

## Response to Reviewers

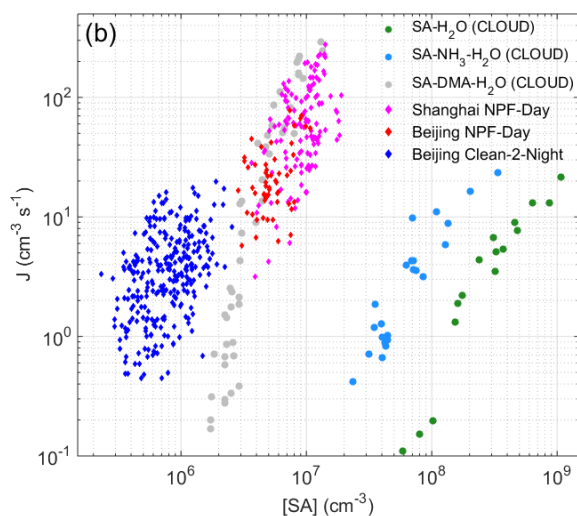
We thank the reviewer for the constructive comments and suggestions. As suggested, we have added some details to make our analysis easier to follow and we hope our point-to-point response to the comments given below can address these concerns. The comments, our replies, and the corresponding changes in the manuscript and supplementary information are marked in black, blue, and green, respectively.

1) It looks to me that most of revisions were not made on the text or SI, though the authors tried to include additional figures to address comments in their response. I would like these figures to be included in revised manuscript.

Response: The previous changes made in the manuscript and supplement are marked in orange. Please note that in the following replies, the acronym SA stands for sulfuric acid, which has also been defined in the manuscript.

As suggested, Fig. 6 (b) and the corresponding illustration have been additionally added in the revised manuscript:

“Fig. 6 (b) shows that the particle nucleation rates ( $J$ ) in the nighttime and the daytime roughly fall on the same line. Especially, the daytime values agree well with those from previous observations in Shanghai and CLOUD chamber SA-DMA (dimethylamine)-H<sub>2</sub>O experiment. The similar  $J - SA$  relationship between the nighttime and the daytime suggests a similar nucleation mechanism as SA-base clustering. Lei Yao et al. proposed that in urban megacities, high concentration of DMA together with SA were enough to explain the particle growth to  $\sim 3$  nanometers (Yao et al., 2018). Therefore, the formation of nighttime as well as daytime sub-3nm particles at our site was more likely a result of SA-DMA-H<sub>2</sub>O nucleation.” (Line 284-289, Page 11)



**Fig. 6 (b)** Comparison of Beijing ambient, Shanghai ambient and CLOUD experimental cluster formation rates against SA concentration. Green, light blue and grey dots denote CLOUD  $J_{1.7}$  data for SA-H<sub>2</sub>O, SA-NH<sub>3</sub>-H<sub>2</sub>O and SA-DMA-H<sub>2</sub>O nucleation respectively (Almeida et al., 2013; Kirkby et al., 2011). Magenta diamonds represent Shanghai NPF  $J_{1.7}$  data (Yao et al., 2018). Red and blue diamonds are Beijing  $J_{1.5}$  data for NPF day (10:00-14:00) and Clean-2 night (20:00-04:00), respectively.

Besides, Fig. S9 and Table S5 have also been added to the revised supplement with the following explanation being added in the revised manuscript:

“Besides, João Almeida et al. suggested that when SA concentration doesn't exceed  $3.0 \times 10^7 \text{ cm}^{-3}$ , the level of amines above 5 ppt are sufficient to reach the rate limit for amine ternary nucleation (Almeida et al., 2013). Although the median nighttime concentration of C2 amines (very likely DMA) was around 2.4 ppt (Fig. S9 and Table S5), there were also other base species (e.g., C3-amines,  $\text{NH}_3$ ) co-existing. Altogether, they are sufficient to stabilize SA clusters. (Line 289-293, Page 11)

Please also note that Fig. 6 now is Fig. 6 (a).

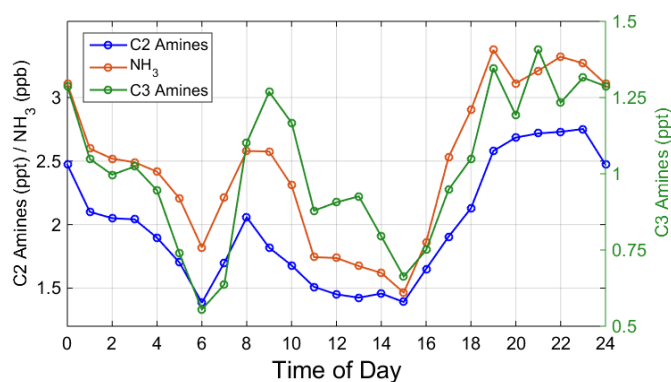


Fig. S9 Median diurnal variation of  $\text{NH}_3$ , C2 amines and C3 amines from 10<sup>th</sup> December, 2018 to 6<sup>th</sup> January, 2019.

Table S5 Median concentrations of  $\text{NH}_3$ , C2 amines and C3 amines from 10<sup>th</sup> December 2018 to 6<sup>th</sup> January 2019.

Species	Unit	Night	Polluted Night	Clean-2 Night (Vis $\geq$
		(20:00-04:00)	(Vis < 12 km)	16km, $[\text{O}_3] \geq 2 \times 10^{11} \text{ cm}^{-3}$ )
$\text{NH}_3$	Mixing ratio in ppb	2.8	3.3	1.9
	Concentration in $\text{cm}^{-3}$	$7.6 \times 10^{10}$	$8.9 \times 10^{10}$	$5.1 \times 10^{10}$
C2 Amines	Mixing ratio in ppt	2.4	2.6	1.6
	Concentration in $\text{cm}^{-3}$	$6.3 \times 10^7$	$7.0 \times 10^7$	$4.4 \times 10^7$
C3 Amines	Mixing ratio in ppt	1.2	1.4	0.74
	Concentration in $\text{cm}^{-3}$	$3.1 \times 10^7$	$3.9 \times 10^7$	$2.0 \times 10^7$

2) Also, in a new ESTlett paper that came out recently (<https://pubs-acscorg.elib.uah.edu/doi/10.1021/acs.estlett.0c00615>), the authors showed  $\text{SO}_3$  formation (hence, sulfuric acid and even sub-3 nm particles) during the night due to heterogeneous reactions of  $\text{SO}_2$  on soot particles. Then the steady state of sulfuric acid must include this production route as well.

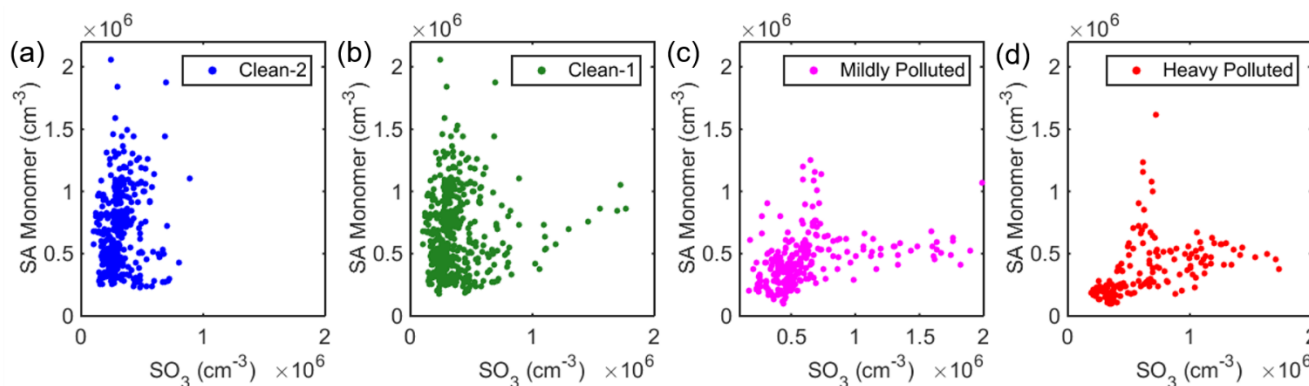
Response: Thanks a lot for your suggestion.

The ambient  $\text{SO}_3$  was indeed observed. We first look into the correlation between the measured concentrations of  $\text{SO}_3$  and SA. As shown in Fig. S10 (a), under Clean-2 condition when the oxidation from alkenes ozonolysis pathway dominates the formation of SA, there is almost no apparent correlation between SA and  $\text{SO}_3$ . With the increase of pollution level, the positive correlation shows up. Under polluted condition, high aerosol surface could favor the heterogeneous production of  $\text{SO}_3$ , which might, at least to some extent, explain the extra SA sources. For this reason, we mentioned in the manuscript that there could be additional sources of SA under polluted condition.

It should be pointed out that, by assuming the pseudo-steady state, we calculated the concentration of SA based on the measured SO<sub>3</sub> data:

$$k_6[\text{SO}_3][\text{H}_2\text{O}]^2 = [\text{SA}]CS + \beta[\text{SA}]^2$$

where  $k_6 = 3.9 \times 10^{-41} \exp(6830.6/T) \text{ cm}^{-6} \text{ s}^{-1}$  (Jayne et al., 1997). The calculated SA concentration was over 10 times higher than the measured one. As mentioned in the ESTLett paper, “SO<sub>3</sub> concentration could be overestimated because the influence of ambient ions (i.e., SO<sub>3</sub>·NO<sub>3</sub><sup>-</sup>) was not excluded and some of the hydrate complex intermediate (SO<sub>3</sub>·H<sub>2</sub>O) also could be detected as SO<sub>3</sub>·NO<sub>3</sub><sup>-</sup>”. This means that not all measured SO<sub>3</sub> molecules/clusters were the ones producing SA. Due to the remaining uncertainties in the measured SO<sub>3</sub> concentration and the unclear mechanism of the SO<sub>2</sub> heterogeneous pathway, we are not able to quantify the formation of SO<sub>3</sub> and SA from the heterogeneous reactions of SO<sub>2</sub> on soot particles. Therefore, we can’t include this SO<sub>2</sub> heterogeneous term in the production of SA.



**Fig. S10** Correlation between sulfuric acid monomer and SO<sub>3</sub> measured by CI-APi-TOF during nighttime (20:00 – 04:00 next day) from 18<sup>th</sup> January to 15<sup>th</sup> March 2019 for (a) Clean-2 condition with visibility larger than 16.0 km and O<sub>3</sub> concentration higher than  $2.0 \times 10^{11} \text{ cm}^{-3}$  (~ 7 ppb), (b) Clean-1 condition with visibility larger than 12.0 km, (c) mildly polluted condition with visibility in the range of 4.0 - 12.0 km, and (d) heavy polluted condition with visibility smaller than 4.0 km.

To clarify this consideration, we added Fig. S10 in the revised supplement and the following interpretation in the revised manuscript:

“Besides, a recent study shows that SO<sub>3</sub> generated from the reaction of SO<sub>2</sub> on the surface of soot particles potentially leads to the formation of SA during nighttime and early morning (Yao et al., 2020). However, the correlation between the nighttime SA and SO<sub>3</sub> was only found during polluted periods (Fig. S10), suggesting that it might have an important contribution during polluted cases. This may, at least to some extent, explain the extra SA sources under polluted condition. (Line 256-260, Page 10)

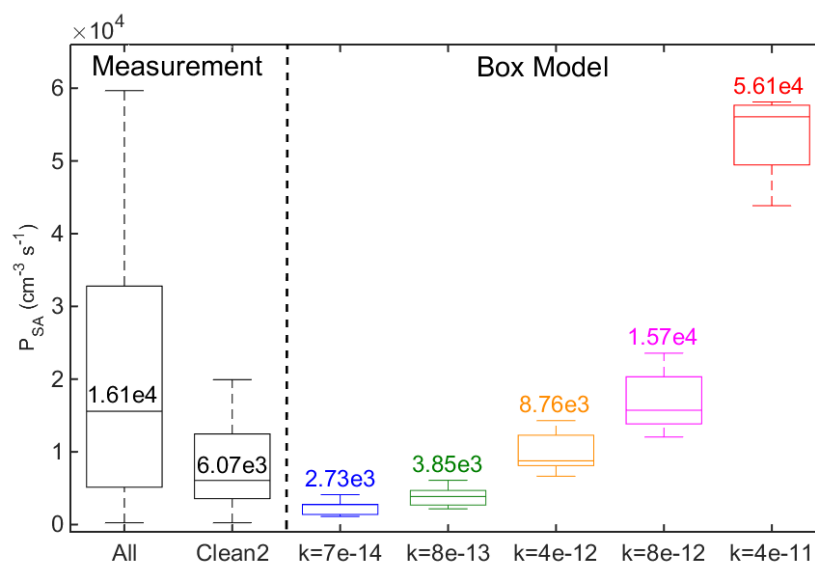
3) Nevertheless, a simple 0-D box model simulations will be most useful.

Response: Thanks for your suggestion.

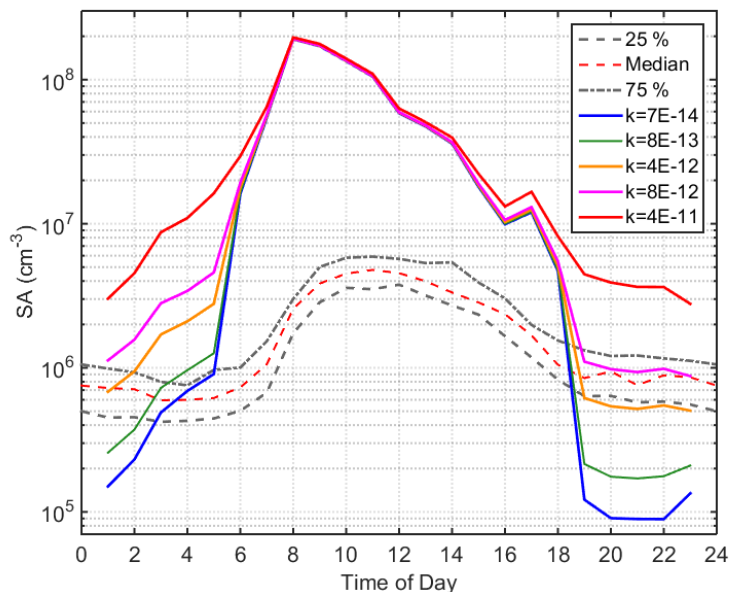
As suggested, the MCMv3.3.1 was used to simulate the production rate of SA ( $P_{SA}$ ) from the alkenes ozonolysis route. In total, 26 VOCs, including 6 alkenes, and 5 trace gases were added as input parameters (Table R1). It should be noted that the isomers of VOCs molecules cannot be distinguished due to the lack of structure information, and fractions of different isomers

were roughly set to be equal. Both the sCI and OH pathways were simulated and their production reactions are listed in Table R2 and Table R3.

Fig. R2 shows that the median values of  $P_{SA}$  for all nights (20:00-04:00) and Clean-2 nights during the measurement period (from 18<sup>th</sup> January to 16<sup>th</sup> March 2019) are  $1.61 \times 10^4 \text{ cm}^{-3} \text{ s}^{-1}$  and  $6.07 \times 10^3 \text{ cm}^{-3} \text{ s}^{-1}$  respectively. As mentioned in the manuscript, the rate constant between stabilized Criegee intermediate (sCI) and  $\text{SO}_2$  ( $k_{\text{sCI-SO}_2}$ ) spans over several orders of magnitude, from  $7.0 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$  (MCMv3.3.1) to  $4.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  (Ahrens et al., 2014). As expected, with the increase of  $k_{\text{sCI-SO}_2}$ , the modelled  $P_{SA}$  also increases dramatically, varying from  $2.73 \times 10^3 \text{ cm}^{-3} \text{ s}^{-1}$  to  $5.61 \times 10^4 \text{ cm}^{-3} \text{ s}^{-1}$ . Although a uniform  $k_{\text{sCI-SO}_2}$  can be adjusted to match the measured SA values, but it also reflects a large uncertainty of the model. Besides, there exist large deviations between the modelled and measured concentrations of SA, with daytime SA exceedingly higher than the measured one no matter what  $k_{\text{sCI-SO}_2}$  value is chosen (Fig. R3), which further reveals the uncertainty in modeling  $P_{SA}$  and SA concentration. Therefore, we still feel it is unnecessary to add the box model results in this study. However, we did mention in the manuscript that “A well-tuned box model is a useful tool to resolve it and verify the role of the ozonolysis of alkenes on the nighttime SA formation. However, such a modeling work is not included in our study, as the lacking of a complete VOC datasets and the large uncertainties in yields of sCI and oxidation rate constants of  $\text{SO}_2$  by sCI have posed challenges in ensuring the precision of the box-model.”. (Line 266-269, Page 10)



**Fig. R2** Production rate of SA ( $P_{SA}$ ) from measurement and box model simulation. The ‘All’ and ‘Clean2’ represent dataset belonging to all night and clean-2 night. The ‘ $k=7\text{e-}14$ ’, ‘ $k=8\text{e-}13$ ’, ‘ $k=4\text{e-}12$ ’, ‘ $k=8\text{e-}12$ ’, and ‘ $k=4\text{e-}11$ ’ are the reaction rate constants between sCI and  $\text{SO}_2$  with unit of  $\text{cm}^3 \text{ s}^{-1}$ . The rate constant of  $7.0 \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$  is chosen from MCMv3.3.1 as a lower limit. The rate constants of  $8.0 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$  and  $4.0 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  are taken from literature (Mauldin et al., 2012; Ahrens et al., 2014) and latter one is regarded as the upper limit. The middle two  $4.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  and  $8.0 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  are used for sensitivity analysis for the box model. The black and colored values are the corresponding median values of  $P_{SA}$ .



**Fig. R3** Diurnal variations of measured and modelled SA concentration. The grey dashed line, red dashed line and grey dot-dashed line represent the 25 %, median and 75 % values of measured SA concentrations. The blue, green, orange, magenta and red solid lines are simulated SA concentrations from box model with different values of  $k_{sCl-SO_2}$  with unit of  $cm^3 s^{-1}$ .

**Table R1** Input VOCs and trace gases for box model simulation

Group	Name of Species	Formula
Trace Gases	Sulfur Dioxide	SO <sub>2</sub>
	Ozone	O <sub>3</sub>
	Carbon Monoxide	CO
	Nitrogen Dioxide	NO <sub>2</sub>
	Nitric Oxide	NO
Alkenes	Propylene	C <sub>3</sub> H <sub>6</sub>
	Butadiene	C <sub>4</sub> H <sub>6</sub>
	Butene	C <sub>4</sub> H <sub>8</sub>
	Isoprene	C <sub>5</sub> H <sub>8</sub>
	Pentene	C <sub>5</sub> H <sub>10</sub>
	Hexene	C <sub>6</sub> H <sub>12</sub>
Other VOCs	Butane	C <sub>4</sub> H <sub>10</sub>
	Acetone	C <sub>3</sub> H <sub>6</sub> O
	Pentane	C <sub>5</sub> H <sub>12</sub>
	Methyl Ethyl Ketone	C <sub>4</sub> H <sub>8</sub> O
	Hexane	C <sub>6</sub> H <sub>14</sub>
	Methylcyclohexane	C <sub>7</sub> H <sub>14</sub>
	Heptane	C <sub>7</sub> H <sub>16</sub>
	Octane	C <sub>8</sub> H <sub>18</sub>
	Nonane	C <sub>9</sub> H <sub>20</sub>
	Decane	C <sub>10</sub> H <sub>22</sub>
	Undecane	C <sub>11</sub> H <sub>24</sub>
	Dodecane	C <sub>12</sub> H <sub>26</sub>

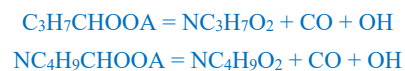
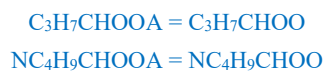
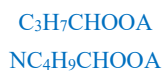
Benzene	C <sub>6</sub> H <sub>6</sub>
Toluene	C <sub>7</sub> H <sub>8</sub>
Styrene	C <sub>8</sub> H <sub>8</sub>
Xylene	C <sub>8</sub> H <sub>10</sub>
Ethylbenzene	C <sub>8</sub> H <sub>10</sub>
Trimethylbenzene	C <sub>9</sub> H <sub>12</sub>
Ethyltoluene	C <sub>9</sub> H <sub>12</sub>
Propylbenzene	C <sub>9</sub> H <sub>12</sub>

**Table R2** Production reactions of Criegee intermediate

Species	Formula	Reactions
Propylene	C <sub>3</sub> H <sub>6</sub>	O <sub>3</sub> + C <sub>3</sub> H <sub>6</sub> = CH <sub>2</sub> OOB + CH <sub>3</sub> CHO
		O <sub>3</sub> + C <sub>3</sub> H <sub>6</sub> = CH <sub>3</sub> CHOOA + HCHO
Butadiene	C <sub>4</sub> H <sub>6</sub>	O <sub>3</sub> + C <sub>4</sub> H <sub>6</sub> = ACR + CH <sub>2</sub> OOD
		O <sub>3</sub> + C <sub>4</sub> H <sub>6</sub> = HCHO + ACROOA
1-Butene	C <sub>4</sub> H <sub>8</sub>	BUT1ENE + O <sub>3</sub> = CH <sub>2</sub> OOB + C <sub>2</sub> H <sub>5</sub> CHO
Trans-2-Butene		BUT1ENE + O <sub>3</sub> = C <sub>2</sub> H <sub>5</sub> CHOOA + HCHO
Cis-2-Butene		TBUT2ENE + O <sub>3</sub> = CH <sub>3</sub> CHO + CH <sub>3</sub> CHOOB
		CBUT2ENE + O <sub>3</sub> = CH <sub>3</sub> CHO + CH <sub>3</sub> CHOOB
Isoprene	C <sub>5</sub> H <sub>8</sub>	O <sub>3</sub> + C <sub>5</sub> H <sub>8</sub> = CH <sub>2</sub> OOE + MVK
		O <sub>3</sub> + C <sub>5</sub> H <sub>8</sub> = CH <sub>2</sub> OOE + MACR
		O <sub>3</sub> + C <sub>5</sub> H <sub>8</sub> = HCHO + MVKOOA
		O <sub>3</sub> + C <sub>5</sub> H <sub>8</sub> = HCHO + MACROOA
1-Pentene	C <sub>5</sub> H <sub>10</sub>	PENT1ENE + O <sub>3</sub> = CH <sub>2</sub> OOB + C <sub>3</sub> H <sub>7</sub> CHO
Trans-2-Pentene		PENT1ENE + O <sub>3</sub> = C <sub>3</sub> H <sub>7</sub> CHOOA + HCHO
		TPENT2ENE + O <sub>3</sub> = C <sub>2</sub> H <sub>5</sub> CHOOB + CH <sub>3</sub> CHO
Cis-2-Pentene		TPENT2ENE + O <sub>3</sub> = CH <sub>3</sub> CHOOB + C <sub>2</sub> H <sub>5</sub> CHO
		CPENT2ENE + O <sub>3</sub> = CH <sub>3</sub> CHOOB + C <sub>2</sub> H <sub>5</sub> CHO
		CPENT2ENE + O <sub>3</sub> = C <sub>2</sub> H <sub>5</sub> CHOOB + CH <sub>3</sub> CHO
Hexene	C <sub>6</sub> H <sub>12</sub>	HEX1ENE + O <sub>3</sub> = C <sub>4</sub> H <sub>9</sub> CHO + CH <sub>2</sub> OOB
		HEX1ENE + O <sub>3</sub> = HCHO + NC <sub>4</sub> H <sub>9</sub> CHOOA

**Table R3** Production reactions of stabilized Criegee intermediate (sCI) and OH radical

Species	Production Reactions of sCI	Production Reactions OH radical
CH <sub>2</sub> OOB	CH <sub>2</sub> OOB = CH <sub>2</sub> OO	CH <sub>2</sub> OOB = HO <sub>2</sub> + CO + OH
CH <sub>2</sub> OOD	CH <sub>2</sub> OOD = CH <sub>2</sub> OO	CH <sub>2</sub> OOD = HO <sub>2</sub> + CO + OH
CH <sub>2</sub> OOE	CH <sub>2</sub> OOE = CH <sub>2</sub> OO	CH <sub>2</sub> OOE = HO <sub>2</sub> + CO + OH
ACROOA	ACROOA = ACROO	ACROOA = HO <sub>2</sub> + CO + HCHO + CO + OH
MVKOOA	MVKOOA = MVKOO	MVKOOA = OH + MVKO <sub>2</sub>
MACROOA	MACROOA = MACROO	MACROOA = OH + CO + CH <sub>3</sub> CO <sub>3</sub> + HCHO
CH <sub>3</sub> CHOOA	CH <sub>3</sub> CHOOA = CH <sub>3</sub> CHOO	CH <sub>3</sub> CHOOA = CH <sub>3</sub> O <sub>2</sub> + CO + OH
CH <sub>3</sub> CHOOB	CH <sub>3</sub> CHOOB = CH <sub>3</sub> CHOO	CH <sub>3</sub> CHOOB = CH <sub>3</sub> O <sub>2</sub> + CO + OH
C <sub>2</sub> H <sub>5</sub> CHOOA	C <sub>2</sub> H <sub>5</sub> CHOOA = C <sub>2</sub> H <sub>5</sub> CHOO	C <sub>2</sub> H <sub>5</sub> CHOOA = C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> + CO + OH
C <sub>2</sub> H <sub>5</sub> CHOOB	C <sub>2</sub> H <sub>5</sub> CHOOB = C <sub>2</sub> H <sub>5</sub> CHOO	C <sub>2</sub> H <sub>5</sub> CHOOB = C <sub>2</sub> H <sub>5</sub> O <sub>2</sub> + CO + OH

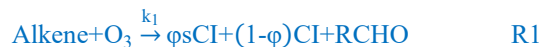


4) It is still not clear to me how the authors retrieved the equation in Line 218 (main text) – I would like the authors to show the derivation of this equation.

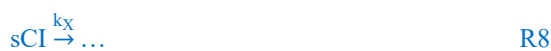
$$k_{\text{app}}[\text{Alkene}][\text{O}_3][\text{SO}_2] = [\text{SA}]\text{CS} + \beta[\text{SA}]^2 \quad (\text{Line 218 in the main text})$$

Response: Since the detailed sources of SA in the real atmosphere is really complex, e.g., the varied role of each alkene in producing OH radical, sCI, and SA, we did not intend to precisely calculate the  $P_{\text{SA}}$  from each of these individual sources. But instead, we use an approximation as indicated by the equation. As mentioned in the manuscript, the two terms on the right side denote the sink of SA, i.e., the condensation of SA onto particles and the collision of SA monomers with each other to form SA dimers. The term on the left side is an empirical one that accounts for the formation from the ozonolysis-of-alkenes-initiated oxidation of  $\text{SO}_2$ . Here, both the OH radical produced from the decomposition of Criegee intermediate (CI) (R3) and stabilized Criegee intermediate (sCI) (R2) are potentially important for oxidizing  $\text{SO}_2$ . As such oxidation is very complicated and reaction dynamics are largely unknown, precise calculation of different reactions is impossible. Therefore, we apply an empirical parameter, i.e., apparent reaction constant ( $k_{\text{app}}$ ) to show the general rate of all reactions. The derivation of  $k_{\text{app}}$  is shown below.

The non-photochemical oxidation pathway for  $\text{SO}_2$  to form SA mainly includes the following reactions (which have been listed in the manuscript, Line 75, 77, 80-83, Page 3):



where  $k_i$  is the rate constant of each reaction,  $\phi$  is the yield of sCI in the ozonolysis of alkenes, and CI is the chemically activated Criegee intermediate. Besides, there are four additional reactions concerning the loss of sCI, CI and OH:



where  $k_{\text{XX}}$  is the bimolecular reaction constant for sCI with other species except from  $\text{SO}_2$ ,  $k_{\text{X}}$  is the decomposition rate of sCI,  $k_{\text{Y}}$  is the deposition rate of CI which do not generate OH, and  $k_{\text{ZZ}}$  is the bimolecular constant reaction for OH with other species excluding  $\text{SO}_2$ .

Then the net production rate of SA can be expressed as:

$$P_{SA}=k_6[SO_3][H_2O]^2 \quad (1)$$

sCI, CI, OH, SO<sub>3</sub> and HSO<sub>3</sub> are short-lived intermediates, so that a PSS assumption can be applied. PSS equations for sCI, CI, OH, SO<sub>3</sub> and HSO<sub>3</sub> are as follows:

$$sCI: \quad k_1[Alkene][O_3]\phi=k_2[sCI][SO_2]+k_{XX}[sCI][X]+k_X[sCI] \quad (2)$$

$$CI: \quad k_1[Alkene][O_3](1-\phi)=k_3[CI]+k_Y[CI] \quad (3)$$

$$OH: \quad k_3[CI]=k_4[SO_2][OH]+k_{ZZ}[Z][OH] \quad (4)$$

$$SO_3: \quad k_2[sCI][SO_2]+k_5[HSO_3][O_2]=k_6[SO_3][H_2O]^2 \quad (5)$$

$$HSO_3: \quad k_4[SO_2][OH]=k_5[HSO_3][O_2] \quad (6)$$

then, the concentrations of sCI, CI and OH are calculated as:

$$[sCI]=\frac{k_1[Alkene][O_3]\phi}{k_2[SO_2]+k_{XX}[X]+k_X} \quad (7)$$

$$[CI]=\frac{k_1[Alkene][O_3](1-\phi)}{k_3+k_Y} \quad (8)$$

$$[OH]=\frac{k_3[CI]}{k_4[SO_2]+k_{ZZ}[Z]} \quad (9)$$

bring (5), (6), (7), (8) and (9) to (1) gives:

$$\begin{cases} P_{SA} = k_{app}[Alkene][O_3][SO_2] \\ k_{app} = k_1 k_2 \phi \tau_{sCI} + k_1 k_4 (1-\phi) \tau_{OH} \frac{k_3}{k_3+k_Y} \\ \tau_{sCI} = \frac{1}{k_2[SO_2]+k_{XX}[X]+k_X} \\ \tau_{OH} = \frac{1}{k_4[SO_2]+k_{ZZ}[Z]} \end{cases} \quad (10)$$

The first term and second term for  $k_{app}$  in equation (10) represent the sCI and non-photochemical OH oxidation pathways respectively.  $k_1$ ,  $k_2$  and  $k_4$  are chosen to be  $1.29 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$ ,  $8.0 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ , and  $1.38 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  separately according to previous studies (Sipila et al., 2014; Mauldin et al., 2012; Wine et al., 1984).  $\frac{k_3}{k_3+k_Y}$  is the fraction of CI decomposition leading the formation of OH radical, which is around 0.4 according to MCMv3.3.1.  $\tau_{sCI}$  and  $\tau_{OH}$  are the lifetimes of sCI and OH radical respectively.

It can be seen that  $k_{app}$  is highly environment-dependent, as  $k_{app}$  is not only influenced by the yields of OH radical and sCI, but also determined by the rate constants of various reactions as well as the concentration of enormous atmospheric species. As discussed in the response to Comment #3, these parameters for each individual alkene are with large uncertainty, and hence, this “bulk oxidant” method is an appropriate option. It should be noted that, the 25%, median, and 75% values of  $\tau_{sCI}$  during nighttime under clean condition were 0.012 s, 0.017 s, and 0.021 s, respectively. Similarly, the 25%, median, and 75% values of  $\tau_{OH}$  were  $1.27 \times 10^{-3}$  s,  $1.73 \times 10^{-3}$  s and  $2.42 \times 10^{-3}$  s, respectively. The variation of  $\tau_{sCI}$  and  $\tau_{OH}$  (roughly  $\pm 50\%$ ) could be even smaller than the variation of the rate constants for different alkenes. So, the value of  $k_{app}$  may depend more on the mixing ratios of different alkenes.

Besides, the rate constants concerning the lifetime calculation for reactions of sCI with SO<sub>2</sub>, H<sub>2</sub>O, CO, NO<sub>2</sub>, and NO as well as OH radical with VOCs, O<sub>3</sub>, SO<sub>2</sub>, CO, NO<sub>2</sub> and NO are listed below in Table S4.



**Table R4** Rate constants for reactions of sCl and OH radical used for lifetime calculation

Compound	Reaction Constant (cm <sup>-3</sup> s <sup>-1</sup> )*	Reference
Propylene	k <sub>OH</sub>	3.19E-11
Butadiene	k <sub>OH</sub>	7.45E-11
1-Butene	k <sub>OH</sub>	3.53E-11
Trans-2-Butene	k <sub>OH</sub>	7.35E-11
Cis-2-Butene	k <sub>OH</sub>	6.37E-11
Isoprene	k <sub>OH</sub>	1.11E-10
1-Pentene	k <sub>OH</sub>	3.56E-11
Trans-2-Pentene	k <sub>OH</sub>	6.69E-11
Cis-2-Pentene	k <sub>OH</sub>	6.54E-11
1-Hexene	k <sub>OH</sub>	3.70E-11
Butane	k <sub>OH</sub>	2.19E-12
Acetone	k <sub>OH</sub>	1.80E-13
Pentane	k <sub>OH</sub>	3.63E-12
Methyl Ethyl Ketone (MEK)	k <sub>OH</sub>	1.11E-12
Hexane	k <sub>OH</sub>	1.77E-12
Octane	k <sub>OH</sub>	8.30E-12
Nonane	k <sub>OH</sub>	9.68E-12
Decane	k <sub>OH</sub>	1.08E-11
Undecane	k <sub>OH</sub>	1.29E-11
Dodecane	k <sub>OH</sub>	1.39E-11
Benzene	k <sub>OH</sub>	1.16E-12
Toluene	k <sub>OH</sub>	6.13E-12
Styrene	k <sub>OH</sub>	5.80E-11
m-Xylene	k <sub>OH</sub>	2.31E-11
p-Xylene	k <sub>OH</sub>	1.43E-11
o-Xylene	k <sub>OH</sub>	1.36E-11
Ethylbenzene	k <sub>OH</sub>	7.00E-12
1,3,5-Trimethylbenzene	k <sub>OH</sub>	5.67E-11
1,2,4-Trimethylbenzene	k <sub>OH</sub>	3.25E-11
1,2,3-Trimethylbenzene	k <sub>OH</sub>	3.27E-11
m-Ethyltoluene	k <sub>OH</sub>	1.86E-11
p-Ethyltoluene	k <sub>OH</sub>	1.18E-11
o-Ethyltoluene	k <sub>OH</sub>	1.19E-11
Propylbenzene	k <sub>OH</sub>	6.30E-12
Heptane	k <sub>OH</sub>	6.86E-12
Chloroform	k <sub>OH</sub>	8.71E-14
O <sub>3</sub>	k <sub>OH</sub>	5.75E-14
SO <sub>2</sub>	k <sub>OH</sub>	1.37E-12
CO	k <sub>OH</sub>	5.64E-11

MCMv3.3.1

NO <sub>2</sub>	koH	3.65E-11	
NO	koH	1.81E-10	
SO <sub>2</sub>	k <sub>sCl</sub>	8.00E-13	(Mauldin et al., 2012)
H <sub>2</sub> O	k <sub>sCl</sub>	1.20E-15	(Newland et al., 2015)
CO	k <sub>sCl</sub>	1.20E-15	MCMv3.3.1
NO <sub>2</sub>	k <sub>sCl</sub>	1.00E-15	MCMv3.3.1
NO	k <sub>sCl</sub>	1.00E-14	MCMv3.3.1
sCl	k <sub>sCl-dec</sub>	12.0 s	(Newland et al., 2015)

\* The unit for rate constant is  $\text{cm}^3 \text{s}^{-1}$  if not specified.

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