

Response to reviewers' comments on "Molecular Analysis of Secondary Organic Aerosol and Brown Carbon from the Oxidation of Indole" (egusphere-2023-1804)

The authors kindly thank the reviews for the careful review of the manuscript, and the helpful comments and suggestions, which improve the manuscript a lot. All the comments are addressed below point by point, with our responses in blue, and the corresponding revisions to the manuscript in red. All updates of the original manuscript are marked in the revised version.

Editor

Both the referees and I have gone through the authors' revisions and comments carefully. We are of the opinion that the FIGAERO thermograms need further analysis. Based on the FIGAERO thermograms that the authors' provided in the revised version, some of their thermograms could be fitted using multiple peaks (not single peaks). This indicates that they likely had thermal decomposition occurring for some of the thermograms of the products that they were tracking. This is especially obvious for the $C_8H_5O_3N$ thermogram, but the $C_8H_7O_4N$ and $C_8H_7O_3N$ thermograms could be fitted with multiple peaks as well. In addition, the peaks of these three thermograms were centered at high temperatures (>100 C), which is another indication of thermal decomposition. Based on the authors' replies to the comments in the initial round of reviews, it sounds like the authors may have prematurely discounted the possibility of thermal decomposition in their analysis. While this may not affect their overall conclusions, it is still important to get this analysis done correctly. The two referees have also made other minor comments that needs addressing before this manuscript can be accepted for publication.

Thank you for pointing to the analysis of the thermograms in our manuscript. We agree that the complexity of the thermograms needs to be addressed properly. Consequently, we have added more details on this in our answers to the reviewer comments below.

Reviewer #1

This study by Jiang et al. investigated the formation, chemical composition, and optical properties of secondary organic aerosol (SOA) formed from ozonolysis and OH radical oxidation of indole, one of the important nitrogen-containing heterocyclic VOCs. With the presence of NO_2 , indole SOA formation potential decreased by a factor of two, but the light absorbing potential per mass was higher by a factor of 5. Using mass spectrometric techniques, the authors showed that the presence of NO_2 shifted the indole SOA formation chemical pathways, in which the formation of 3-nitroindole was significantly enhanced, hence affecting the overall SOA chemical composition and optical properties. This is an interesting study and valuable to the community of Atmospheric Chemistry and Physics. Overall, the authors appear to have addressed the reviewers' comments but there are some additional concerns associated with their responses.

Specific comments:

1. Figure S10: While the thermogram of $C_8H_6O_2N_2$ indeed looks a single peak, other compounds (i.e., $C_8H_7O_4N$, $C_8H_7O_3N$, and $C_8H_5O_3N$) show much broader peaks, which are characteristics of multi-modal peaks. At least from calibrations, a single compound shows a very similar peak width (Lopez-Hilfiker et al., 2014; Stark et al., 2017), meaning that wider peaks indicate the presence of multiple peaks next to each other. This may be due to the

presence of isomers with different volatilities or due to the effect of thermal decomposition. Therefore, I suggest rephrasing the sentence "... detected by FIGAERO-CIMS exhibit only one peak in the thermogram and no substantial fragmentation." 2-D thermogram (Wang and Ruiz, 2018; Takeuchi et al., 2022) may be a better way to illustrate the absence/presence of thermal decomposition in a holistic manner.

Indeed, we didn't discuss the complexity of the thermograms sufficiently as we focused on the molecular composition of *ind*-SOA and potential reaction pathways. Broader thermograms, like those of $C_8H_7O_4N$, $C_8H_7O_3N$, and especially $C_8H_5O_3N$, may be caused by the presence of isomers of different volatility and thermal decomposition of larger molecules. Furthermore, the thermograms are also influenced by the overall composition of the matrix on the filter e.g. the ratio of the salts to the organics. To make the reader aware of this, we have modified the text in the manuscript as follows and we have also added 2-D thermograms as Figure S13. However, a detailed discussion of the SOA volatility is beyond the scope of our manuscript.

"Figure S10 shows the thermograms of four major compounds detected. For 3-nitroindole ($C_8H_6O_2N_2$) a single peak gives no indication for isomers or fragmentation. However, broader thermograms, like those of $C_8H_7O_4N$, $C_8H_7O_3N$, and especially $C_8H_5O_3N$, may be caused by the presence of isomers of different volatility or thermal decomposition of larger molecules or oligomers (Lopez-Hilfiker et al., 2014). Furthermore, the thermograms are also influenced by the overall composition of the matrix on the filter e.g. the ratio of the salts to the organics. This is shown in Figure S13 with overall higher desorption temperatures for the experiment without ammonium sulfate. In this study we will focus on the molecular composition of *ind*-SOA but not discuss the details of its volatility."

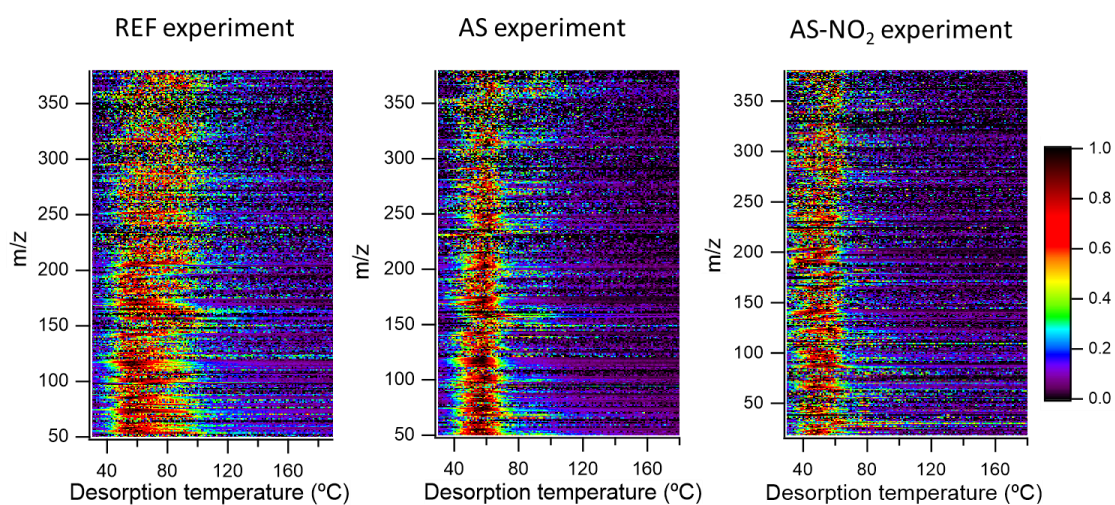


Figure S13. Two-dimensional thermograms of indole SOA at REF, AS, and AS-NO₂ experiments. The contour colors indicate normalized intensities.

2. Line 166: I agree with the authors that at this current moment, it is very difficult to do calibrations of all the detected organic compounds and it is not unreasonable to assume uniform sensitivity. However, I believe it is still important to note here that I-CIMS sensitivity could easily vary by a few order of magnitude reported in literature (Aljawhary et al., 2013; Lee et al., 2014), and therefore the reported fractions do not speak to the actual abundance. One idea is to explicitly say XXX% of the sum "signals" so it is obvious that percentage does not correspond to mass fraction.

We agree that it is important to point out the uncertainties of the CIMS measurements. Therefore, we added the following sentence to the manuscript.

“Since it was not possible for us to calibrate the sensitivities of all organic molecules, we assume the same sensitivity of 22 cps/ppt for all compounds (Lopez-Hilfiker et al., 2016). Please note that the CIMS sensitivity of different organic compounds can vary by a few orders of magnitude. Part of these uncertainties were taken into account in the estimation of the overall uncertainties of CIMS concentrations ($\pm 60\%$) following the approach by Thompson et al. (2017). Therefore, the mass fractions calculated from the CIMS measurements are actually percentages of the sum of the CIMS signals.”

3. Line 200: I suggest rephrasing this sentence. Reaction of gas-phase RO_2 with NO_2 produces peroxy nitrate (RO_2NO_2), which is thermally in equilibrium with RO_2 and NO_2 (Orlando and Tyndall, 2012). Production of fragments is typically from reaction of RO_2 with NO , RO_2 , and NO_3 that generate alkoxy radical (RO), which may undergo fragmentation pathways.

We agree and modified the sentence as follows.

“However, in the presence of NO_2 , gas-phase RO_2 intermediates can form peroxy nitrates (Orlando and Tyndall, 2012). In contrast, reactions of RO_2 with NO , RO_2 , and NO_3 can produce alkoxy radicals which may undergo fragmentation.”

4. Section 3.4 and Figure 5: Do you know how much indole reacted with ozone vs. OH vs. NO_3 radical? From Figure S2, almost all indole appears to have reacted away before the addition of TME (source of OH radical), and I wonder if that means NO_3 radical oxidation was the major oxidation pathway of indole in AS- NO_2 experiment, as opposed to ozonolysis.

As shown in Figure S2, in the reference and seed particle experiments (S2a&b), the indole was depleted quickly by high concentrations of O_3 . However, substantial SOA production only started after further oxidation of the reaction products by OH radicals. Atkinson et al. (1995) have reported a high-rate coefficient for reactions of indole with NO_3 radicals ($1.3 \pm 0.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$), while the reaction with ozone is much slower ($4.9 \pm 1.8 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Therefore, in AS- NO_2 experiment, with initially lower ozone levels (see Figure S2c), the indole was mainly oxidized by NO_3 radicals. Already a significant amount of SOA mass formed by NO_3 radical reactions. However, also in this case sub sequential reactions with OH radicals lead to a further substantial increase in SOA mass. The major product from oxidation of indole in presence of NO_2 was 3-nitroindole.

5. Table 1: I suggest adding $[\text{O}_3]$ as well because it is one important parameter of experimental condition. Also, the SOA mass concentration should be added next to the SOA yield because the SOA yield is a function of the SOA mass concentration and cannot be simply compared without it.

We agree and modified Table 1 accordingly.

Table 1. Summary of indole SOA experimental conditions.

Experiment ID	Indole (ppb)	NO ₂ (ppb)	O ₃ (ppb)	(NH ₄) ₂ SO ₄ seed	RH (%)	Temperature (K)	SOA density (g cm ⁻³)	SOA yield	SOA mass (ug m ⁻³)
REF	20.5	–	698	–	29	303	0.8 ± 0.2	0.45 ± 0.1	45 ± 9.0
AS	24.5	–	700	√	28	303	0.9 ± 0.2	0.44 ± 0.1	52 ± 10.4
AS-NO ₂	18.6	60	776	√	29	303	1.3 ± 0.3	0.19 ± 0.04	21 ± 4.2

6. SI Text 3 (SOA density): I suggest that the authors consider revising this paragraph incorporating their response to the comment 8 by the reviewer 1 to be complete.

We agree and modified the Text 3 in the supplement. We added more information to describe how to calculate the density, especially for AS and AS-NO₂ experiments, as shown the below:

“As shown in Figure S11, in the AS experiment, the nucleation peaks of the size distributions were from pure indole SOA. Therefore, the seed particles do not affect the indole SOA density determination. However, in the AS-NO₂ experiment, the indole SOA density was calculated by the major peaks of coated particles as shown in Figure S12. Therefore, we used an average particle density including the AS seed and the indole SOA coating. The particle mass concentration was calculated from particle volume and average density. The seed particle mass and volume can be determined by SMPS. We obtained the pure indole SOA mass and volume. Then we calculated the pure indole SOA density.”

Reference

- Atkinson, R., Tuazon, E. C., Arey, J., and Aschmann, S. M.: Atmospheric and Indoor Chemistry of Gas-phase Indole, Quinoline, and Isoquinoline, *Atmospheric Environment*, 29, 3423-3432, 10.1016/1352-2310(95)00103-6, 1995.
- Lopez-Hilfiker, F. D., Mohr, C., Ehn, M., Rubach, F., Kleist, E., Wildt, J., Mentel, T. F., Lutz, A., Hallquist, M., Worsnop, D., and Thornton, J. A.: A novel method for online analysis of gas and particle composition: description and evaluation of a Filter Inlet for Gases and AEROSols (FIGAERO), *Atmospheric Measurement Techniques*, 7, 983-1001, 10.5194/amt-7-983-2014, 2014.
- Lopez-Hilfiker, F. D., Iyer, S., Mohr, C., Lee, B. H., D'Ambro, E. L., Kurten, T., and Thornton, J. A.: Constraining the sensitivity of iodide adduct chemical ionization mass spectrometry to multifunctional organic molecules using the collision limit and thermodynamic stability of iodide ion adducts, *Atmospheric Measurement Techniques*, 9, 1505-1512, 10.5194/amt-9-1505-2016, 2016.
- Orlando, J. J., and Tyndall, G. S.: Laboratory studies of organic peroxy radical chemistry: an overview with emphasis on recent issues of atmospheric significance, *Chemical Society reviews*, 41 19, 6294-6317, 2012.
- Thompson, S. L., Yataavelli, R. L. N., Stark, H., Kimmel, J. R., Krechmer, J. E., Day, D. A., Hu, W., Isaacman-VanWertz, G., Yee, L., Goldstein, A. H., Khan, M. A. H., Holzinger, R., Kreisberg, N., Lopez-Hilfiker, F. D., Mohr, C., Thornton, J. A., Jayne, J. T., Canagaratna, M., Worsnop, D. R., and Jimenez, J. L.: Field intercomparison of the gas/particle partitioning of oxygenated organics during the Southern Oxidant and Aerosol Study (SOAS) in 2013, *Aerosol Science and Technology*, 51, 30-56, 10.1080/02786826.2016.1254719, 2017.

Reviewer #2

The authors have generally responded well to the reviewer's comments. However, I would like to draw attention to a few areas that need further clarification or correction:

1. Figure S10: In the revised manuscript, the thermograms from Figaero CIMS measurements are presented. The thermogram for $C_8H_5O_3N$ displays multiple peaks. Despite this compound not being predominantly abundant in *ind*-SOA, and the possibility that the general findings remain valid, this particular detail merits closer scrutiny to ensure the robustness of the data.

Despite the complexity of the thermograms we still consider our interpretation of the molecular composition of the indole SOA as valid. It is beyond the scope of this manuscript to do a detailed discussion of the SOA volatility. However, to explain the differences in the thermograms we have added the following text and a 2-D representation of the thermograms.

“Figure S10 shows the thermograms of four major compounds detected. For 3-nitroindole ($C_8H_6O_2N_2$) a single peak gives no indication for isomers or fragmentation. However, broader thermograms, like those of $C_8H_7O_4N$, $C_8H_7O_3N$, and especially $C_8H_5O_3N$, may be caused by the presence of isomers of different volatility or thermal decomposition of larger molecules or oligomers (Lopez-Hilfiker et al., 2014). Furthermore, the thermograms are also influenced by the overall composition of the matrix on the filter e.g. the ratio of the salts to the organics. This is shown in Figure S13 with overall higher desorption temperatures for the experiment without ammonium sulfate. In this study we will focus on the molecular composition of *ind*-SOA but not discuss the details of its volatility.”

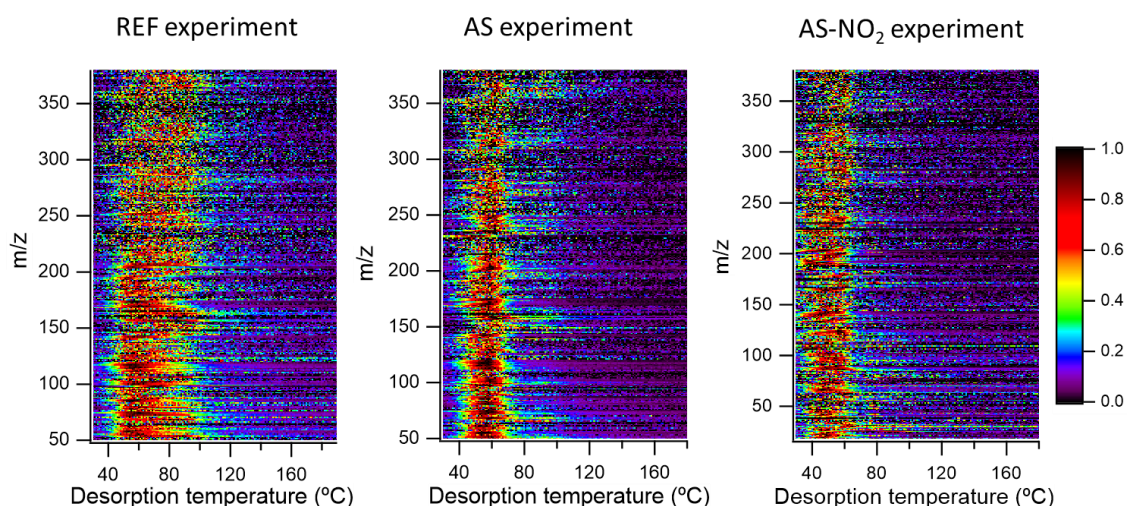


Figure S13. Two-dimensional thermograms of indole SOA at REF, AS, and AS-NO₂ experiments. The contour colors indicate normalized intensities.

2. Line 95: “Following injection of OH radicals”: It's stated that OH radicals were injected, which is inaccurate. I recommend revising this statement.

We agree and modified it as follows.

“Following injection of TME, rapid growth of *ind*-SOA was observed in each of the experiments”.

3. The MAC₃₆₅ data as discussed seem to be primarily based on the findings from Figure 2, which were derived from methanol-extracted samples analyzed through Aqualog measurement. Notably, these values differ from those obtained via UPLC-PDA, as shown in Figure 4. It is essential for the author to offer a more comprehensive explanation for this discrepancy. Additionally, justification for the preference of Aqualog measurement data in this context would further enhance the clarity and validity of the findings.

The light absorption from Aqualog measurement was from methanol extracted samples. However, the light absorption from UPLC-PDA measurement were from acetonitrile extracted samples. The different MAC values could be due to the different solvent. In addition, before UPLC-PDA measurement, the extracted samples were dried with pure nitrogen. This step could lead to vaporize volatile organic compounds. Furthermore, the Aqualog and UPLC-PDA are different instrumental techniques. For Aqualog measurement, the attenuation was from the cuvette. For HPLC-PDA measurement, the chromophores were separated by HPLC and then detected by a diode array detector. These could be the reasons why the MAC values are different between UPLC-PDA and Aqualog measurement. We added the following text in line 270-273 to explain this.

“Please note that the MAC values determined from Aqualog and UPLC-PDA measurements show differences (Figure 2 and 4). This could be caused by different solvent extraction, solution preparation, and instrumental differences.”

Reference

Lopez-Hilfiker, F. D., Mohr, C., Ehn, M., Rubach, F., Kleist, E., Wildt, J., Mentel, T. F., Lutz, A., Hallquist, M., Worsnop, D., and Thornton, J. A.: A novel method for online analysis of gas and particle composition: description and evaluation of a Filter Inlet for Gases and AEROSols (FIGAERO), *Atmospheric Measurement Techniques*, 7, 983-1001, 10.5194/amt-7-983-2014, 2014.