Supporting Information

Increased Primary and Secondary H_2SO_4 Showing the Opposing Roles in SOA Formation from Ethyl Methacrylate Ozonolysis

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1. Table S1. Experimental conditions.

			Seed				
[EM] **(ppb)**	**[O_3]** **(ppb)**	**[SO_2]** **(ppb)**	acidity	mass con. (μg m^{-3})	Volume con. (nm^3 m^{-3})	**CO** **(ppm)**	**RH** **(%)**
100	200	55	-	-	4.6×10^9	38	10%
100	202±4	131±3	-	-	7.3×10^9	36±1	10%
100	205±6	138±6	neutral	47±5	-	38±1	10%
100	200	138	acidity	59.3	-	36	10%
100	205±6	135±6	neutral	42±5	-	38±1	45%
100	200	132	acidity	52	-	36	45%

2. Correction of wall loss rate

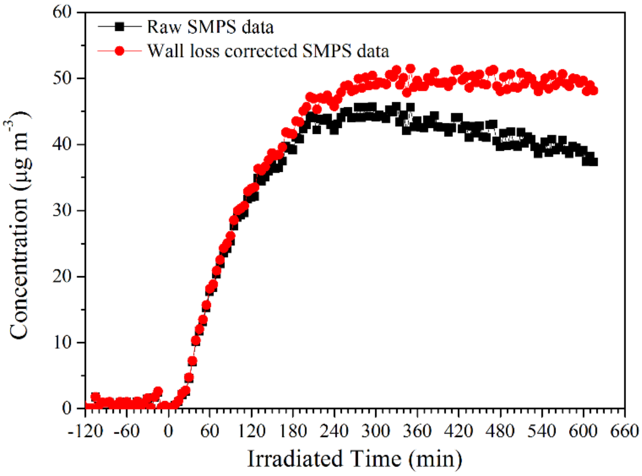


Figure S1. The correction of wall loss rate of $(NH_4)_2SO_4$ particles.

3. Parallel experiments

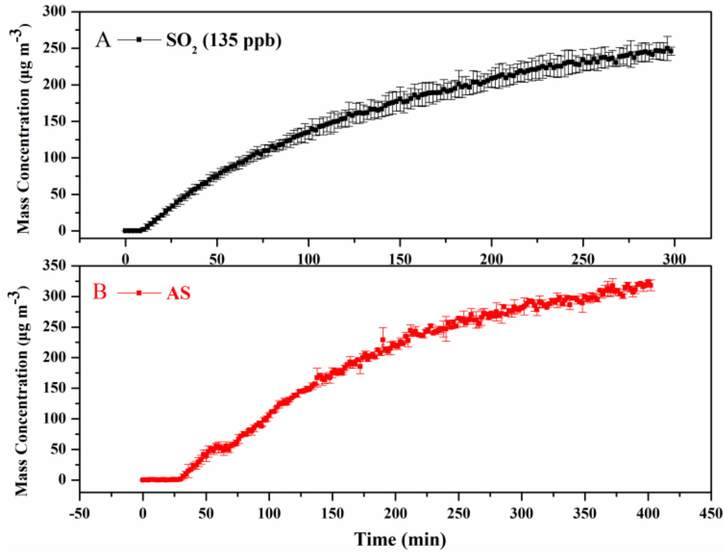


Figure S2. Total mass concentration of secondary particles in parallel experiments at 135 ppb SO_2 in the absence of AS seeds (A) and at 138 ppb SO_2 in the presence of AS seeds (B).

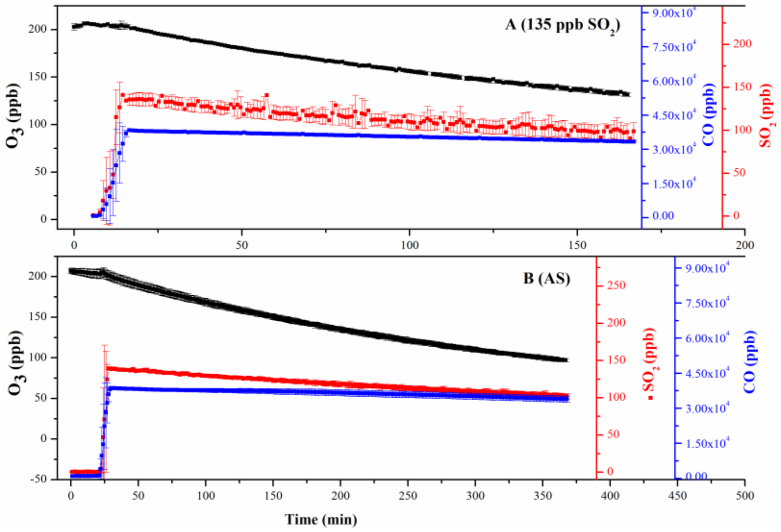


Figure S3. Reaction gas consumption as function of reaction time at 131 ppb SO_2 in the absence of AS seeds (A) and at 138 ppb SO_2 in the presence of AS seeds (B).

4. Background experiments.

In the absence of seed and SO_2, the ozonolysis of alone EM could not produce SOA (Figure S4). Moreover, these background experiments in the absence of SO_2 under AS and AAS condition have been also conducted. As shown in Figure S5, it could be found that the increased particle acidity has a negligible impact on SOA formation in the absence of SO_2. This also further proved that the reducing effect of seed particle on secondary particle formation resulted from the formation of H_2SO_4 particles in the presence of SO_2.

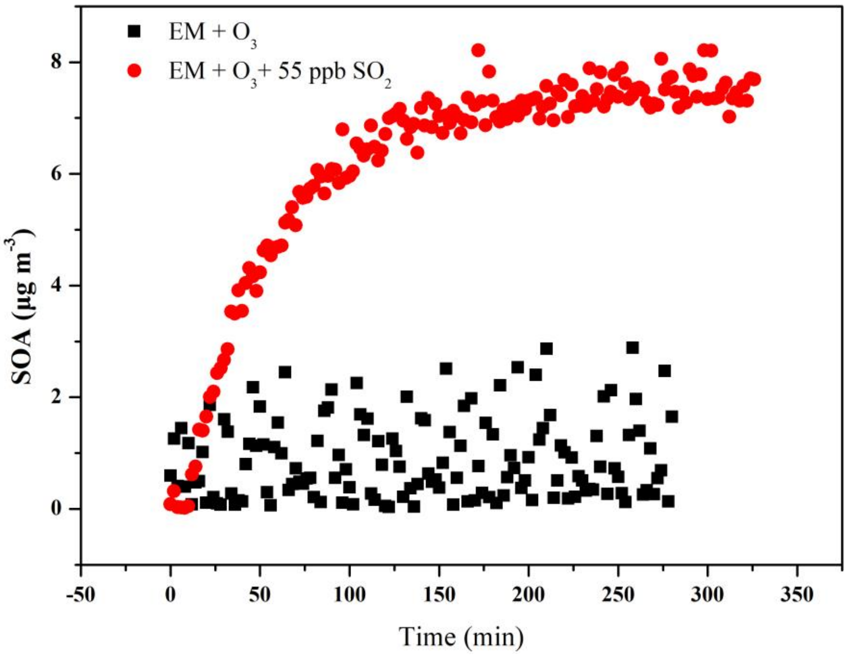


Figure S4. Time-dependent growth curves of SOA in the absence and presence of SO_2

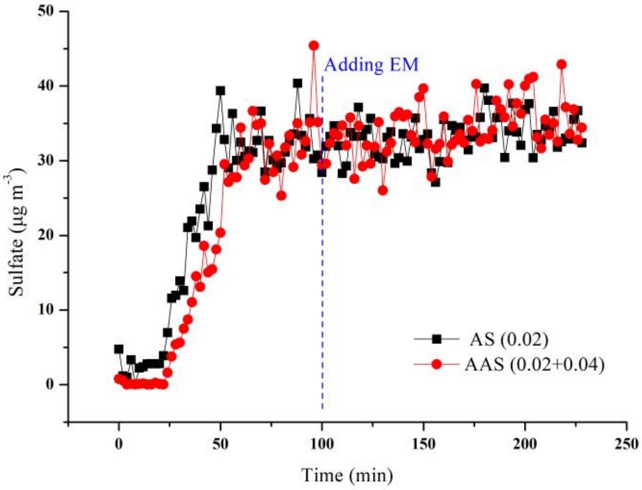


Figure S5. Evolution of secondary particles mass concentration with AS (black) and AAS (red) in the absence of SO_2.

5. Seed acidity experiments of EM ozonolysis at higher RH.

In order to better relate to the real atmosphere and increase the significance of this work, these experiments on the seed particle role were also conducted at higher RH (45-50% RH). As shown in Figure S6, it could be found that increased particle acidity similarly suppressed the formation of SOA and sulfate at higher RH. This indicated that the suppressed role of increased acidity to SOA and sulfate formation should be ubiquitous in the real atmosphere.

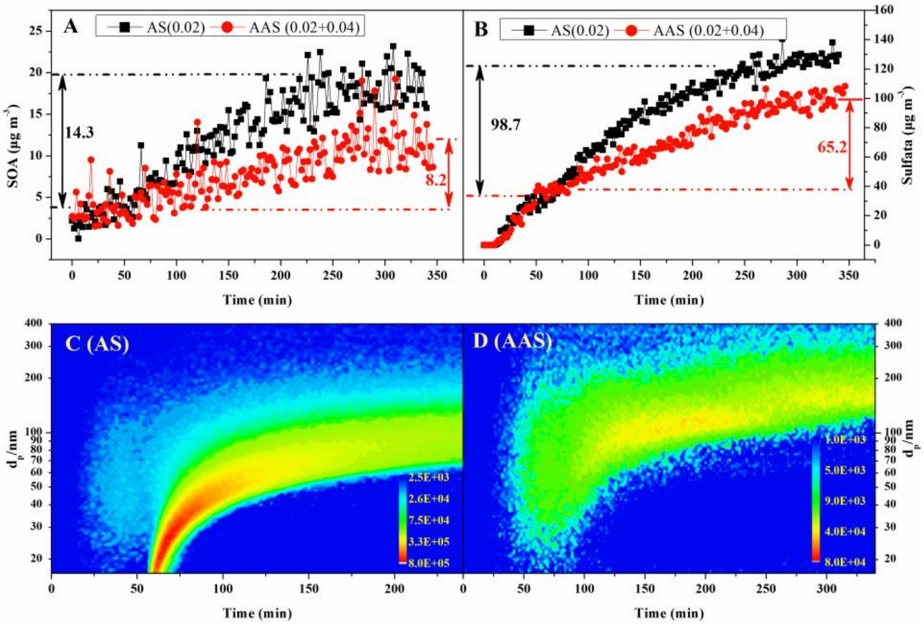


Figure S6. Time-dependent growth curves of both SOA (A) and sulfate (B) in presence of AS seed (red) and acidic AAS seed particles. Size distribution of secondary aerosol as a function of time under AS seed particle (C) and Acidic AAS seed particle (D)

The lower the concentration of both SOA and sulfate at 45% RH relative to 10% RH proved that increased RH was adverse to SOA and sulfate formation (Figure S7).

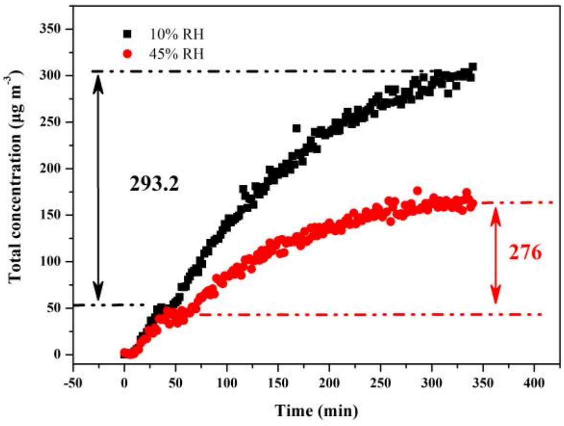


Figure S7. Total mass concentration at 10% RH (black) and 45% RH (red)

6. The uptake of EM on the surface of seed solutions.

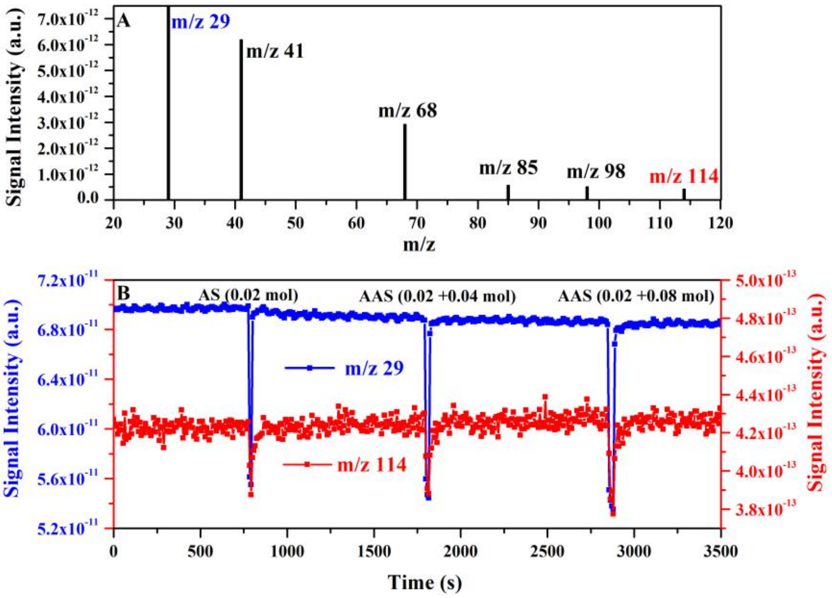


Figure S8. Mass spectrum of EM and its uptakes in AS (0.02 mol), AAS (0.02+0.02 mol), and AAS (0.02+0.04 mol) solutions.

7. The ozonolysis of surface EM with SO_2 and without SO_2

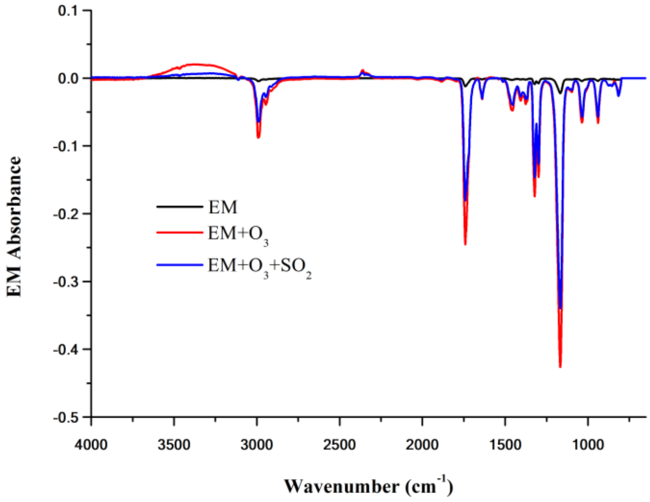


Figure S9. Absorbance of EM ozonolysis in the absence and presence of SO_2.

To further verify the presence of SO_2 could hamper the ozonolysis of adsorbed EM due to surface H_2SO_4 formation, we check the absorbance of EM ozonolysis in the absence and presence of SO_2. 50 μL EM was first added in the Attenuated Total Reflection (ATR). At 10% RH, EM will gradually volatilize in the purge gas with the rate of 200 ml min^{-1}. Reactant gas (O_3 and SO_2) was subsequently introduced along with purge gas when liquid EM could not be observed in ATR. As shown in Figure S, it could be found that EM consumption in the presence of SO_2 was slower than that in the absence of SO_2. This indicated the presence of SO_2 indeed suppressed the ozonolysis of absorbed EM in ATR surface.

8. Seed acidity experiments of α-pinene ozonolysis at 45% RH.

To further verify whether these observations could happen for other systems, the ozonolysis experiments of α-pinene at 45% RH in the presence of seed particles with different acidity were also conducted in the chamber. As shown in Figure S8, increased particle acidity similarly suppressed the formation of SOA and sulfate during α-pinene ozonolysis at higher RH. These results indicated that the suppressed role of increased acidity to SOA and sulfate formation should be ubiquitous in the real atmosphere.

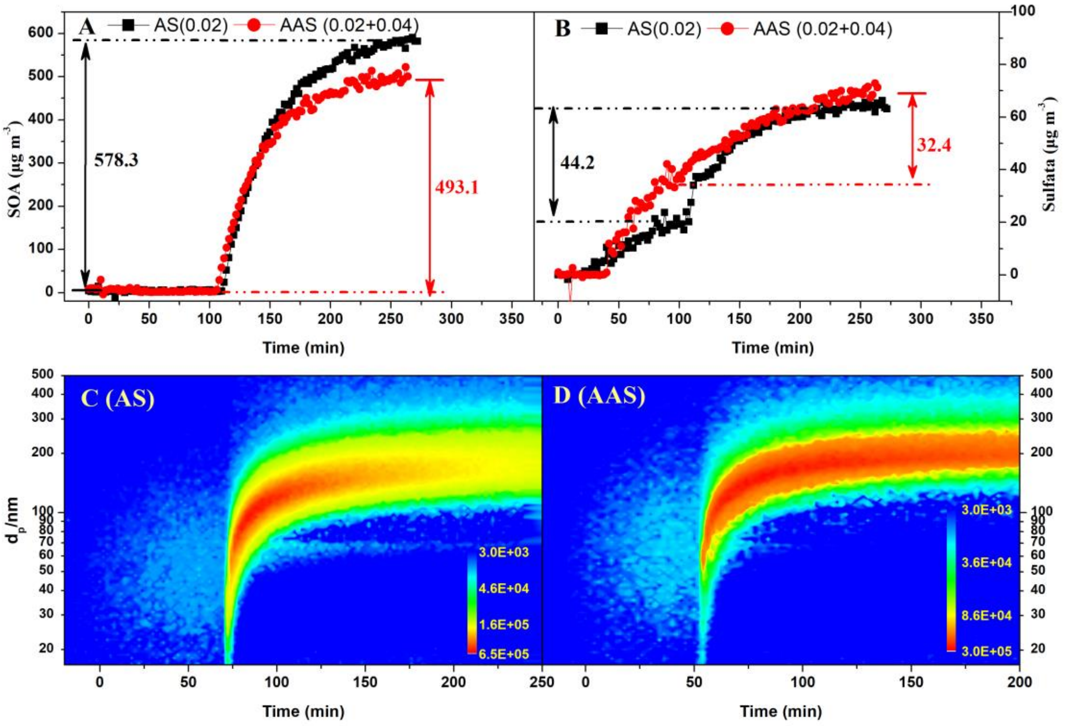


Figure S10. Time-dependent growth curves of both SOA (A) and sulfate (B) in presence of AS seed (red) and acidic AAS seed particles. Size distribution of secondary aerosol as a function of time under AS seed particle (C) and Acidic AAS seed particle (D)

9. The methodological of PMF analysis

We utilized these organic data matrices and the corresponding error matrices after SQUIRREL 1.57 analysis for the PMF analyses (Execute Calcs Tool v2.06). According to the procedures supplied by Zhang et al. (2011) and Ulbrich et al. (2009),(Ulbrich et al., 2009; Zhang et al., 2011) we carefully evaluated the PMF results and solution. The m/z ranges of data from SQUIRREL in PMF analyses are 12-115. The error matrices were pretreated using PMF evaluation toolkit following the described in Huang et al.(Huang et al., 2018)

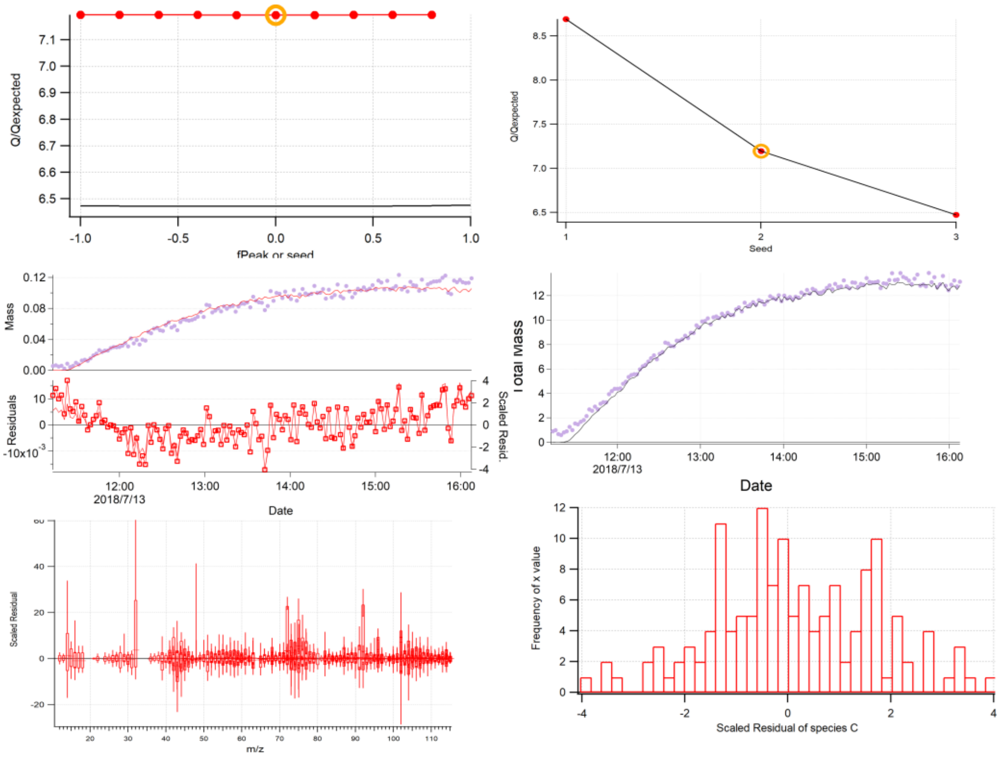


Figure S11. Two-factor solution for PMF analysis of EM-derived SOA at 93 ppb SO_2 in the absence of seeds, Diagnostic plot, fPeak=0, Seed varies from -1 to 1

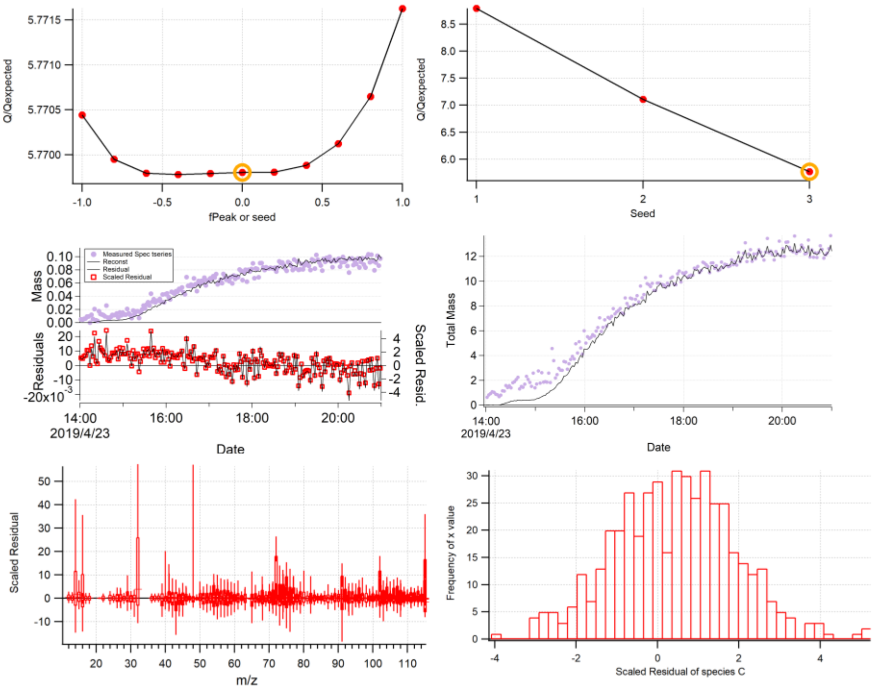


Figure S12. Three-factor solution for PMF analysis of EM-derived SOA at 135 ppb SO_2 in the presence of AS seeds, Diagnostic plot, fPeak=0, Seed varies from -1 to 1

10. Normalized spectra of Factor 3 and adsorbed EM.

The blank experiment of just EM and AAS was also conducted. As shown in Figure S, the mass spectrum of adsorbed EM was similar with Factor 3, especially for the ratio of m/z 43 and 44.

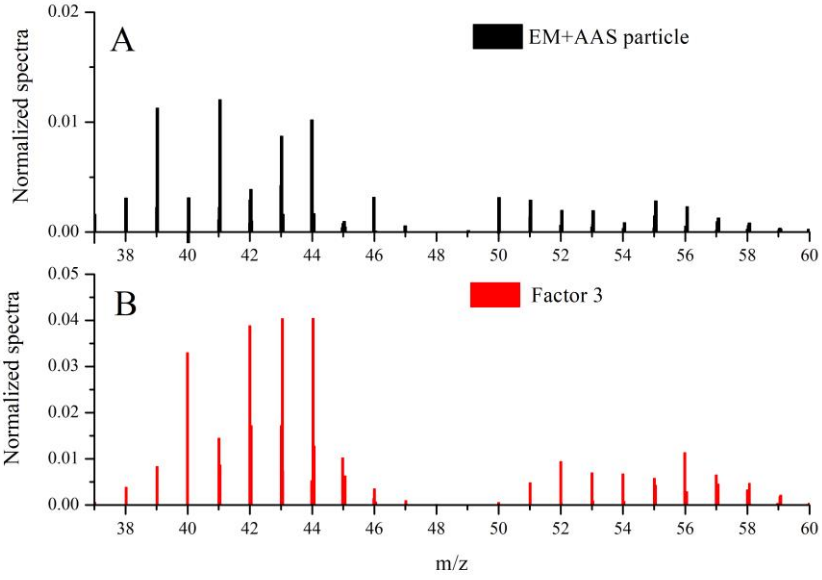


Figure S13. normalized spectra of Factor 3 and adsorbed EM in AAS particles.

11. The S/C ratio and sulfate fragments between neutral and acidity.

Chen et al. suggested that the difference in sulfate fragments between AS and organosulfate could be used to verify the organosulfate formation.(Chen et al., 2019) In order to make clear whether organosulfates were produced during EM ozonolysis, thus the sulfate fragments between AS and AAS experiments were also compared. As shown in Figure S, it could be found that the distributions of sulfate in both of seed experiments were almost the similar. Moreover, the S/C ratio were also the same in both of seed experiments. Taken together, it could be concluded that the contribution of organosulfates to SOA formation and OSc could be ignored. The increased oxidation state (OSc) of the aerosol may be attribute to the formation of more highly functionalized products.

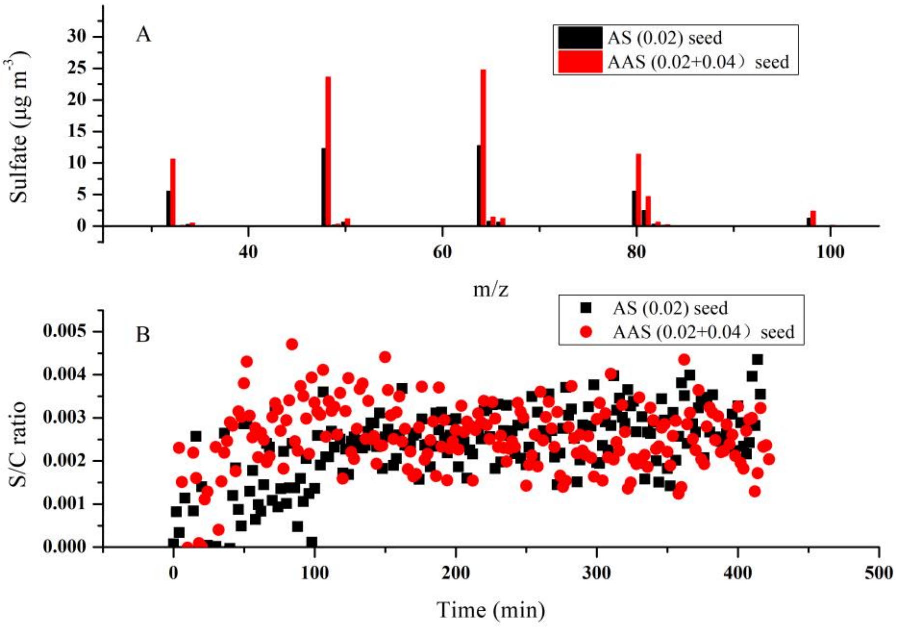


Figure S14. Mass spectrum (A) and S/C ratio (B) of sulfate in the presence of AS and AAS seed particles.

12. Evolutions of major SOA molecules

The evolutions of some molecule ions peaks have been shown in Figure S. The increase of their mass concentrations indicated that these molecular ions peaks with m/z 116, 130, 132, 140, 146, 148, 158, 162, 164, 176, 178, 180, 194, 196, and 212 should be the major ozonolysis products.

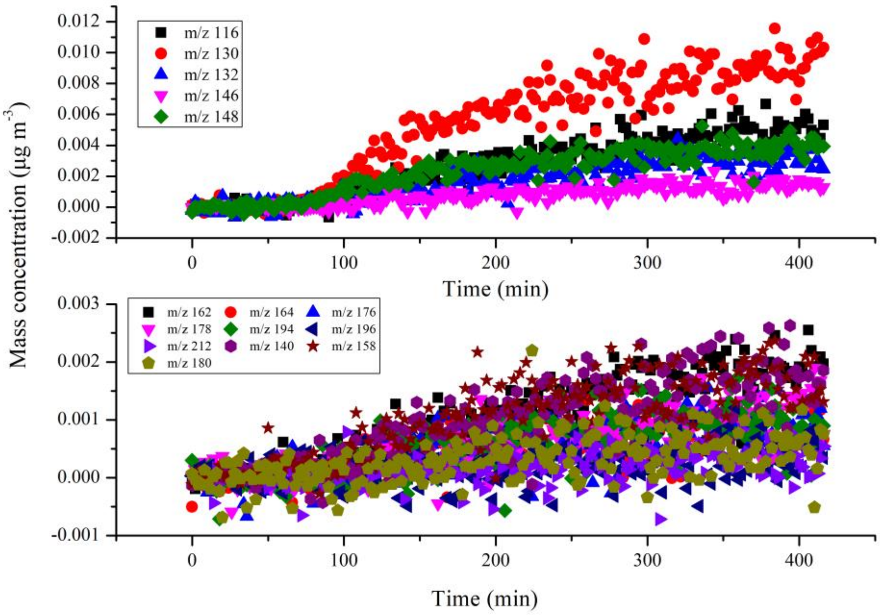
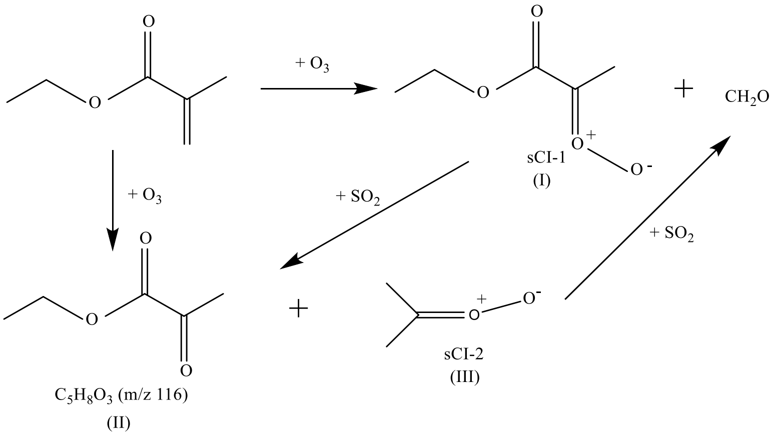


Figure S15. Time evolution of major oxidation products in presence of AS seed

13. General mechanism of the ozonolysis of EM and the formation mechanism of sulfuric acid



Scheme S1. General mechanism of the ozonolysis of EM

The reaction mechanism of sulfuric acid during alkene ozonolysis has been shown as following:

$$R_1R_2COO + SO_2 \rightarrow R_1R_2CO + SO_3 \qquad (1)$$

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad (2)$$

10% RH has been proved to be sufficient in SA formation via the sCI+SO$_2$ reaction based on some previous studies.(Berndt et al., 2014; Diaz de Mera et al., 2017; Zhang et al., 2019)

Reference

Berndt, T., Voigtländer, J., Stratmann, F., Junninen, H., Mauldin III, R.L., Sipilä, M., Kulmala, M., Herrmann, H., 2014. Competing atmospheric reactions of CH_2OO with SO_2 and water vapour. Phys. Chem. Chem. Phys. 16, 19130-19136.

Chen, Y., Xu, L., Humphry, T., Hettiyadura, A.P., Ovadnevaite, J., Huang, S., Poulain, L., Schroder, J.C., Campuzano-Jost, P., Jimenez, J.L., 2019. Response of the aerodyne aerosol mass spectrometer to inorganic sulfates and organosulfur compounds: Applications in field and laboratory measurements. Environ. Sci. Tech. 53, 5176-5186.

Diaz de Mera, Y., Aranda, A., Bracco, L.L., Rodriguez, D., Rodriguez, A., 2017. Formation of secondary organic aerosols from the ozonolysis of dihydrofurans. Atmos. Chem. Phys.17. 2347–2357.

Huang, D.D., Zhang, Q., Cheung, H.H., Yu, L., Zhou, S., Anastasio, C., Smith, J.D., Chan, C.K., 2018. Formation and evolution of aqSOA from aqueous-phase reactions of phenolic carbonyls: comparison between ammonium sulfate and ammonium nitrate solutions. Environ. Sci. Tech. 52, 9215-9224.

Ulbrich, I.M., Canagaratna, M.R., Zhang, Q., Worsnop, D.R., Jimenez, J.L., 2009. Interpretation of organic components from Positive Matrix Factorization of aerosol mass spectrometric data. Atmos. Chem. Phys. 9, 2891-2918.

Zhang, P., Chen, T., Liu, J., Liu, C., Ma, J., Ma, Q., Chu, B., He, H., 2019. Impacts of SO_2, Relative Humidity, and Seed Acidity on Secondary Organic Aerosol Formation in the Ozonolysis of Butyl Vinyl Ether. Environ. Sci. Tech. 53, 8845-8853.

Zhang, Q., Jimenez, J.L., Canagaratna, M.R., Ulbrich, I.M., Ng, N.L., Worsnop, D.R., Sun, Y., 2011. Understanding atmospheric organic aerosols via factor analysis of aerosol mass spectrometry: a review. Anal. Bioanal. Chem. 401, 3045-3067.