Review of "New insights into the nonlinear effects of NOx on SOA formation from isoprene photo-oxidation" by Xinbei Xu et al.

General comments

The authors report on their research results on the mechanism of secondary aerosol formation from the photochemical oxidation of isoprene as a function of initial NOx concentration. The results of the chemical ionization mass spectrometer and secondary aerosol yield measurements examined as a function of initial NOx concentration presented in this paper are similar to the results of previous papers (D'Ambro et al., 2017; Kroll et al., 2005; 2006). The new experimental results of this study are the systematic investigation of online measurements of secondary products as a function of NOx, but the NOx dependence is not discussed in detail in Figs. 3-4 of this paper, and it is difficult to say that the results are sufficiently presented. There is concern about the generality of the conclusions, as the initial VOC concentration is a single point. There is a lack of specific comparison with previous studies. There are related papers that are not cited. The order of explanation of the results is not appropriate in some places. The explanation of the calculation method for Figures 5a and 5b, which are related to the conclusions, is insufficient. Based on the above, I think that this paper needs significant revision. The detailed points are listed below.

Major comments

(1) I think that the experimental results of the chemical analysis of SOA composition using CIMS with systematically varied NOx are new primary information obtained in this study. However, with regard to the CIMS analysis results, only the similarity to previous reports is discussed in the first paragraph of section 3.2, and two points with different NOx concentrations are shown in Fig. 3. I think that the value of this research as an original paper would be enhanced if detailed experimental results on the initial NOx concentration dependence of the chemical composition were presented and compared with the results of the SOA yield. I have written specific comments in Comment (17), so please refer to that as well.

(2) Page 12, lines 315-326. This study discusses the results of experiments conducted under conditions where the initial isoprene concentration is kept constant. If the initial isoprene concentration decreases, the concentration of SOA produced also decreases, and the gas particle partitioning shifts to the gas phase side. If the gas particle partitioning shifts to the gas phase side, there is a possibility that the β value, which is the maximum SOA yield, will be affected. In this study, it was concluded that the SOA yield is maximized when $\beta = 0.5$, but it is unclear how universal this conclusion is based on the experimental evidence presented in

this study alone. The conclusion should be toned down, or the discussion should be based on additional experiments or additional MCM calculations to confirm the universality of the conclusion under conditions with different isoprene concentrations.

(3) Abstract, lines 46-47. As far as I can tell, this is a sentence that is not discussed in the main text. What does it mean that β can be used as a reference? What is the significance of discussing only the yield of isoprene-derived SOA in outdoor observations and atmospheric 3D model calculations, and is it even possible to do so? Or are you saying that future research should focus on the fact that β, which is evaluated for all RO2, not just isoprene-derived RO2, can be used as an indicator to evaluate the generation rate of all SOA? There must be differences in volatility between isoprene-derived SOA and other SOA, so it cannot be said that β can be used as a reference based on the results of this study alone. The above points should be discussed in the main text and clarified in terms of their meaning before this sentence is added to the abstract.

Other comments

(4) Lines 39-40 of the abstract. It is difficult to understand why the "fraction" of RO2+HO2 and RO2+NO increases at the same time, when there is a competitive relationship between RO2+HO2 and RO2+NO. Are you referring to the total loss rate caused by RO2+HO2 and RO2+NO?

(5) Page 3, line 62. In this paragraph, the effect of NOx on the oxidation reaction of isoprene is discussed from the perspective of physical chemistry. However, I feel that the discussion would be enhanced if the significance of the reaction between biogenic isoprene and anthropogenic NOx in the atmospheric environment were discussed first. For example, the importance of BVOCs is increasing in countries that have taken measures to combat air pollution due to the reduction of emissions of anthropogenic VOCs and the increase in emissions of plant-derived VOCs caused by global warming (Pfannerstill et al., 2024). We need a more sophisticated understanding of the interaction between biogenic VOCs and anthropogenic NOx in order to control air pollution.

Ref.: Pfannerstill et al., Temperature-dependent emissions dominate aerosol and ozone formation in Los Angeles, Science, 384, 1324-1329, 2024.

(6) Page 6, line 141. The concentration of OH radicals suddenly appears as an experimental result. How was the concentration of OH radicals determined? You need to include an explanation somewhere before here or here.

(7) Page 6, lines 145-147. The oxygen atoms that react with H2O are produced by the photolysis of O3, not by the photolysis of NO2. Although this is how it is written in the reaction equation, it seems to me that the text says that the O atoms produced by the photolysis of NO2 react with H2O. Please fix this.

(8) Page 6, lines 150-154. This paragraph discusses the results of Fig. 1. However, the description of the product in the previous paper (Jiang et al., 2017) is not directly related to the results of Fig. 1. If this description is necessary here, the relationship with Fig. 1 should be clarified. Alternatively, the discussion of the product should be made in the section on the results of chemical composition analysis.

(9) Page 6. The chemical reaction formula in Eq. 1-5 is easy to read immediately after the explanation in the main text (pp. 144-147).

(10) Page 6, lines 158-163. Regarding the NOx dependence of the chemical mechanism, the RO2 chemistry described by the authors is important, but consideration of HOx chemistry, which is involved in the formation of OH, is also important. Kroll et al. supply high concentrations of OH radicals by photolysis of H2O2. In this study, on the other hand, RO2+HO2 acts as a reaction that stops the HOx cycle during the reaction time after NOx is consumed under low NOx conditions. The yield of SOA may decrease due to the decrease in the generation rate of ELVOC and ULVOC and the increase in their wall loss. In fact, the results of Kroll et al. did not show such a decrease in the SOA yield on the low-NOx side as in the present study. In order to explain the difference with the results of Kroll et al., it is also necessary to discuss the effect of HOx chemistry.

(11) Page 7, line 174. Is OSc the average carbon oxidation state? Explain, as this is the first time it has been mentioned.

(12) Figure 3. Change the abbreviations LVOC, ELVOC, and ULVOC in the figure to the same notation as in the abstract.

(13) Page 7, lines 187-191. Zhao et al. and Chen et al. focused on the dark reaction of NO3+isoprene. If you are going to explain the products detected in this study by citing Zhao et al. and Chen et al., you should explain why there are similarities between the NO3 reaction and the photo-oxidation in this study, either here or before. In addition, the results of D'Ambro et al. (2017), who detected the products of photo-oxidation using CIMS in the same way as this study, should be compared with the results of this study, and the similarities and differences should be discussed.

(14) Page 7, lines 192-193. Regarding the conditions of this study, it is necessary to discuss the possibility that the addition reaction of the reagent ion NO3- affects the measured signal. If it has been confirmed in other studies, please show that as well.

(15) Page 8, lines 201-204. It says "rate coefficient of OH oxidation", but based on the context, isn't it actually the rate (k[OH]) rather than the rate coefficient (k)?

(16) Page 8, lines 217-222. The explanation that new particle formation occurs due to the ULVOC of the nitrate oligomers detected in this study does not necessarily match the argument based on the MCM calculation results that the decrease in NO causes auto-oxidation and the formation of HOM, which triggers SOA formation. According to Figure 4, the concentration of oligomers increases between 15 and 30 minutes, but the concentration of SOA increases at 30 minutes. It is also possible that new particle formation is triggered by the formation of nitrate-free HOMs, which occur when NO concentrations are low at 30 minutes. The discussion of the mechanism of new particle formation in this paragraph needs to be carefully considered.

(17) Page 8-9, lines 223-232. I understand that the NOx dependence of the concentration of nitrate oligomers is consistent with previous research by Rissanen et al. However, I wonder if there is something new that the authors could investigate by systematically varying the NOx level. For example, the authors state in the results of Fig. 4 that nitrate oligomers are related to new particle formation. If this is the case, when the NOx concentration is systematically changed, is there always a consistency between the time when the concentration of nitrate oligomers increases and the time when the concentration of SOA increases? The presentation of such results enhances the value of this research as an original paper and leads to a discussion evaluating the relationship between nitrate oligomers and new particle formation.

(18) Page 9, lines 235-245. I think it would be better to have this discussion after the author presents the experimental results on the NOx dependence of SOA yield (Fig. 2). I don't think it is necessary to present the CIMS results between Fig. 2 and this discussion.

(19) Pages 9-10, lines 246-258. The authors cited a previous NO3+ isoprene paper in the section explaining the results of the CIMS. The importance of NO3 in this paragraph should be discussed before that section. Also, since black light (~365 nm) is used in this study, photodegradation of NO3 (>400 nm) hardly occurs, and this point should be discussed as being different from the reaction of sunlight in the atmosphere (see, for example, Fig. 6 of Reed et al., 2016).

Ref. Reed et al., Interferences in photolytic NO2 measurements: explanation for an apparent missing oxidant? Atmos. Chem. Phys., 16, 4707-4724, 2016.

(20) Page 10, lines 261-265. Does the NOx concentration in Fig. 5 represent the initial concentration? Also, what point in the reaction does the loss rate, NO concentration, and HO2 concentration represent? Or are they the average values for the entire calculation interval? A detailed explanation of what the authors calculated is needed.

(21) Page 10, lines 267-268. The same as the abstract. Are you referring to the total loss rate of RO2+HO2 and RO2+NO, rather than the "proportion" of RO2+HO2 and RO2+NO?

(22) Page 10, lines 271-274. The text is difficult to understand. Explain it in plain English. Also, explain the meaning of "no" in "p-HOMs-RO2 (no<7)".

(23) Page 12, lines 315-326. The same as comment 20. How were the concentrations of [NO] and [HO2] determined here? It would be meaningless to conclude that the SOA yield is maximized when β is 0.5 without clearly defining the concentrations.

(24) In this study, do the wall adsorption losses of LVOC, ELVOC, and ULVOC, etc. have any effect on the conclusions? Some discussion of this is needed somewhere in the main text.