

Interactive comment on “Influence of NO₂ on secondary organic aerosol formation from ozonolysis of limonene” by Changjin Hu et al.

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Received and published: 22 September 2017

Answer to comment of Referee#1 on “Influence of NO₂ on secondary organic aerosol formation from ozonolysis of limonene” by Changjin Hu et al.

Reviewer Comment - OVERVIEW:

This manuscript describes a laboratory and modeling study of SOA formation from the ozonolysis of limonene in the presence of NO₂. The manuscript is topically relevant to ACP. The authors need to make clearer the unique contribution of this research, and how this manuscript advances the field. Specifically, I have two main criticisms: (1) Are the SOA yield differences meaningful for cases when similar delta SOA is observed with and without NO₂? (2) Are the resulting changes in SOA yield and composition a

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consequence of different O₃ chemistry or do they just reflect NO₃ chemistry at high NO₂? The impact of the research is clearly reduced if the authors are merely reproducing NO₃ oxidation experiments under high NO₂ conditions.

REPLY: We appreciate the referee for the constructive comments that will contribute to improve our original manuscript. Regarding to the importance of understanding the effects of anthropogenic emissions on aerosol formation from biogenic emissions and to what extent can biogenic SOA be controlled (Ng et al., 2017), as well as the situations of high emission of limonene (Guenther et al., 1995, 2000; Griffin et al., 1999) and the increasing tropospheric NO₂ (He et al., 2007), this work has uncovered the underground reaction mechanism of limonene ozonolysis at the presence of NO₂ when anthropogenic and biogenic emissions are entangled together, which is more complicated than that the observed aerosol mass or yield shows. (1) Firstly, NO₂ effect, not only NO as mainly investigated before (Presto et al., 2005; Kroll and Seinfeld, 2008), on SOA yields has been proved experimentally to be very important, which is more pivotal to real atmosphere (Ng, et al., 2017). (2) Secondly, even the observed aerosol mass or yield are similar, the underground formation mechanism may be different, for example, different [O₃]₀/[VOC]₀ ratio or different NO₂ concentration, which is most important to control strategy. (3) Thirdly, NO₂ effect on SOA formation from ozonolysis of limonene is not only related to the competition between O₃- and NO₃-initiated oxidation of limonene, but also the competition between RO₂+HO₂ and RO₂+NO₂ (or NO₃) following the O₃ initiated oxidation. Under the different [O₃]₀/[VOC]₀ ratio, the presence of NO₂ may have different effect on the SOA formation. So it is believed that this work is helpful to understand to what extent can biogenic SOA be controlled when anthropogenic emissions coexists. Please find below the point-by-point responses (in blue) to each comment (in black italics). And we have made corresponding modifications/revisions based on these in the revised manuscript and supplement (the changes are marked in red).

(1) Are the SOA yield differences meaningful for cases when similar delta SOA is ob-

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served with and without NO₂?

REPLY: By comparing Exp. N1-N7 (without NO₂) with Exp. N8-N16 (with NO₂), although they have similar [O₃]₀ and [VOC]₀, they have different SOA formation yield. And the most important is that even for the cases when they have similar Δ SOA, for example, N3 (Δ M₀=211 μ g/m³) and N12 (Δ M₀=218 μ g/m³) (See Table 1 in the manuscript), they have different reaction mechanism. For N3, all of SOA formed from ozonolysis of limonene, while for N12, there was about 40% limonene reacted with NO₃ (See Fig. R1). Even the exact ratio of SOA formation from NO₃ chemistry was hard to decide, it is believed that there should be organic nitrates in aerosol particles in N12 while there is not any organic nitrates in aerosol particles formed in N3. So, similar Δ SOA may have different formation yield; even similar Δ SOA have similar formation yield, they have different formation mechanism. For field, different formation mechanism means different sources and different control strategy, which is the most important for pollution or climate.

(Figure 1 here is corresponding to Figure R1)

(2) Are the resulting changes in SOA yield and composition a consequence of different O₃ chemistry or do they just reflect NO₃ chemistry at high NO₂?

REPLY: It is believed that the changes in SOA yield and composition is the combined action of O₃ chemistry and NO₂ chemistry (NO₃ chemistry and direct reaction of NO₂ with the intermediates of limonene+O₃). As shown in Fig. R1, for Exp. N8-N11, the SOA yields increased in turn from N8 to N11 with the percentages of total limonene reacted by NO₃ increasing, while they are still lower than the corresponding SOA yields without NO₂ (Exp. N1-N4, see Table 1). However, it is interesting to find that although the percentages of total limonene reacted by NO₃ for Exp. N11-N16 were almost the same (~42%), the SOA yields still increased from N11 to N16, and in high [O₃]₀ conditions, the SOA yields with NO₂ even are higher than that of without NO₂ (for example, N16 to N7, see Table 1)). If the [VOC]₀ and [O₃]₀, as well as their ratio

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([O₃]₀/[VOC]₀ ~2.4), are fixed (Exp. N17-N21), it can be seen from Fig. R2 that the fraction of limonene reacted with NO₃ increases monotonically and that reacted with O₃ decreases monotonically with the increasing of NO₂. Under this kind of conditions, the SOA yield first increases rapidly, and then levels off or decreases at last according to the increasing of NO₂ (See experimental work shown in Fig.3, and modeling work in Fig. S5c). Based on mechanism analysis, it is believed that in very high NO₂ level, the increase of PANs and nitrates cannot compensate the decrease of ROOHs and acids in aerosol phase with the increase of NO₂, which indicates again the competition between NO₃- and O₃- initiated oxidation. So, it is seemed that neither O₃ chemistry nor NO₃ chemistry can result in the changes in SOA yield and composition alone.

(Figure 2 here is corresponding to Figure R2)

CHANGES IN THE REVISED MANUSCRIPT:

Based on Figure R1 and Figure R2 here, Figure 8 concerning to the fraction of the limonene reacts with O₃ versus NO₃ and the corresponding SOA yields has been added in the revised manuscript, and the original fraction of limonene reacted with different oxidants for Exp. N8-N21 has been shown in Figure S7 and Figure S8 in the revised supplement (See the revised supplement). And we have re-written the corresponding paragraph from line 546 to line 568 in 3.4. part in the revised manuscript as the following: "For example, given the fixed [VOC]₀, [O₃]₀ and their ratio ([O₃]₀/[VOC]₀ ~2.4) for Exp. N17-N21, it can be found that the fraction of limonene reacted with NO₃ increases monotonically with the increasing of NO₂, and the observed SOA yield also increases accordingly under the same conditions (Figure 8a and Figure S7). It is believed that in this case, NO₃- initiated oxidation of limonene can produce some condensable organic nitrates, such as NLIMOOH and LIMBNO₃(Figure 7), which compensate the decrease of ROOHs and acids in aerosol phase leading to the increase of SOA formation. In fact, large amounts of organic nitrates have also been observed experimentally as the major reaction product of limonene oxidation by NO₃ (Spittler et al., 2006; Fry et al., 2011), which substantiates the observation in this work. However,

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NO₂ effect on SOA formation is embodied not only in the initial competition between NO₃ and O₃ oxidation. As shown in Figure 8b and Figure S8, although the SOA yields increased with the increasing of the percentages of total limonene consumed by NO₃ for Exp. N8-N11, it is interesting to find that the SOA yields still increased from Exp. N11 to N16 even the percentages of total limonene reacted by NO₃ were almost the same (~42%). It is worthy to point out that despite increasing in turn from N8 to N11, the SOA yields in N8-N11 are lower than the corresponding SOA yields without NO₂ under the similar [O₃]₀ and [VOC]₀ conditions (Exp. N1-N4, see Table 1). On the contrary, in high [O₃]₀ conditions, the SOA yields with NO₂ (Exp. N14-N16) are even higher than that without NO₂ (Exp. N5 - N7, see Table 1). So it is presumed that NO₂ (or NO₃) also participates in participation in the production of PANs and nitrates following ozonolysis of limonene. "

(Figure 3 here is corresponding to Figure 8 in the revised manuscript)

(Figure 4 here is corresponding to Figure S7 in the revised supplement)

(Figure 5 here is corresponding to Figure S8 in the revised supplement)

References:

Griffin, R. J., Cocker III, D. R., Flagan, R. C., Seinfeld, J. H., and Dabdub, D.: Estimate of global atmospheric organic aerosol formation from the oxidation of biogenic hydrocarbons, *Geophys. Res. Lett.* 26, 2721–2724, 1999. Guenther, A., Hewitt, C. N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., McKay, W. A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J., and Zimmerman, P.: A global model of natural volatile organic compound emissions, *J. Geophys. Res.-Atmos.*, 100, 8873–8892, doi:10.1029/94JD02950, 1995. Guenther, A., Geron, C., Pierce, T., Lamb, B., Harley, P., and Fall, R.: Natural emissions of non-methane volatile organic compounds, carbon monoxide, and oxides of nitrogen from North America. *Atmos. Environ.*, 34, 2205–2230, 2000. He, Y., Uno, I., Wang, Z., Ohara, T., Sugimoto, N., Shimizu, A., Richter, A., and Burrows J. P.: Variations of the

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increasing trend of tropospheric NO₂ over central east China during the past decade. *Atmos. Environ.*, 41, 4865–4876, 2007. Kroll, J. H. and Seinfeld, J. H.: Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere, *Atmos. Environ.*, 42, 3593–3624, 2008. Ng, N. L., Brown, S.S., Archibald, A.T., Atlas, E., Cohen, R.C., Crowley, J. N., Day, D. A., Donahue, N. M., Fry, J. L., Fuchs, H., Griffin, R. J., Guzman, M. I., Herrmann, H., Hodzic, A., Iinuma, Y., Jimenez, J. L., Kiendler-Scharr, A., Lee, B. H., Luecken, D. J., Mao, J., McLaren, R., Mutzel, A., Osthoff, H. D., Ouyang, B., Picquet-Varrault, B., Platt, U., Pye, H. O. T., Rudich, Y., Schwantes, R. H., Shiraiwa, M., Stutz, J., Thornton, J. A., Tilgner, A., Williams, B. J., and Zaveri, R. A.: Nitrate radicals and biogenic volatile organic compounds: oxidation, mechanisms, and organic aerosol, *Atmos. Chem. Phys.*, 17, 2103–2162, 2017. Presto, A. A., Hartz, K. E. H., and Donahue, N. M.: Secondary organic aerosol production from terpene ozonolysis. 2. Effect of NO_x concentration, *Environ. Sci. Technol.*, 39, 7046–7054, 2005.

Specific comments:

1. Experimental methods - were these experiments conducted in the dark? REPLY: Sure, these experiments were conducted in the dark. Please see "...21 darkened chamber experiments were carried out at room temperature..." in Line 233 in the revised manuscript.

2. Figure 2 - I suggest that the authors place error bars on the yield data. Is the difference between NO₂ and non-NO₂ experiments truly meaningful?

REPLY: Thank you very much for your suggestion. As aforementioned in the reply to the main criticisms, it is believed that the difference between NO₂ and non-NO₂ experiments is truly meaningful. In compare with that of Exp. N1-N7 (without NO₂), the SOA yields for Exp. N8-N16 (with NO₂) show complicated variation under the similar [VOC]₀ and [O₃]₀. Under [O₃]₀/[VOC]₀ < 2 conditions (N8-N12), the introduction of NO₂ results in a weak negative effect on the SOA yields compared to that without NO₂.

C6

While at $[O_3]/[VOC] > 2$ conditions (N13-N16), SOA yields increase substantially, far exceeding those without NO₂ at a similar mixing ratio of $[O_3]$ and [limonene]. And it is believed that NO₃ chemistry plays an important role with the introducing of NO₂. So, the observed difference of SOA yield between NO₂ and non-NO₂ experiments indicates the different source and underground competition between O₃ chemistry and NO₃ chemistry, and the different chemical composition of aerosol particles.

CHANGES IN THE REVISED MANUSCRIPT: We have added the error bars in Fig.2 and the corresponding change in figure caption in the revised manuscript as " Each data point represents an individual experiment, and has an estimated uncertainty of $\pm 15\%$."

(Figure 6 here is corresponding to Figure 2 in the revised manuscript)

3. Figure 2, Lines 295-310. The figure shows that the experiments with the highest SOA yield had NO₂. But I am unconvinced by the argument NO₂ is causing the higher yields, because it is extremely difficult to compare "paired" sets of experiments (e.g., X ppb limonene and no NO₂ versus X ppb limonene and Y ppb NO₂).

REPLY: Thank you very much for your observation. Maybe it's better to give an example here. It seems that NO₂ effect on SOA formation is related to the $[O_3]/[VOC]$ ratio. For clarity, two "paired" sets of experiments are presented here. Both of Exp. N2 and N10 have similar $[O_3]$, $[VOC]$ and the $[O_3]/[VOC]$ ratios are nearly to 1 (see Table 1), where the introduction of NO₂ in Exp.N10 resulted in the decrease of SOA yield compared to Exp. N2. However, for Exp. N7 and N16, both of them have similar $[O_3]$, $[VOC]$ and the $[O_3]/[VOC]$ ratios of them are > 5 (see Table 1), where the introduction of NO₂ in Exp.N16 resulted in the increase of SOA formation. Similarly, N5 vs. N14, and N6 vs. N15 can also affirm that the introducing of NO₂ has led to the increasing of SOA yields under the $[O_3]/[VOC] > 2$ conditions.

CHANGES IN THE REVISED MANUSCRIPT: We have added the two pair of experiments as example in the corresponding paragraph. "For example, Exp. N2 and N10

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have similar $[O_3]$, $[VOC]$ and $[O_3]/[VOC]$ ratios (~ 1) (see Table 1), while the introducing of NO₂ in N10 resulted in the decrease of SOA yield compared to N2." in line 307-309 and "For example, N16 has similar $[O_3]$, $[VOC]$ and $[O_3]/[VOC]$ ratios (> 5) to N7 (see Table 1), where the introduction of NO₂ in N16 resulted in the increase of SOA formation compared to N7" in line 313-316 of the revised manuscript.

4. Line 367 - what drove the temperature difference between the sets of experiments?

REPLY: Thank you very much for your observation. The case is that the two sets of experiments has been performed in different seasons. N17-N21 were carried in summer season, whereas N1-N16 were carried in winter season. Although with air conditioner in the lab, there was still temperature difference between the two sets of experiments.

5. Figure 4 would benefit from having a 1:1 line

REPLY: Thank you very much for your suggestion. We agree with you that the linear fit line is not the best way to illustrate the relativity between the predicted SOA yield and the observed SOA yield, so the 1:1 line has been added in new Fig. 4.

CHANGES IN THE REVISED MANUSCRIPT: We have added 1:1 line in new Fig.4, and revised the corresponding figure caption. We have re-written the paragraph: "It is shown that almost all the data points lie above the 1:1 line and the slope of the linear fit line of the points is 1.4, which indicates that the predicted results are higher than the observed ones."

(Figure 7 here is corresponding to Figure 4 in the revised manuscript)

6. The authors should comment on what fraction of the limonene reacts with O₃ versus NO₃ - at least for the endo bond - in the various experiments. It seems like this should be retrievable from the MCM runs.

REPLY: Thank you very much for your valuable suggestion. We agree with you that if the fraction of the limonene reacts with O₃ versus NO₃ is added, the role of the competition between O₃ with NO₃ initiated limonene oxidation on SOA formation will

C8

be more explicit. So we have investigated the fractions of the limonene reacts with O₃ versus NO₃ for the experiments (N8-N21) as shown in Figure S7 and Figure S8 in the revised supplement.

CHANGES IN THE REVISED MANUSCRIPT: We have re-written the corresponding paragraph from line 539 to line 561 in 3.4. part in the revised manuscript, and added the fraction of the limonene reacts with O₃ versus NO₃ in Figure 8 in the revised manuscript, as well as Figure S7 and Figure S8 in the revised supplement.

7. Is scheme 1 new - generated as a result of this work - or reproduced from the MCM? If it is from the MCM, the authors need to clearly state that the Scheme is not their original work. The same applies to Table 2.

REPLY: Thank you very much for your suggestion. Scheme 1, as well as the contents in Table 2, was reproduced from the MCM.

CHANGES IN THE REVISED MANUSCRIPT: We have labeled " Reproduced from the MCM " in the corresponding place.

Please also note the supplement to this comment:

<https://www.atmos-chem-phys-discuss.net/acp-2017-433/acp-2017-433-AC1-supplement.pdf>

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2017-433>, 2017.

C9

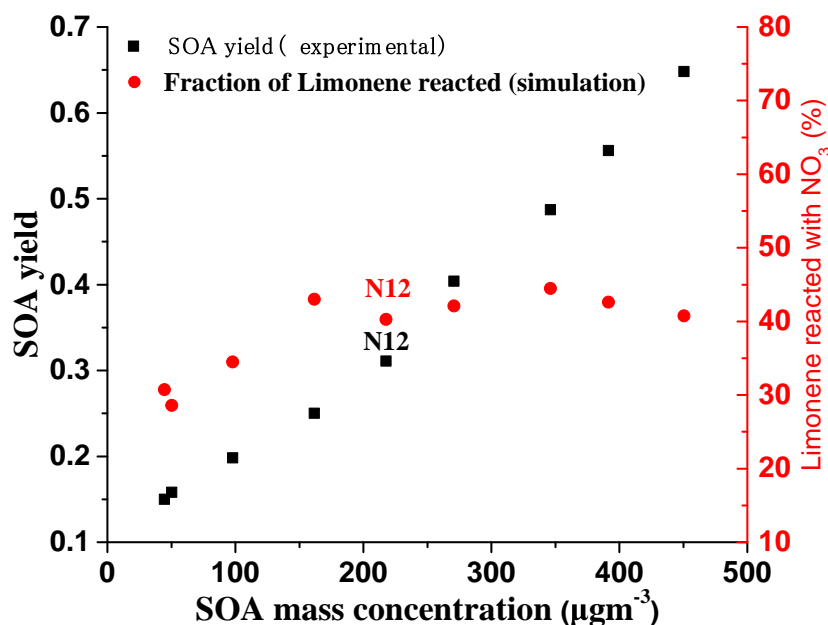


Fig. 1. Figure R1. The fraction of the limonene reacted with NO_3 (model study) and the corresponding SOA yields (experimental work) for Exp. N8-N16.

C10

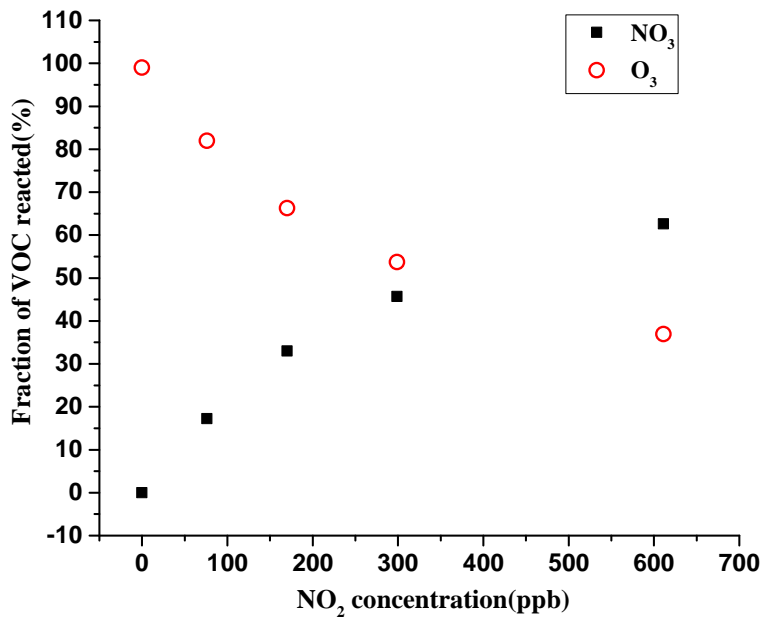


Fig. 2. Figure R2. The fraction of limonene reacted with the different oxidants according to the changing of NO₂ (simulation for Exp. N19-N21).

C11

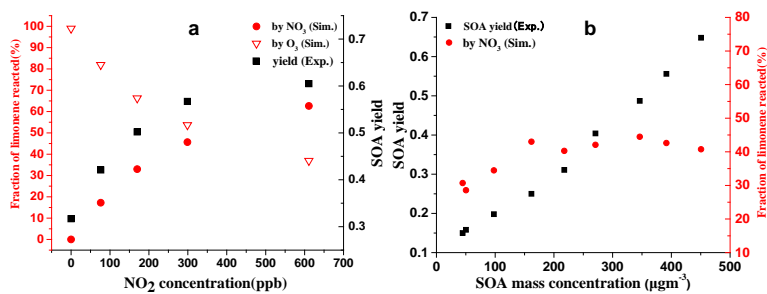


Fig. 3. Figure 8. The fraction of the limonene reacted with oxidant (O₃ or NO₃, model study) and the corresponding SOA yields (experimental work) for Exp. N8-N16(a) and Exp. N17-N21(b).

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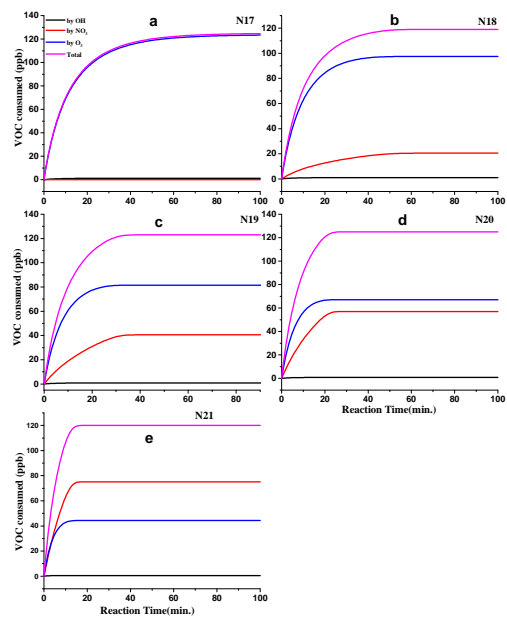


Fig. 4. Figure S7. The evolution of the limonene consumed by different oxidants for Exp. N17-N21 (Simulation based on MCM model). In order to show the consuming rate of limonene, only the initial stage of rea

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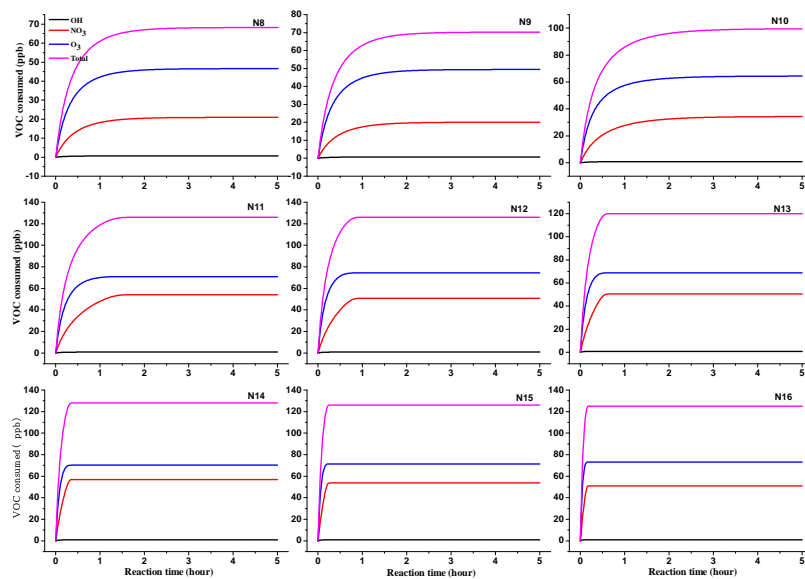


Fig. 5. Figure S8. The evolution of the limonene consumed by different oxidants for Exp. N8-N16 (Simulation based on MCM model).

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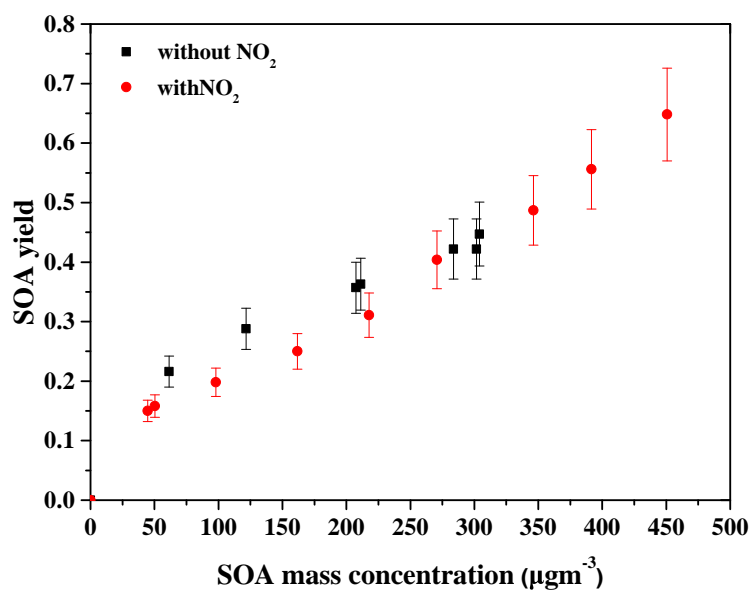


Fig. 6. Figure 2. Aerosol yield for the limonene/O₃/NO₂ system for the initial terpene mixing ratios of ~ 125 ppb with NO₂ (~250 ppbv) or without NO₂. Each data point represents an individual experiment, and

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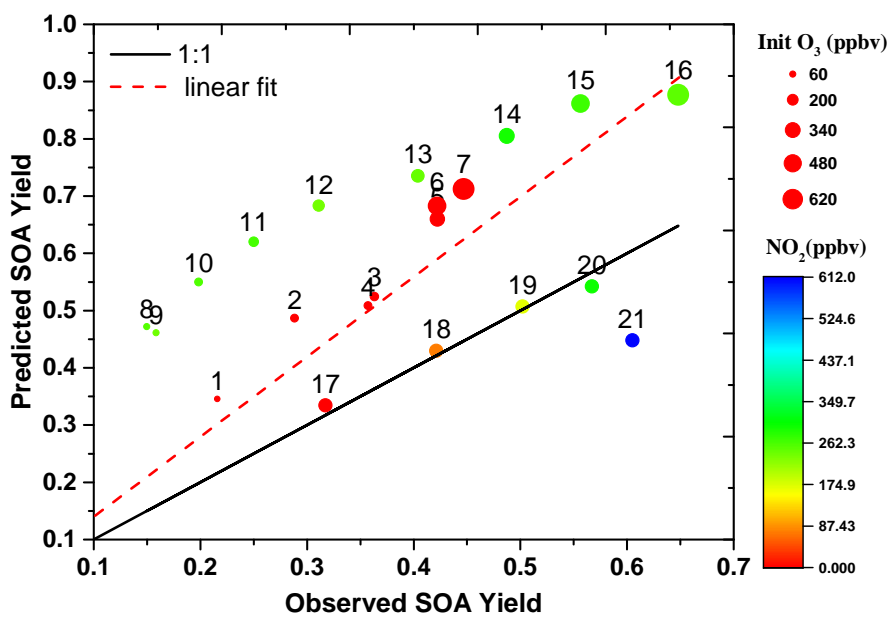


Fig. 7. Figure 4. Comparison of the observed SOA yield and the predicted SOA yield for all the smog chamber experiments. The sizes of the data points represent the corresponding initial O₃ levels of the simul

C16