum-Wolff, L., Grayson, J. W., Bateman, A. P., Kuwata, M., Sellier, M., Murray, B. J., Shilling, J. E., Martin, S. T., and Bertram, A. K.: Viscosity of  $\alpha$ -pinene secondary organic material and implications for particle growth and reactivity, *Proceedings of the National Academy of Sciences*, 110, 8014-8019, 10.1073/pnas.1219548110, 2013.

Surratt, J. D., Chan, A. W. H., Eddingsaas, N. C., Chan, M. N., Loza, C. L., Kwan, A. J., Hersey, S. P., Flagan, R. C., Wennberg, P. O., and Seinfeld, J. H.: Reactive intermediates revealed in secondary organic aerosol formation from isoprene, *P Natl Acad Sci USA*, 107, 6640-6645, DOI 10.1073/pnas.0911114107, 2010.

Xu, L., Kollman, M. S., Song, C., Shilling, J. E., and Ng, N. L.: Effects of NO<sub>x</sub> on the Volatility of Secondary Organic Aerosol from Isoprene Photooxidation, *Environ Sci Technol*, 48, 2253-2262, 10.1021/es404842g, 2014.

Xu, L., Guo, H., Boyd, C. M., Klein, M., Bougiatioti, A., Cerully, K. M., Hite, J. R., Isaacman-VanWertz, G., Kreisberg, N. M., Knote, C., Olson, K., Koss, A., Goldstein, A. H., Hering, S. V., de Gouw, J., Baumann, K., Lee, S.-H., Nenes, A., Weber, R. J., and Ng, N. L.: Effects of anthropogenic emissions on aerosol formation from isoprene and monoterpenes in the southeastern United States, *Proceedings of the National Academy of Sciences*, 112, 37-42, 10.1073/pnas.1417609112, 2015a.

Xu, L., Suresh, S., Guo, H., Weber, R. J., and Ng, N. L.: Aerosol characterization over the southeastern United States using high-resolution aerosol mass spectrometry: spatial and seasonal variation of aerosol composition and sources with a focus on organic nitrates, *Atmos. Chem. Phys.*, 15, 7307-7336, 10.5194/acp-15-7307-2015, 2015b.