Response to reviewers

We gratefully appreciate the reviewers for the valuable time and insightful comments. The manuscript has been greatly improved based on these comments and suggestions. All the comments have been addressed point by point in the revised manuscript, and the revisions are marked in red colour. The responses to the specific comments are listed as follows.

Response to the Comments from Reviewer #1:

Reviewer #1: *The clarification of the formation mechanism of HOMs/OOMs is of great importance for atmospheric chemistry. In this study, the authors investigated the elaborate oxidation mechanisms of terpinolene initiated by OH and* NO_3*, elucidating the new formation mechanism of OOMs, the molecular structures of the products, and their time-dependent yields and volatility. These findings contribute to the molecular structure identification of OOMs in atmospheric monitoring and the refinement of atmospheric chemical models. Overall, the work is well-presented and innovative. I recommend publication after the following issues are addressed:*

Response: Response: Thank you for the positive and valuable comments. We have revised the manuscript carefully according to the comments and suggestions, and marked them in red in the manuscript.

Comment #1: *Line 21-21, the logic flow of the context is not smooth and should be revised.*
Response to Comment #1: Thank you for the valuable comment. We have revised this description in the manuscript, specifically as follows:
Measurements in forested areas revealed that monoterpene oxidation products played a dominant role in driving new particle growth (Mohr et al., 2019; Huang et al., 2016), while the atmospheric oxidation mechanisms of monoterpenes, especially the formation of OOMs, have not been fully elucidated.

Comment #2: *Line 162, here "dominant reaction" or "rate-determining step"?*
Response to Comment #2: Thank you for pointing out. "Rate-determining step" is more accurate herein, and we have revised this expression and marked the change in red in the manuscript.

Comment #3: *Line 203, how do free radical centers migrate? It should be specified in the manuscript for better understanding.*
Response to Comment #3: Thank you for the valuable comment. The radical center of 2-IM3b migrates from the oxygen atom to the carbon atom, due to the cleavage of the C-C bond. The revision is supplemented in the manuscript, as detailed below:
Besides, Fig.4(c) indicates that the radical center of 2-IM3b migrates from the oxygen atom to the

carbon atom via C-C bond cleavage, and consecutively reacts with O_2 and HO_2 to generate 2-P5.

Comment #4: *Why was the NO_3-Terpinolene-R• (2-IM3) chosen for subsequent oxidation mechanism research? A justification should be provided.*

Response to Comment #4: Thank you for the valuable comment. Since the formation reaction of the NO_3-Terpinolene-R• (2-IM3) is barrierless and releases more heat, being the dominant intermediate, 2-IM3 is selected for the investigation of subsequent oxidation mechanisms.

Comment #5: *In Figure 8, the values of C* for different isomers are difficult to distinguish. The figure format should be modified for better readability.*

Response to Comment #5: Thank you for pointing out this problem. We have modified Figure 8 for clarity in the manuscript.

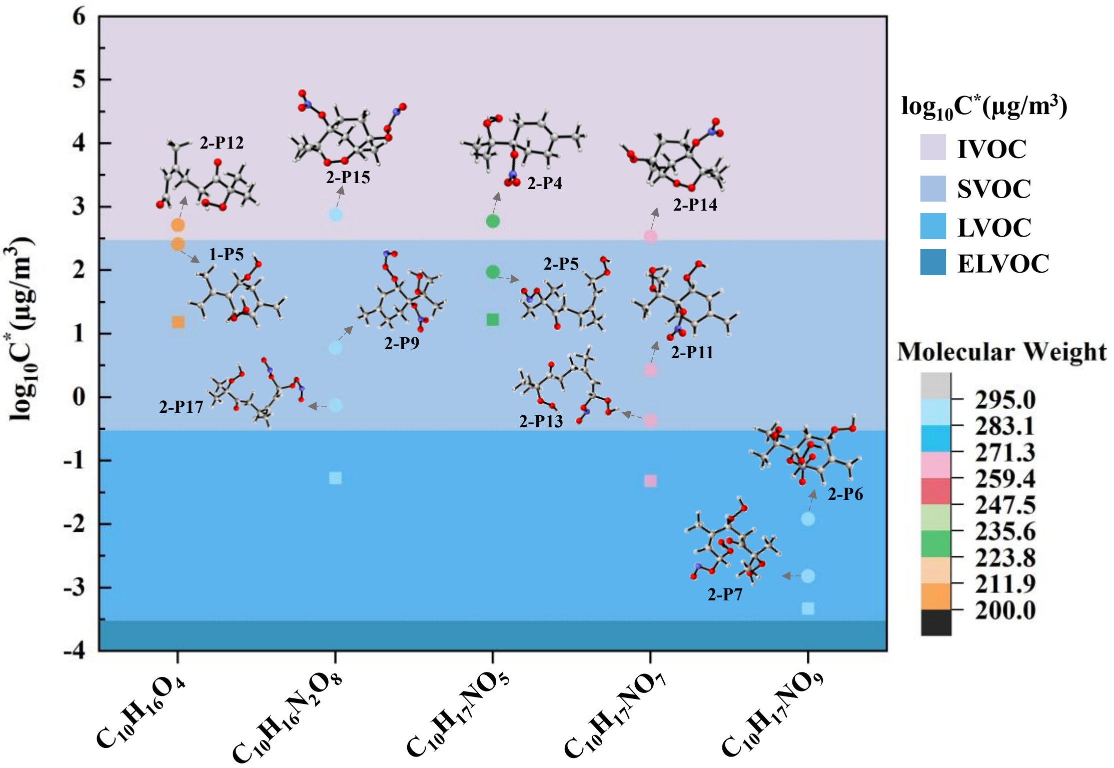

Figure 8. The molecular weight ranges and volatility classifications of C10-OOMs isomers. (Volatility prediction methods: (○) the functional group contribution method(SIMPOL.1), (☐) the molecular formula parameterization method)

Comment #6: *Language: The manuscript should be carefully revised for grammar and style. Several sentences contain errors, such as verb tense errors.*

Response to Comment #6: Thank you for the valuable comment. We have checked the whole manuscript carefully and modified formatting problems and grammatical errors.

Response to the Comments from Reviewer #2:

Reviewer #2: *This study explores terpinolene's oxidation mechanisms initiated by OH (daytime) and NO_3 (nocturnal) radicals, finding H shift limits continuous autoxidation in OH-induced reactions while radical center transfer via bond breaking drives new autoxidation for high-yield nitrogen-containing OOMs in NO_3-induced ones. it also finds nitrogen-containing OOMs have lower C* (more prone to enter particle phase), significant C* differences among OOM isomers emphasize determining molecular structures (especially ring numbers), and comparing the two mechanisms aids OOM identification in atmospheric monitoring and model refinement. It can be published after addressing the following concerns:*

Response: Response: Thank you for the positive and valuable comments. We have revised the manuscript carefully according to the comments and suggestions, and marked them in red in the manuscript.

Comment #1: *Abstract: Line 3. Higher SOA yield than what? Higher than other limonene-based systems? What is the specific magnitude of this higher yield? SOA yield varies significantly depending on multiple factors and is not a fixed value.*

Response to Comment #1: Thank you for pointing out. We totally agree with the reviewer's comment; the expression "Terpinolene is an isomeride of limonene, with an even higher SOA yield" is not accurate, since the SOA yields of terpinolene and limonene are largely dependent on the experimental conditions. According to the experimental results from Friedman and Farmer (2018), the SOA yields from the sequential photooxidation of seven monoterpene isomers (α-pinene, β-pinene, limonene, sabinene, terpinolene, α-terpinene, and γ-terpinene) using an Oxidative Flow Reactor under dry conditions. SOA yields were highest for terpinolene (33% at 5.7 days of aging), followed by sabinene, β-pinene, α-pinene, limonene, γ-terpinene, and α-terpinene. Whereas, based on the results (Figure 3) from Griffin et al. (1999), the SOA yield of limonene is evidently higher than that of terpinolene. Therefore, we have revised this sentence in the Abstract, as detailed below: Terpinolene is an isomeride of limonene, with a high SOA yield.

Comment #2: *Introduction: Authors should review existing literature to clarify whether nitrogen-containing species have lower or higher saturation concentrations compared to non-nitrogen-containing species. Additionally, is organic nitrate or peroxy organic nitrate considered in this context?*

Response to Comment #2: Thank you for the valuable comment. We have supplemented the related literature review in the section of Introduction. For the estimation of the vapor pressure, Isaacman-VanWertz and Aumont (2021) assumed that the impact of a nitrate group on the vapor pressure is equivalent to a hydroxyl group, which was considered reasonable for the reaction system dominated by $R\text{-}ONO_2$ and peroxynitrates in organic nitrogen gas-phase oxidation products. Besides, according to the chamber experiments and structure-activity relationships, adding $\text{-}ONO_2$ functional groups to C10 and larger molecules could reduce the vapor pressure (Rollins et al. 2013).
In our work, both organic nitrate and peroxy organic nitrate were considered.

Comment #3: *Method: The approach for evaluating uncertainties associated with the calculations is missing.*

Response to Comment #3: Thank you for pointing out. To evaluate the reliability of the computational method used in our work, the accuracy of the computational level in determining the energy barriers of the rate-determining steps was compared with the calculated results obtained by the highly time-consuming "gold standard" method CBS-QB3(Dunn et al. 2004), which shows good consistency, as shown in the table below.

Table S1. Energy Barriers calculated by CBS-QB3 and the method used in this study

Reactions	Energy Barrier (kcal/mol) (CBS-QB3)	Energy Barrier (kcal/mol) (M06-2X/6-311++G(3df,3pd))
1-IM4 → 1-IM41b	21.5	21.3
1-IM4 → 1-IM41a	18.3	19.6
1-IM4 →1-IM41d	22.1	23.0

In addition, we also compared our results of key reactions with the previous work of structurally similar monoterpenes (Møller et al. 2020), and the deviations are within a reasonable range, which is summarized in the following table.

Table S2. Energy Barriers calculated by CCSD(T)-F12a/VDZ-F12 (abbreviated F12) and ωB97X-D/aug-cc-pVTZ, and the method used in this study (unit: kcal/mol).

Reactions	CCSD(T)-F12a/VDZ-F12	ωB97X-D/aug-cc-pVTZ	This work
1-IM4 → 1-IM41d	26.3	25.5	23.0
1-IM4 → 1-IM41b	21.7	22.2	21.3
1-IM4 → 1-IM41g	18.5	19.4	20.9

Comment #4: *Line 153: Previous studies suggest that NO_2 release was derived from experimental data, whereas HONO release in this study is based on energy barrier calculations. If NO_2 was indeed measured experimentally, should this be more reliable than theoretical calculations? If so, how can the calculation results in this study be validated? Conversely, if NO_2 was not measured directly (e.g., its signal could be interfered with by HONO), then HONO should be the correct pathway. Are you implying that the NO_2 measurements reported in previous studies originated from HONO signals?*

Response to Comment #4: Thank you for pointing out this problem. As shown in Figure 2 in the manuscript, the subsequent reactions of 1-IM42, formed by the reaction of the peroxy radical 1-IM41 and NO, have two possible pathways: a. the elimination of HONO to produce 1-P1 overcoming a high energy barrier of 43.6 kcal/mol; b. the formation of 1-P1 via sequential H abstraction by OH, the cleavage of C-C bond and the barrierless elimination of NO_2, overcoming low barriers of 10.6 and 6.5 kcal/mol. Therefore, the generation of NO_2 is evidently more feasible, which is consistent with the experimental results. Although the formation of HONO from the above reaction pathway is difficult, the possibility that HONO is produced by the atmospheric oxidation of other organic compounds cannot be ruled out. For the NO_2 measurements, the influence of HONO signals could not be completely excluded.

Comment #5: *HONO can release HONO upon photolysis—do you have any data to demonstrate the yield of HONO from this process?*

Response to Comment #5: Thank you for your valuable comment. As the formation of HONO is not the dominant pathway, it was not considered in the zero-dimensional chemical model, and therefore, the yield of HONO cannot be determined in this work.

Comment #6: *Line 236: NO_2 is not specified; I assume its concentration is set to 0 in your model? In forested areas and remote regions with low NO levels, most NO is converted to NO_2. NO_2 can undergo photolysis to form NO, so total NO_x ($NO + NO_2$) should be a more representative metric.*

Response to Comment #6: Thank you for your valuable comment. We agree with your view, in the atmosphere, the conversion between NO and NO_2 can readily occur, with the concentrations reaching a dynamic equilibrium. In our work, the initial concentrations of NO_2 were set in the model, and the re-simulations were conducted under different atmospheric conditions, i.e., (a) in a urban area (50 ppb NO, 39 ppb NO_2, 1 ppt HO_2), (b) in a surburban area (3 ppb NO, 9 ppb NO_2, 3 ppt HO_2), and (c) in a forested area (0.5 ppb NO, 4 ppb NO_2, 40 ppt HO_2) (Guo et al. 2024, Kieloaho et al. 2013, Klemm et al. 2006, Lew et al. 2020, Ma et al. 2019, Mao et al. 2010, Mavroidis and Ilia 2012, Mazzeo et al. 2005, Zhang et al. 2022).

Comment #7: *I am also curious why NO concentrations in forests are set to be lower than in "remote areas". Soil NO_x emissions are a substantial source of NO_x in forest environments.*

Response to Comment #7: Thank you for your valuable comment. We agree with your point of view; soil emission is an important source of NO_x in the forest areas. According to the literature, NO concentration over the forests is not fixed, varying from tens of ppt to hundreds of ppt or even several ppb in different regions, with higher concentration in the low atmosphere due to the soil emission (Kieloaho et al. 2013, Klemm et al. 2006). In our work, we referred to the literature and determined the atmospheric conditions in a suburban area (3 ppb NO, 9 ppb NO_2, 3 ppt HO_2) and a forested area (0.5 ppb NO, 4 ppb NO_2, 40 ppt HO_2) in our simulation (Guo et al. 2024, Kieloaho et al. 2013, Klemm et al. 2006, Lew et al. 2020, Mavroidis and Ilia 2012).

Comment #8: *Line 237: Why is HO_2 concentration fixed at 50 ppt across all scenarios? HO_2 is an intermediate radical, and its formation and levels depend on factors such as VOCs and NO_x. It is not typically constrained to a fixed value in box models.*

Response to Comment #8: Thank you for pointing out. We have modified the setting of HO_2 concentrations in the model based on the previous research. In our simulation, the initial concentrations of HO_2 were set to be 1 ppt in an urban area, 3 ppt in a suburban area, and 40 ppt in a forested area. In addition, the HO_2 concentration is not constrained to a fixed value in our box models.

Comment #9: *Line 349: Can you provide a more detailed description of the results presented in Figure 8? For example, are you stating that $C_{10}H_{16}O_4$ (classified as an OOM) is identified as an SVOC with a C* of 1 in your analysis, but would be categorized as an SVOC with a C* of 2.5 if calculated using the functional group method?*

Response to Comment #9: Thank you for your valuable comment. For instance, for the product $C_{10}H_{16}O_4$ (two isomers: 2-P12 & 1-P5), the values of lg C* for two isomers are both ~1 μg/m^3

estimated by the molecular formula parameterization method, belonging to SVOC. Whereas, using the functional group contribution method (SIMPOL.1), the lg C* values of the isomers 1-P5 and 2-P12 are calculated to be 2.4 and 2.7 μg/m^3, respectively, of which 2-P12 can be categorized as an IVOC.

Comment #10: *Line 350: Which method for volatility estimation—molecular formula-based or functional group-based—is more reliable? Can you discuss the reasons for the discrepancies between these two methods? Additionally, does organic nitrate influence volatility calculations?*

Response to Comment #10: Thank you for your valuable comment. The functional group-based method could be more reliable, since within each compound category the variations in vapor pressure can be attributed to the number and size of functional groups present and the relative positions of those functional groups to each other both positionally and geometrically, these two factors impact upon both the molecules' dipole moments and upon their ability to interact both intramolecularly and intermolecularly via hydrogen bonding (Dang et al. 2019), thus explaining the differences in the estimated vapor pressure.

Yes, organic nitrate can influence the volatility calculations; the reactions of volatile organic precursors with NOx lead to the formation of nitro and nitrate groups. There exists some data in the literature for polynitrates, but few data are available for compounds with combinations of nitro and/or nitrate with −COOH and −OH groups. Hence, the previous work assumed that nitrogen is predominantly present as nitrate groups, and each nitrate group is treated as being equivalent to a hydroxyl group; this assumption is reasonable for a system dominated by products of gas-phase oxidation, in which R-ONO$_2$ compounds and peroxynitrates are the dominant source of organic nitrogen (Bilde et al. 2015, Isaacman-VanWertz and Aumont 2021).

Comment #11: *Results section: Organic nitrate is a key component of nitrogen-containing OOMs. Given this, I recommend focusing discussions on organic nitrate (RONO$_2$) OOMs specifically, rather than attributing all relevant observations to "nitrogen-containing OOMs" in general.*

Response to Comment #11: Thank you for pointing out. We have modified the description in the revised manuscript for specificity and clarity.

Reference:

Bilde, M., Barsanti, K., Booth, M., Cappa, C.D., Donahue, N.M., Emanuelsson, E.U., McFiggans, G., Krieger, U.K., Marcolli, C., Topping, D., Ziemann, P., Barley, M., Clegg, S., Dennis-Smither, B., Hallquist, M., Hallquist, Å.M., Khlystov, A., Kulmala, M., Mogensen, D., Percival, C.J., Pope, F., Reid, J.P., Ribeiro da Silva, M.A.V., Rosenoern, T., Salo, K., Soonsin, V.P., Yli-Juuti, T., Prisle, N.L., Pagels, J., Rarey, J., Zardini, A.A. and Riipinen, I. (2015) Saturation Vapor Pressures and Transition Enthalpies of Low-Volatility Organic Molecules of Atmospheric Relevance: From Dicarboxylic Acids to Complex Mixtures. Chemical Reviews 115(10), 4115-4156.

Dang, C., Bannan, T., Shelley, P., Priestley, M., Worrall, S.D., Waters, J., Coe, H., Percival, C.J. and Topping, D. (2019) The effect of structure and isomerism on the vapor pressures of organic molecules and its potential atmospheric relevance. Aerosol Science and Technology 53(9), 1040-1055.

Dunn, M.E., Pokon, E.K. and Shields, G.C. (2004) Thermodynamics of Forming Water Clusters at Various Temperatures and Pressures by Gaussian-2, Gaussian-3, Complete Basis Set-QB3, and Complete Basis Set-APNO Model Chemistries; Implications for Atmospheric Chemistry. Journal of the American

Chemical Society 126(8), 2647-2653.

Friedman, B. and Farmer, D.K. (2018) SOA and gas phase organic acid yields from the sequential photooxidation of seven monoterpenes. Atmospheric Environment 187, 335-345.

Griffin, R.J., Cocker Iii, D.R., Flagan, R.C. and Seinfeld, J.H. (1999) Organic aerosol formation from the oxidation of biogenic hydrocarbons. Journal of Geophysical Research: Atmospheres 104(D3), 3555-3567.

Guo, P., Su, Y., Sun, X., Liu, C., Cui, B., Xu, X., Ouyang, Z. and Wang, X. (2024) Urban–Rural Comparisons of Biogenic Volatile Organic Compounds and Ground-Level Ozone in Beijing, 15(3), 508.

Isaacman-VanWertz, G. and Aumont, B. (2021) Impact of organic molecular structure on the estimation of atmospherically relevant physicochemical parameters. Atmos. Chem. Phys. 21(8), 6541-6563.

Kieloaho, A.-J., Hellén, H., Hakola, H., Manninen, H.E., Nieminen, T., Kulmala, M. and Pihlatie, M. (2013) Gas-phase alkylamines in a boreal Scots pine forest air. Atmospheric Environment 80, 369-377.

Klemm, O., Held, A., Forkel, R., Gasche, R., Kanter, H.J., Rappenglück, B., Steinbrecher, R., Müller, K., Plewka, A., Cojocariu, C., Kreuzwieser, J., Valverde-Canossa, J., Schuster, G., Moortgat, G.K., Graus, M. and Hansel, A. (2006) Experiments on forest/atmosphere exchange: Climatology and fluxes during two summer campaigns in NE Bavaria. Atmospheric Environment 40, 3-20.

Lew, M.M., Rickly, P.S., Bottorff, B.P., Reidy, E., Sklaveniti, S., Léonardis, T., Locoge, N., Dusanter, S., Kundu, S., Wood, E. and Stevens, P.S. (2020) OH and HO2 radical chemistry in a midlatitude forest: measurements and model comparisons. Atmos. Chem. Phys. 20(15), 9209-9230.

Ma, X., Tan, Z., Lu, K., Yang, X., Liu, Y., Li, S., Li, X., Chen, S., Novelli, A., Cho, C., Zeng, L., Wahner, A. and Zhang, Y. (2019) Winter photochemistry in Beijing: Observation and model simulation of OH and HO2 radicals at an urban site. Science of The Total Environment 685, 85-95.

Mao, J., Ren, X., Chen, S., Brune, W.H., Chen, Z., Martinez, M., Harder, H., Lefer, B., Rappenglück, B., Flynn, J. and Leuchner, M. (2010) Atmospheric oxidation capacity in the summer of Houston 2006: Comparison with summer measurements in other metropolitan studies. Atmospheric Environment 44(33), 4107-4115.

Mavroidis, I. and Ilia, M. (2012) Trends of NOx, NO2 and O3 concentrations at three different types of air quality monitoring stations in Athens, Greece. Atmospheric Environment 63, 135-147.

Mazzeo, N.A., Venegas, L.E. and Choren, H. (2005) Analysis of NO, NO2, O3 and NOx concentrations measured at a green area of Buenos Aires City during wintertime. Atmospheric Environment 39(17), 3055-3068.

Møller, K.H., Otkjær, R.V., Chen, J. and Kjaergaard, H.G. (2020) Double Bonds Are Key to Fast Unimolecular Reactivity in First-Generation Monoterpene Hydroxy Peroxy Radicals. The Journal of Physical Chemistry A 124(14), 2885-2896.

Zhang, G., Hu, R., Xie, P., Lou, S., Wang, F., Wang, Y., Qin, M., Li, X., Liu, X., Wang, Y. and Liu, W. (2022) Observation and simulation of HOx radicals in an urban area in Shanghai, China. Science of The Total Environment 810, 152275.