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Supplement of

Increased primary and secondary $\text{H}_2\text{SO}_4$ showing the opposing roles in secondary organic aerosol formation from ethyl methacrylate ozonolysis

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1. Table S1. Experimental conditions.

<table>
<thead>
<tr>
<th>No.</th>
<th>[EM] (ppb)</th>
<th>[O₃] (ppb)</th>
<th>[SO₂] (ppb)</th>
<th>Seed acidity</th>
<th>mass con. (μg m⁻³)</th>
<th>CO (ppm)</th>
<th>RH (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>100</td>
<td>200</td>
<td>55</td>
<td>-</td>
<td>-</td>
<td>38</td>
<td>10%</td>
</tr>
<tr>
<td>#2</td>
<td>100</td>
<td>202±4</td>
<td>131±3</td>
<td>-</td>
<td>-</td>
<td>36±1</td>
<td>10%</td>
</tr>
<tr>
<td>#3</td>
<td>100</td>
<td>205±6</td>
<td>138±6</td>
<td>neutral</td>
<td>47±5</td>
<td>38±1</td>
<td>10%</td>
</tr>
<tr>
<td>#4</td>
<td>100</td>
<td>200</td>
<td>138</td>
<td>acidity</td>
<td>59.3</td>
<td>36</td>
<td>10%</td>
</tr>
<tr>
<td>#5</td>
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<td>205±6</td>
<td>135±6</td>
<td>neutral</td>
<td>42±5</td>
<td>38±1</td>
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</tr>
<tr>
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<td>100</td>
<td>200</td>
<td>132</td>
<td>acidity</td>
<td>52</td>
<td>36</td>
<td>45%</td>
</tr>
</tbody>
</table>

2. Correction of wall loss rate

![Figure S1](image_url)

**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 of AS (A) and AAS (B).

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 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 S5). Moreover, these background experiments in the absence of SO$_2$ 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 SO$_2$. This also further proved that the reducing effect of seed particle on secondary particle formation resulted from the formation of H$_2$SO$_4$ particles in the presence of SO$_2$. 

![Graph showing reaction gas consumption as a function of reaction time]
Figure S5. Time-dependent growth curves of SOA in the absence and presence of SO₂.

Figure S6. Evolution of secondary particles mass concentration with AS (black) and AAS (red) in the absence of SO₂.

Figure S7. Evolution of SOA mass concentration with AS (black) and AAS (red) in the absence of SO₂ (AMS data).

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 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.

**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% RH proved that increased RH was adverse to SOA and sulfate formation (Figure S9).
6. **Figure S9.** Total mass concentration at 10% RH (black) and 45% RH (red)

The mean PToF size of sulfate at 135 ppb SO$_2$ was also higher than that at 55 ppb SO$_2$ (Figure S10).

Moreover, the mean surface concentration and mean size of new particles at 135 SO$_2$ were also higher than that at 55 ppb SO$_2$ (Figure S11A). This indicated that high SO$_2$ level promoted the rapid homogeneous nucleation of H$_2$SO$_4$, which providing greater surface area and volume for the condensation of low-volatile products.

**Figure S10.** PToF size of sulfate at 55 ppb SO$_2$ and 135 ppb SO$_2$.

**Figure S11.** Number distribution of secondary particle at 55 ppb SO$_2$ and 135 ppb SO$_2$
(A) when the number concentration was maximum; Size distribution of seed particle: AS and AAS seed particle (B).

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

![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.]

8. The ozonolysis of surface EM with SO$_2$ and without SO$_2$

![Absorbance of EM ozonolysis in the absence and presence of SO$_2$.]

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 N$_2$. 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 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.

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 S14. 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 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

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

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 spectrum (f44) were observed to continually increased with the decrease of m/z 43 (the characterized fragment of carbonyl species) and the ratio of m/z 43 to total signal (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 oxidized species to more oxidized species could occur when the H₂SO₄ proportion (acidity) in the particle-phase reached a certain concentration.
**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).

11. The estimation of particle acidity

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.

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

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

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

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 same. 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 S17.** Mass spectrum (A) and S/C ratio (B) of sulfate in the presence of AS and AAS seed particles.

**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.

14. 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:

\[ R_1R_2COO + SO_2 \rightarrow R_1R_2CO + SO_3 \]  \hspace{1cm} (1)

\[ SO_3 + H_2O \rightarrow H_2SO_4 \]  \hspace{1cm} (2)

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


Ulbrich, I. M., Canagaratna, M. R., Zhang, Q., Worsnop, D. R., and Jimenez, J. L.:
