

Interactive comment on “Increased Primary and Secondary H₂SO₄ Showing the Opposing Roles in SOA Formation from Ethyl Methacrylate Ozonolysis” by Peng Zhang et al.

Anonymous Referee #1

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SUMMARY This paper investigated the SOA formation from the ozonolysis of ethyl methacrylate (EM) in the presence of acidic sulfate seed, which was nebulized using aqueous sulfuric acid solution or/and SO₂ oxidation, in the indoor chamber. The resulting SOA and acidic sulfate were characterized using HR-ToF-AMS fragmentation patterns and the Van Krevelen diagram under varying the amount of acidic sulfate. Overall, it is difficult to follow the flow of the manuscript. The interpretation for the impact of aerosol acidity on SOA yields and the trend in product distributions was somewhat weak. In addition, the implication of the resulting study to the ambient air was not well described.

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1. Gas product aging. For the chamber study, the authors included CO to remove OH radicals that were yielded from the decomposition of ozonolysis products of EM. The experimental condition in the absence of UV light and OH radicals suggests that further oxidation of ozonolysis products in the gas phase can be very slow or insignificant. It is unclear how the ozonolysis products of this study can be further oxidized under such experimental conditions.

2. 2nd paragraph in page 5, Cleaning chamber. The paper described that the smog chamber was cleaned for at least 24 h until certain condition were reached. Authors need to explain the cleaning procedure with more details. In addition to the concentrations of background gas and particles, the cleaning procedure can influence the wall conditions. Off-gassing of some preexisting organic gases from chamber takes time. No chamber can be perfectly sealed. The organic compounds deposited on the chamber wall can influence atmospheric chemistry and SOA formation. Ammonia can slowly intrude to the chamber wall and stick to chamber wall. This ammonia can be off-gassing from the wall and neutralize acidic seed in the absence of SO₂.

3. Missing of EM profiles: Authors showed the time profiles of ozone and SO₂ (Figure S2) but did not show EM time profiles. Please include the EM time profiles. No SOA yield was reported.

4. Impact of acidic aerosol on SOA formation (Section 3.1). The explanation for the influence of acidic inorganic seed on SOA needs to be more clarified by characterizing the impact of the wall on SOA formation. Most explanations in this paper are qualitative. SOA growth need to be explained with mathematical parameters. SOA growth mechanisms should be explained based on thermodynamic partitioning and the kinetic factor in heterogeneous chemistry. (1) SOA formation is not necessarily dependent of the quantity of acidic aerosol or the quantity of wet-inorganic aerosol because SOA growth via aqueous reactions of organic species can be limited by the quantity of reactive chemical species in gas phase. The significance of the aqueous reaction of organic species are related to the characteristic time of heterogeneous chemistry. The

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lifetime of EM could be several hours (longer than experimental duration). The gaseous organic products formed in the experimental condition of this study may be relatively stable in the absence of OH radicals and UV light. In the case when the characteristic time of the aqueous reaction or organic products is relatively short, the aqueous phase reaction does not need the high concentration of wet-seed. The authors did not show the profile of EM as well as the consumption of EM over the course of the experiment. Based on Figure 1, sulfate concentrations were much higher than SOA. In the presence of the high concentration of acidic sulfate, the sensitivity of reactive chemical species to aerosol acidity can be small. On the other hand, if aqueous reaction is relatively slower than ozonolysis, heterogeneous reactions can be sensitive to the quantity of acidic wet-seed. In this case, the impact of the wall can be significant because both the characteristic time of particle loss to the wall and characteristic time for organic deposition can be relatively important. Therefore the experimental data reported in this study need in-depth analyses. Overall, experimental data is not strong to support the author's explanation on the impact of acidic sulfate on SOA growth.

(2) Figure 1: Authors need to explain how Figure 1 was obtained (what instrument and what procedure?). The subtraction of the large quantity of sulfate aerosol from the total aerosol is not appropriate to accurately quantify the SOA mass produced. The acidic aerosol deposition to the chamber wall can acidify the chamber wall and actively absorb the reactive gas species. The characteristic time of the wall loss of organic compounds can be influenced by the dimension of the chamber. In general, the surface area of wall can be larger than the surface area of aerosol. If the oxidized products from the ozonolysis of precursor hydrocarbons are not highly reactive for aerosol phase reactions, the impact of the wall can be high as discussed above. To demonstrate the actual impact of acidic aerosol, the characterization of the chamber wall should be performed.

(3) SO₂ oxidation in the absence of preexisting wet aerosol produces many small particles increasing the surface area of aerosols (Figure 7). In the presence of wet-

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ammonium sulfate, SO₂ can partition to aqueous phase and SO₂ can be heterogeneously oxidized with ozone. Thus, wet-seed can suppress the formation of new sulfuric acid particles that can increase surface areas of particles. In the presence of wet-AS aerosol, it will take time to build up aerosol acidity as increasing sulfate fraction in the internal mix of ammonium sulfate and sulfuric acid. I do not convince that SOA formation is suppressed in the presence of more acidic sulfate because the large amount of acidic seed is not necessarily linked to the large SOA mass except a slow organic heterogeneous reaction. The quantity of reactive organic species may be relatively small compared to the large quantify of acidic sulfate.

5. Line 233. What is Fourier spectra ? Please also clarify what is mass spectrum instrument.

6. Line 241. Please check “Sci”.

7. Line 244-247. The connection of alpha-pinene data with EM ozonolysis data is unclear. The appearance of alpha-pinene SOA data is somewhat awkward in the flow of the paper. The SOA from EM ozonolysis will be different from the SOA from alpha-pinene ozonolysis in hydrocarbon lifetime, volatility of products, reactivity in aerosol phase, organic vapor deposition to the wall, and solubility of products in salted aqueous phase. It is hard to understand why alpha-pinene SOA behaves in the same with EM SOA for the impact of sulfate on SOA.

8. Lines 257-260. For the last two decades, there have been numerous studies to investigate the impact of sulfuric acid on SOA formation. The authors' citations mainly pointed the publication from own lab. There were landmark publications to launch the investigation of acid-catalyzed reactions of organics in the aerosol phase. The authors need to give a credit to early scientific efforts by citing land breaking publications in this area.

9. PMF analysis (page 10-13) (1) In page 10, authors mentioned that Factor 1 is for less-oxygenated organic aerosol (carbonyls) and factor 2 is for more oxygenated

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organic aerosol (carboxylic acid). Authors mentioned that after 200 min, Factor 1 continuously increased but Factor 2 decreased suggesting chemical conversion of part of less-oxygenated species in Factor 2 to more-oxygenated products in Factor 1 in the latter period of reaction. Authors need to rationale how this conversion occurs. In addition, the description in page 10 is contradicted between several sentences

(2) Lines 288-293. Authors mentioned condensation of both less oxidized species and more oxidized species. However, this description cannot be connected to acid-catalyzed heterogenous reaction. What does the condensation means in this paper? The authors need to clarify aerosol growth mechanisms that mainly influence EM SOA.

(3) In general, if aerosol growth is dominated by acid-catalyzed heterogeneous chemistry, the concentration of carbonyl species can significantly decreases due to the reaction of carbonyl species. Authors need to clarify the mechanistic role of sulfuric acid on SOA growth on the trend of mass peaks.

10. Lines 346-347. "SOA increased with decreasing particulate pH" This sentence may be true for a specific situation when aerosol composition changes (neutralization with ammonia and change in humidity). The concern is what is the definition of aerosol acidity in the authors' point. The pH is calculated from the proton concentration (mol/L) in aqueous phase. The increasing of the quantity of acidic sulfate cannot necessarily increase pH. pH mainly changes with inorganic composition and humidity. Authors should clarify how pH changes in the paper and how to define aerosol acidity in the discussion in the numerous places. The change in pH is different from the change in the quantity of sulfate without changing aerosol composition.

11. Figure 7. The curved arrow points in clockwise direction with different reasons in both the left side and the right side boxes. It is difficult to understand the information in the right side.

12 Kinetic mechanisms on page 18. Reaction III may represent the H-shift followed by autoxidation. In general, H-shift occurs 5-membered geometry or 6-membered ge-

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ometry. The H-shift that is depicted in III is based on a 8-membered ring. The H-shift with a higher than 6-member ring geometry may unlikely occurs. The authors need to clarify this.

13. Lack of the description of atmospheric implication of this study. In general the concentration of EM in ambient air will be much lower than the chamber condition and their oxidation will be processed in the presence of OH radicals and UV light (daytime). Is ozonolysis is the main mechanisms of EM oxidation in ambient air?. If the OH radical is not scavenged, what are the impacts of acidic sulfate on EM SOA formation?. In polluted ambient areas, there is preexisting particulate matter. Is the EM ozonolysis + SO₂ (Craigie intermediate + SO₂) mechanism significant in such ambient air?

14. The author needs to discuss about organosulfate (OS) formation in different acidic aerosols and the potential impact of OS on SOA growth.

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