



Supplement of

Increased primary and secondary H_2SO_4 showing the opposing roles in secondary organic aerosol formation from ethyl methacrylate ozonolysis

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				Seed			
No.	[EM]	[O ₃]	[SO ₂]	acidity	mass con. (µg m ⁻³)	CO (ppm)	RH (%)
	(ppb)	(ppb)	(ppb)				
#1	100	200	55	-	-	38	10%
#2	100	202±4	131±3	-	-	36±1	10%
#3	100	205±6	138±6	neutral	47±5	38±1	10%
#4	100	200	138	acidity	59.3	36	10%
#5	100	205±6	135±6	neutral	42±5	38±1	45%
#6	100	200	132	acidity	52	36	45%

1. Table S1. Experimental conditions.

2. Correction of wall loss rate



Figure S1. The correction of wall loss rate of (NH₄)₂SO₄ particles.





Figure S2. Time-dependent growth curves of ammonium and sulfate in the presence

38 **3. Parallel experiments**



Figure S3. Total mass concentration of secondary particles in parallel experiments at
135 ppb SO₂ in the absence of AS seeds (A) and at 138 ppb SO₂ in the presence of AS
seeds (B).





Figure S4. Reaction gas consumption as function of reaction time at 131 ppb SO₂ in
the absence of AS seeds (A) and at 138 ppb SO₂ in the presence of AS seeds (B).

4. Background experiments.

In the absence of seed and SO₂, the ozonolysis of alone EM could not produce SOA (Figure S5). Moreover, these background experiments in the absence of SO₂ under AS and AAS condition have been also conducted. As shown in Figure S6 and S7, it could be found that the increased particle acidity has a negligible impact on SOA formation in the absence of SO₂. This also further proved that the reducing effect of seed particle on secondary particle formation resulted from the formation of H₂SO₄ particles in the presence of SO₂.



Figure S5. Time-dependent growth curves of SOA in the absence and presence of



56 SO₂



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Figure S6. Evolution of secondary particles mass concentration with AS (black) and

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AAS (red) in the absence of SO₂.



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Figure S7. Evolution of SOA mass concentration with AS (black) and AAS (red) in

 $62 \qquad \text{the absence of } SO_2 \text{ (AMS data).}$

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

64 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 S8, 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.



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Figure S8. 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%





Figure S9. Total mass concentration at 10% RH (black) and 45% RH (red)

6. Mean size and surface concentration of seed particles and new particles under different condition.

- 81 The mean PTof size of sulfate at 135 ppb SO_2 was also higher than that at 55 ppb SO_2
- 82 (Figure S10).



83 84

89

Figure S10, PTof size of sulfate at 55 ppb SO₂and 135 ppb SO₂.

Moreover, the mean surface concentration and mean size of new particles at 135 SO₂were also higher than that at 55 ppb SO₂ (Figure S11A). This indicated that high SO₂ level promoted the rapid homogeneous nucleation of H₂SO₄, which providing greater surface area and volume for the condensation of low-volatile products.



Figure S11. Number distribution of secondary particle at 55 ppb SO₂ and 135 ppb SO₂

- 91 (A) when the number concentration was maximum; Size distribution of seed particle:
- 92 AS and AAS seed particle (B).



93 7. The uptake of EM on the surface of seed solutions.

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Figure S12. Mass spectrum of EM and its uptakes in AS (0.02 mol), AAS (0.02+0.02

96 mol), and AAS (0.02+0.04 mol) solutions.

8. The ozonolysis of surface EM with SO₂ and without SO₂



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99 **Figure S13.** Absorbance of EM ozonolysis in the absence and presence of SO₂.

Fourier spectra represents the in situ attenuated total internal reflection infrared
 (ATR-IR) spectra, which was recorded using a NEXUS 6700 (Thermo Nicolet
 Instrument Corp.) Fourier transform infrared (FT-IR) spectrometer equipped with a

high-sensitivity mercury-cadmium-telluride (MCT) detector cooled by liquid N₂. All spectra reported here were recorded at a resolution of 4 cm⁻¹ for 100 scans in the spectral range of 4000–650 cm⁻¹.(Han et al., 2013; Ma et al., 2019). 50 μ L 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 (O₃ and SO₂) was subsequently introduced along with purge gas when liquid EM could not be observed in ATR.

110 **9.** The methodological of PMF analysis

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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 S15. Three-factor solution for PMF analysis of EM-derived SOA at 135 ppb
SO₂ in the presence of AS seeds, Diagnostic plot, fPeak=0, Seed varies from -1 to 1

125 **10.** The evolution of m/z Org43 and m/z Org44 fragment

126 From Figure S16, the mass concentration of m/z 44 (the characterized fragment of high oxidized species) and the ratio of m/z 44 to total signal in the component mass 127 spectrum (f44) were observed to continuedly increased with the decrease of m/z 43 128 (the characterized fragment of carbonyl species) and the ratio of m/z 43 to total signal 129 130 (f43) after 200 min, which is consistent with that observed in Figure 3B. This analysis also supported our proposed conclusion in which the chemical conversion of less 131 oxidized species to more oxidized species could occur when the H₂SO₄ proportion 132 (acidity) in the particle-phase reached a certain concentration 133



Figure S16, Time-dependent growth curves of m/z Org43 and m/z Org44 fragment (A); the triangle plot of f(43) vs f(44) of SOA (B) at 55 ppb SO₂ in absence of seed particles. f44 (ratio of m/z 44 to total signal in the component mass spectrum) and f43 (defined similarly).

139 **11. The estimation of particle acidity**

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According to the methods reported by Peng et al (Peng et al., 2019) we estimated the pH in the particles. The acidity for nucleated H₂SO₄ particles (pH) under different SO₂ concentration have been estimated to be 3.27 and 3.46, respectively (Figure 5). The acidities for AS and AAS (pH) have been estimated to 7.3 and 4.1, respectively.

144 For the E-AIM model, pH was estimated as follows:

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$$pH = -log_{10}(f_{(H^+)} \times X_{(H^+)})$$

146 Where $f_{(H^+)}$ is the activity coefficient of H^+ , $X_{(H^+)}$ is the molar fraction of H^+ .

147 12. 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.



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159 Figure S17. Mass spectrum (A) and S/C ratio (B) of sulfate in the presence of AS and

160 AAS seed particles.

161 **13. Evolutions of major SOA molecules**

The evolutions of some molecule ions peaks have been shown in Figure S17. 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 S18. Time evolution of major oxidation products in presence of AS seed.

168 14. General mechanism of the ozonolysis of EM and the formation mechanism of

- 169 sulfuric acid
- 170





Scheme S1. General mechanism of the ozonolysis of EM

173 The reaction mechanism of sulfuric acid during alkene ozonolysis has been shown as174 following:

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$$R_1 R_2 COO + SO_2 \to R_1 R_2 CO + SO_3$$
 (1)

$$SO_3 + H_2O \to H_2SO_4 \tag{2}$$

10% RH has been proved to be sufficient in SA formation via the sCI+SO₂ reaction
based on some previous studies.(Zhang et al., 2019; Diaz-De-Mera et al., 2017;
Berndt et al., 2014)

181 **Reference**

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