

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

This work presents laboratory chamber studies on the effect of particle acidity on the secondary organic aerosols (SOA) formation from OH-initiated oxidation of α -pinene, a topic that has received much attention yet still under debate. The authors concentrate their discussions on how seed particle acidity would affect the SOA yield and elemental composition during different stages of photooxidation and under different reaction regimes (high vs. low NO_x). Overall, these experimental observations would certainly contribute a relatively complete dataset to studies that highlight the role of aerosol acidity in SOA production and aging. However, the major conclusions are potentially biased by the experimental protocols, in particular, the interference of NO_2 under low NO_x conditions as well as liquid water contents under different particle acidities. The authors are suggested to conduct additional experiments and perform modeling calculations to strengthen their conclusions prior to consideration of being published on *Atmospheric Chemistry and Physics*.

General Comments

1. Low vs. High NO_x conditions

The authors observed enhanced nitrogen-containing organic fragments formation with increasing aerosol acidity under high NO_x conditions. However, the fraction of these fragments remains constant at different particle acidities under low NO_x conditions, as shown in Figure 6. By examination of the ozone profile shown in Figure 1, one realizes that moderate ozone production is still occurring under the so-called ‘low NO_x conditions’, owing to the photolysis of NO_2 that are either released from the chamber wall or penetrated from the enclosure air, which is OK and cannot be completely avoided in most chamber setups. The production of ozone indicates a rapid recycling of the NO - NO_2 chemistry, and thus the active role of NO in the production of the nitrogen-containing organic fragments via the RO_2+NO pathway under ‘low NO_x conditions’. As

shown in Figure 6, the fraction of these nitrogen-containing organic fragments under low NO_x conditions seems comparable with those under high NO_x conditions, indicating that they cannot be simply artifacts in the AMS measurement. But the question is why the dependence of these nitrogen-containing organic fragments on particle acidity is only observed under high NO_x conditions? The authors need to give a convincing explanation on this inconsistency.

Another issue is that the so-called ‘high NO_x condition’ does not necessarily lead to the RO_2+NO reaction dominant regime over the entire course of the experiment. As shown in Figure 1, NO concentration seems to be completely depleted after a few min of reaction, which is expected due to the intense formation of nitric acid and its rapid deposition on the wall and particles. The authors are suggested to carry out continuous NO injection after the initial consumption of NO to truly achieve the ‘high NO_x condition’. Alternatively, HONO or CH_3ONO can be used as the OH precursor under high NO_x conditions.

2. First vs. later generation SOA products

The strong dependence of SOA yield on particle acidities under high NO_x conditions was only observed during the initial photooxidation stage, where the total SOA mass concentration is less than 2 ug/m^3 . As the reaction proceeds, SOA yields are eventually comparable at different particle acidities and the authors explained this phenomenon as the unavailability of free H^+ due to thick organic coatings. Note that this argument is established under the assumption that the core of the particles are (semi)-solid and there is no particle-phase diffusion over the entire course of several hours of reaction, which is doubtful considering the moderate RH conditions employed in the experiments. One suspects that if the observed SOA yield dependence at the initial particle growth period on the acidity can be simply attributed to the uncertainties in the AMS measurement when the overall organic loadings are extremely low ($< 2 \text{ ug/m}^3$). The authors are suggested to perform additional calibration experiments:

- 1) Prepare a mixture of pinonic acid (a surrogate for α -pinene photo-oxidation products) and ammonium sulfate salt under different acidities, atomize the mixtures into the chamber under controlled RH and T conditions, and sample

the suspended particles by AMS. The authors need to verify if AMS measured organic loadings are identical under different seed acidities even at low organic levels. This calibration experiments can also be used as a means to correct the AMS collection efficiency, if different from the default value used.

- 2) Alternatively, the authors could repeat experiments # 9-12, but adding seed particles after only 30 min of reaction. Would the dependence of SOA yield on the organic loadings still be observed?

3. Aerosol liquid water content

The hygroscopic growth curves for ammonium sulfate seed at different acidities are significantly different. At ~ 50% RH, diameter changes of $(\text{NH}_4)_2\text{SO}_4$ and NH_4HSO_4 are 0% and 20% at equilibrium, respectively, due to water uptake (Seinfeld and Pandis, 2008). For the experimental conditions in this study, i.e., dry seed particles with different acidities at 50-70% RH, the water content would vary significantly from zero to several tens of percentage in mass, depending the amount of sulfuric acid in the particle phase. As a result, the observed ‘acidity effect’, if any, should really be the coupled effect of both acidities and water content in aerosols. Another concern is the different phase states of particles could potentially lead to different bouncing effect on the AMS vaporizer, thus changing the collection efficiency for different seed particles. In view of these uncertainties, the authors are suggested to conduct a series of experiments using hydrated seed particles to begin with.

4. Particle acidity and atmospheric relevant conditions

In view of the main focus of this study, the seed particle acidities need to be estimated based on the AMS measured inorganic composition and thermodynamic models such as E-AIM (<http://www.aim.env.uea.ac.uk/aim/aim.php>). The authors are also suggested to discuss how relevant the acidities used in the chamber experiments with atmospheric conditions.

Minor Comments

1. Page 2, Line 50: Ester dimers are observed as an important class of products from the ozonolysis of α -pinene (e.g., Zhang et al., PNAS, 2015). Epoxides are certainly produced, but from a minor pathway (e.g., Eddingsaas et al., ACP, 2012), and ring-opening reactions proceed rapidly following the reactive uptake of epoxides.
2. Page 2, Line 57: It has been well recognized that sulfate esters contribute to a large fraction of SOA mass via reactive uptake of IEPOX, a second generation oxidation products from isoprene photooxidation under low NO conditions, onto acidified aerosols. However, the exact mass fraction of sulfate esters in the α -pinene system has not yet been determined. Surratt et al. (2007) and (2008) report for the first time the evidence of organosulfate in α -pinene derived SOA, but not quantification.
3. Page 5, Line 132: Have the authors performed experiments monitoring the decay of pure sulfate particles? How was the decay rate compared with particles coated with organics?
4. Page 5, Line 134: How was the 0.1 ug/cm^{-3} mass from self-nucleation estimated?
5. Page 5, Line 139: What is the estimated NO_3 photolysis rate?