RE: A point-to-point response to reviewers' comments

"Secondary OH reactions of aromatics-derived oxygenated organic molecules lead to plentiful highly oxygenated organic molecules within an intraday OH exposure" by Yuwei Wang, Chuang Li, Ying Zhang, Yueyang Li, Gan Yang, Xueyan Yang, Yizhen Wu, Lei Yao, Hefeng Zhang, Lin Wang (egusphere-2023-1702)

Dear Dr. Liggio,

We are very grateful for the comments from the reviewer and your suggestions to improve our work. To address the concerns raised by the reviewer and you, a point-to-point response to the comments, which are repeated in *italic*, is given below.

We are looking forward to your decision at your earliest convenience.

Best regards,

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The manuscript has been improved to make it publishable, after some additional corrections as pointed out by the most recent review. In particular,

(1) A thorough language editing should be performed before the work is accepted for publication.
R1. We are sorry for the language issue. We have carefully edited the texts to enhance the clarity and readability of this manuscript.

We have revised our manuscript (Line 73 – 74) as:

"stand for the number of carbon, hydrogen, and nitrogen atoms, respectively, in a molecular) for HOMs"

(Line 78 – 79) as:
"Autoxidation of BPR could be very fast if it has a favorable structure"

(Line 95) as:
"and those with 14 hydrogen atoms"

(Line 108) as:
"processes that occur at night."

(Line 110) as:
"is a compound"

(Line 114 – 115) as:
"and the quantity of experiments was very finite, restricting the application of their conclusions to atmospheric relevant conditions"

(Line 122) as:
"of the stabilized first-generation oxidation"

(Line 125 – 126) as:
"Atmospheric OH concentration"

(Line 130 – 131) as:
"study chemical characteristics of aromatics-derived HOMs at different OH exposures, especially those that are less than …"

(Line 133 – 136) as:
"In this study, two series of laboratory experiments on OH-initiated oxidation of 1,3,5-TMB, selected as an example of anthropogenic VOCs, were conducted. One was conducted with [OH] ranging from 9.32×10^7 to 1.03×10^9 molecule cm^{-3}, corresponding to an OH exposure …"

(Line 140 – 144) as:
"We explored the evolution of oxidation products to investigate the secondary OH chemistry of stabilized first-generation oxidation products generated by the oxidation of 1,3,5-TMB. Furthermore,

the influence of NO on the formation of HOMs was investigated by introducing N_2O into the reaction system."

(Line 152) as:
"low [OH] ones"

(Line 158 – 159) as:
"four without NO_x (Exp. 2-1 – 2-4) and three with NO_x (Exp. 2-5 – 2-7)."

(Line 161) as:
"and also listed in Table S1."

(Line 172) as:
"a plug flow one in …"

(Line 174 – 175) as:
"6 slpm out of the 15 slpm zero-gas was initially passed through …"

(Line 184) as:
"a HOM compound"

(Line 187) as:
"a steady state was assumed to be reached."

(Line 194 – 197) as:
"… when evaluating the OFR settings, especially under the high UV light dose settings in the 1st-round experiments. Our evaluation on photolysis of the precursor and HOMs shows that photolysis was not a contributor to our observation on C9 and C18 HOM formation."

(Line 200) as:
"photolysis-to-OH reaction for 1,3,5-TMB in"

(Line 205) as:
"Master Chemical Mechanism (MCM)"

(Line 207) as:
"to be around …"

(Line 218 – 219) as:
"while RH and irradiances were not changed, as an increase in the precursor concentration corresponds to a larger sink for OH."

(Line 221) as:
"$O(^1D)$ in the …"

(Line 237) as:

"of our nitrate CIMS …"

(Line 241 – 243) as:

"as discussed below."

(Line 244 – 245) as:

"Vocus PTR was applied to quantify precursor concentrations."

(Line 268) as:

"are thus of a …"

(Line 279) as:

"To compare chemical regimes of two …"

(Line 410) as:

"the Vocus PTR. Consumption of …"

(Line 416) as:

"PAM_chem_v8 model"

(Line 422 – 423) as:

"The ratios of between HO_2/OH and RO_2/OH in the 1st-round experiments were generally in the same order of magnitude as those in with the ambient atmosphere …"

(Line 430) as:

"atmospheres"

(Line 480 – 485) as:

"As a result, relative proportions of autoxidation and condensation were lowered. On the other hand, 1,3,5-TMB-derived BPR was suggested to undergo autoxidation ($R7$) at a reaction rate of 0.078 s^{-1} (Wang et al., 2017), which represented 36.8%, 94.4%, and 92.8% of the overall rates of $R1 – R3$ and $R5 – R7$ in Exp. 1-12, Exp. 2-3, and summertime, urban Beijing, respectively. Because of its dominant proportion in Exp. 2-3 and the ambient, the autoxidation channel is not included for clarity in Figure 1a. Autoxidation did …"

(Line 494) as:

"the other reaction channels"

(Line 503) as:

"in the Exp. 2-3, and were 5.3%, 6.5%, 87.0%, and 1.2%"

(Line 512) as:

"that is at least 2"

(Line 514) as:
"In laboratory experiments"

(Line 529 – 530) as:
"the detailed formulae of monomer RO_2 could be probed"

(Line 554) as:
"Therefore, even if the …"

(Line 560 – 562) as:
"are estimated to have saturation vapor concentrations (C*) of 30.20, 30.20, 0.85, and 3.39 μg/m^3 at 300 K, respectively with the volatility parameterization developed in the CLOUD chamber oxidation experiments of aromatics"

(Line 565 – 566) as:
"Compared to ambient conditions, the proportion of their condensation in the laboratory"

(Line 570) as:
"are completely different for …"

(Line 582 – 588) as:
"By assuming a similar diffusion coefficient of LVOCs and ELVOCs to that of sulfuric acid, the lifetimes of LVOCs and ELVOCs in the ambient still can still be as high as 77 s for the condensation loss, which is close to the residence time of our PAM OFR. Therefore, if they were generated by oxidation of aromatics in the ambient, these LVOCs and ELVOCs should at least have the potential to experience the same OH exposures as those in our low [OH] experiments, i.e., at least 5.86×10^8 molecule cm^{-3} s."

(Line 614 – 616) as:
"compare the abundance of HOM monomer and HOM dimer crossly here, but to pay attention to the molecular characterization."

(Line 643) as:
"as recommended by MCM,"

(Line 810 – 813) as:
"On the other hand, the loss pathways of HOM dimers were not exactly the same as the ambient as discussed in the last two paragraphs of Section 3.1. This …"

(Line 902 – 903) as:
"the larger proportion"

We have also revised the figure and table captions in the supplement.

We have revised the table caption of Table S2 as:

"Table S2. Reactions included in the modified PAM_chem_v8 model under the settings with only 254 nm UV lights on. For experiments in the absence of NO_x, the input value of N_2O is 0 and all the NO_x-related reactions actually proceed with a zero rate. RO_2 is the sum of BPR and $C_9H_{13}O_7\cdot$ for simplification."

the table caption of Table S6 as:

"Table S6. The C9 and C18 products detected by nitrate CI-ToF in Exp. 2-3. The exact mass is the mass without an adduct of a reagent ion of NO_3^-. "--" stands for the signal of a compound was below the detection limit."

the figure caption of Figure S1 as:

"Figure S1. (a) Concentration profiles of OH, HO_2, BPR, and total RO_2 in the 1st-round experiments in the absent of NO_x in the PAM OFR as a function of OH exposures. The average total concentrations of RO_2 and BPR were scaled with a factor of 0.1 for a better visualization. (b) Concentration profiles of OH, HO_2, BPR, and total RO_2 in the 1st-round experiments in the presence of NO_x in the PAM OFR as a function of OH exposures. The average total concentrations of RO_2 were scaled with a factor of 0.9 for a better visualization."

and the figure caption of Figure S2 as:

"Figure S2. MS comparison of the (a) monomer products between Exp. 1-3 and Exp. 1-19, (b) dimer products between Exp. 1-3 and Exp. 1-19, (c) monomer product MS between Exp. 1-12 and Exp. 1-22, and (d) dimer products between Exp. 1-12 and Exp. 1-22. The signals of HOMs were raw ones in the nitrate CIMS."

We have also corrected the incorrect hyphens in our manuscript with En Dashes.

We have revised our manuscript (Line 203) as:

"~ $3.9\times10^{-18} - 3.9\times10^{-17}$"

(Line 438) as:

"and $(4 - 28)\times10^8$, $(0.8 - 2.4)\times10^7$"

(Line 457) as:

"(R1 – R3 and R5 – R9)"

(Line 482) as:

"of $R1 - R3$ and $R5 - R7$"

(Line 496) as:

"($R1 - R3$, $R5 - R6$, and $R8 - R9$)"

(Line 514 – 516) as:

"the proportions of $R8 - R9$, i.e., the NO channel in the urban atmosphere were attributed to termination reactions of $R1 - R6$,"

(Line 853) as:

"($x = 12 - 15$)"

(Line 863) as:

"($m = 7 - 11$)"

(Line 877) as:

"($R8 - R9$)"

(2) Somewhat strange statements persist in the text, like "Formation of HOMs is typically triggered by oxidation of VOCs in the gas phase." – how else they could be formed?

R2. We are sorry for the unsuitable statements in the manuscript. We have revised our manuscript (Line 59) as:

"Formation of HOMs is triggered by oxidation of VOCs in the gas phase."

(3) PAM name comes from "potential aerosol mass". Please correct.

R3.

We have revised our manuscript (Line 29 – 30) as:

"with a potential aerosol mass oxidation flow reactor (PAM OFR)"

and (Line 148 – 149) as:

"investigated in a potential aerosol mass oxidation flow reactor (PAM OFR)"

(4) Add important experimental details to the main paper

R4. We have integrated Section S1 in the supplement into Section 2 in the main text of the manuscript.

We have revised our manuscript (Line 288 – 294) as:

"In this work, autoxidation and accretion of 1,3,5-TMB-derived BPR, as well as subsequent reactions of the autoxidation product of BPR, i.e., $C_9H_{13}O_7\cdot$, are newly implemented or modified in this model (Reaction No. 46 – 62 in Table S2). These two radicals were the most significant RO_2 in the system and represented the whole RO_2 pool in the PAM chemistry model simulation. The pathways of peroxy radicals and their kinetics are discussed below. NO_x-related reactions are also included in the model. When experiments without NO_x are simulated, these NO_x-related reactions do not contribute to the simulation results.

"

(Line 304 – 388) as:

"The reaction rate constants for RO_2 in $R1 - R5$ are obtained by MCM or previous investigations (e.g., Jenkin et al., 2003; Berndt et al., 2018; Peng and Jimenez, 2020). We treat $R1 - R3$ as a total

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reaction with a reaction rate constant of 8.8×10^{-13} molecule^{-1} cm^3 s^{-1}, and branching ratios of $R1 - R3$ of 0.6, 0.2, and 0.2, respectively, as suggested by MCM (Jenkin et al., 2003). The reaction rate constants of BPR and $C_9H_{13}O_7\cdot$ for $R4$ are 1.7×10^{-10} and 2.6×10^{-10} molecule^{-1} cm^3 s^{-1}, respectively (Berndt et al., 2018). The reaction rate constants for $R5$ is 1.5×10^{-11} molecule^{-1} cm^3 s^{-1} (Jenkin et al., 2003).

$R6$ is the reaction between OH and RO$_2$, whose reaction rate constant is 1×10^{-10} molecule^{-1} cm^3 s^{-1} according to previous studies (Bossolasco et al., 2014; Yan et al., 2016; Assaf et al., 2016, 2017; Peng and Jimenez, 2020). Current knowledge on the reaction products for the reaction of $CH_3O_2\cdot$ + OH, the most studied RO$_2$ + OH reaction, is summarized in Table S3. The products of this reaction are suggested to include a Criegee intermediate ($CH_2O_2\cdot$), a stabilized methylhydrotrioxide (CH_3OOOH), an alkoxy radical ($CH_3O\cdot$), and methanol (CH_3OH) (Yan et al., 2016; Fittschen, 2019; Caravan et al., 2018; Müller et al., 2016). Müller et al. (2016) and Caravan et al. (2018) suggested that the formation of $CH_2O_2\cdot$ is actually infeasible, and Yan et al. (2016) estimated an upper limit branching ratio of 5% for this pathway. The branching ratios of stabilized products CH_3OH and CH_3OOOH are 6 – 7% (Caravan et al., 2018; Müller et al., 2016) and 7% (Müller et al., 2016), respectively. The most significant product of this reaction is the alkoxy radical ($CH_3O\cdot$), with a branching ratio of more than 86% (Müller et al., 2016). In the absence of NO$_x$, CH_3OH and $CH_3O\cdot$ can also be formed via the traditional unimolecular reaction between $CH_3O_2\cdot$ and RO$_2$, i.e., $R1$ and $R3$. The possible role of this reaction of large RO$_2$, i.e., BPR and other C9-RO$_2$, with OH has not yet been investigated. However, according to the branching ratios for the reaction of $CH_3O_2\cdot$ + OH, this reaction is likely to form RO instead of stabilized C9 products. Hence, we assume that the branching ratios of hydrotrioxide (ROOOH), RO, and ROH are 0.07, 0.86, and 0.07, respectively, for BPR + OH and C9-RO$_2$ + OH.

$R7$ is the unimolecular reactions of RO$_2$ in the PAM OFR. RO$_2$ isomerization rate coefficients are highly dependent on their structures, spanning from 10^{-3} – 10^6 s^{-1} (Bianchi et al., 2019; Crounse et al., 2013; Knap and Jørgensen, 2017; Praske et al., 2018). However, only some substituted acyl RO$_2$ can undergo rapid isomerization at a reaction rate of 10^6 s^{-1} (Knap and Jørgensen, 2017). 1,3,5-TMB-derived BPR and its autoxidation product, $C_9H_{13}O_7\cdot$, do not belong to this group of substituted acyl RO$_2$ (Molteni et al., 2018; Tsiligiannis et al., 2019). The most important unimolecular reactions for 1,3,5-TMB-derived BPR is likely autoxidation while the precise autoxidation reaction rates of 1,3,5-TMB-derived BPR and other RO$_2$ in this system are currently unclear (Bianchi et al., 2019; Molteni et al., 2018). Previous theoretical investigations suggest that more than 90% BPR generated by the oxidation of 1,3,5-TMB possess a structure favoring autoxidation and thus their overall autoxidation reaction rate is relatively fast (Wang et al., 2017). We follow quantum calculation results on the autoxidation reaction of a methyl group adjacent to the RO$_2$ functionality group (Wang et al. 2017), and time the suggested rate (0.026 s^{-1}) by 3 due to the symmetry with three methyl groups in our parent compound. The obtained autoxidation reaction rate is 0.078 s^{-1}.

$R8$ and $R9$ are the reactions between NO and RO$_2$, generating alkoxy radicals and organonitrates, respectively. The reaction rate for the sum of these two reactions is 8.5×10^{-12} molecule^{-1} cm^3 s^{-1}. The branching ratios of these two reactions are 0.843 and 0.157, respectively, according to MCM (Jenkin et al., 2003).

Alkoxy radicals, RO, will be generated in $R1$, $R6$, and $R8$. The widely used near-explicit mechanism, MCM, assumes that RO formed via the alkoxy channel of BPR ($R1$) will decompose into small molecules. Recently, Xu et al. (2020) probed the chemical fates of BPR-derived RO, hereafter referred to as bicyclic alkoxy radical (BCP-oxy), in the oxidation of benzene by laboratory experiments and model calculations, which can be taken as a reference to induce the mechanism of 135-TMB-

derived BCP-oxy. BCP-oxy can undergo two reactions, i.e., ring-breakage and ring-closure, and a new calculation result suggests that the branching ratio of ring-breakage reaction is larger than 98% (Wang et al., 2013). 56% of ring-breakage reactions will break benzene-derived BCP-oxy into butenedial and glyoxal, and the rest 44% will generate a C6 alkyl radical by a 1,5-aldehydic H-shift. The latter C6 alkyl radical will further undergo other reactions, including a 93% branching ratio for decomposition reactions that results in a reduction of carbon atom number (Xu et al., 2020). Therefore, most of benzene-derived BCP-oxy will likely decompose into compounds with fewer carbon atoms. We assume that 1,3,5-TMB-derived BCP-oxy will undertake these decomposition reactions with a similar branching ratio, which means that these radicals cannot form a large number of stabilized products that can influence the distributions of stabilized C9 products in nitrate CIMS.

R10 is the physical loss of RO_2. The physical loss of RO_2 in the PAM OFR consists of the condensation loss to the aerosol particles and the diffusion loss to the OFR walls. In our experiments, measurement results by a long-SMPS show that the aerosol particles presented in the PAM OFR were few. The long SMPS consisted of a long-DMA (TSI model 3081) and a CPC (TSI model 3787), covering a particle number size distribution from 13.6 nm to 736.5 nm. Thus, though not detected in this study, we cannot absolutely deny the possibility that particles might have been generated, resulting in a larger physical loss of HOMs. This part of physical loss might be underestimated. The first-order loss rate of HOMs to the OFR walls, k_{wall}, is limited by eddy diffusion and can be calculated with the following function (Cheng et al., 2021; Palm et al., 2016; McMurry and Grosjean, 1985):

$$k_{wall} = \frac{A}{V} \cdot \frac{2}{\pi} \cdot \sqrt{k_e D_g} \qquad (Eq1)$$

where the OFR surface-area-volume ratio (A/V) is 25 m^{-1} and the coefficient of eddy diffusion (k_e) is 0.0042 s^{-1}, as estimated by the method utilized in a previous study (Brune, 2019) and given in Eq2.

$$k_e = 0.004 + 10^{-2.25} V^{0.74} \qquad (Eq2)$$

where V is the enclosure volume (m^3). The molecular diffusion coefficient, D_g, is estimated with the method as described by Fuller et al. (1966) and is around 5×10^{-6} m^2 s^{-1} with 1,3,5-TMB derived BPR as an example. Hence, k_{wall} is around 0.0023 s^{-1} in the PAM OFR.

Other kinetic data in the modified PAM_chem_v8 model are obtained from the IUPAC (International Union of Pure and Applied Chemistry) dataset (https://iupac-aeris.ipsl.fr, last access: 26 October 2023) and the MCM dataset (MCM v3.3.1, https://mcm.york.ac.uk/MCM/, last access: 9 October 2023).
"

(Line 533 – 534) as:
"as discussed in the fourth last paragraph of Section 2."

(Line 538 – 539) as:
"The concentrations of these two radicals were estimated by PAM_chem_v8."

and (Line 579 – 580) as:
"the physical loss in our PAM OFR, i.e., 0.0023 s^{-}"

(5) Please use consistent concentration units throughout the text.

R5. We have used the concentration unit of molecular cm^{-3} throughout the manuscript and supplement.

We have revised our manuscript (Line 166 – 168) as:

"leading to 7.08×10^{11} – 1.54×10^{12} molecule cm^{-3} of 1,3,5-TMB in the 1st-round experiments, and 7.55×10^{11} or 8.45×10^{11} molecule cm^{-3} of 1,3,5-TMB in the 2nd-round experiments …"

(Line 179 – 181) as:

"resulting in an initial ozone concentration of around 1.05×10^{13} – 2.16×10^{13} molecule cm^{-3} in the OFR in the 1st-round experiments and 3.01×10^{12} – 3.72×10^{12} molecule cm^{-3} in the 2nd-round experiments, respectively."

(Line 213 – 216) as:

"generally resulting in two NO$_x$ levels, 4.41×10^{10} molecule cm^{-3} NO + 1.72×10^{12} molecule cm^{-3} NO$_2$ (Exp. 1-41 – 1-54) and 1.18×10^{11} molecule cm^{-3} NO + 2.94×10^{12} molecule cm^{-3} NO$_2$ (Exp. 1-55 – 1-68) at the exit of the OFR."

(Line 218) as:

"were adjusted in a large range from 4.09×10^{11} to 2.06×10^{12} molecule cm^{-3}"

(Line 223 – 225) as:

"which also resulted in fluctuations in the NO concentrations ([NO]) from 3.19×10^{10} to 1.74×10^{11} molecule cm^{-3} and the NO$_2$ concentrations ([NO$_2$]) from 2.70×10^{11} to 9.31×10^{11} molecule cm^{-3}."

(Line 403 – 406) as:

"53 s, 0.63%, 1.23×10^{13} molecule cm^{-3}, and 1.23×10^{12} molecule cm^{-3}, respectively, as measured directly. For the 2nd-round experiments, the input parameters of O$_3$ concentration and the initial 1,3,5-TMB concentration were updated as 3.68×10^{12} molecule cm^{-3} and 7.55×10^{11} molecule cm^{-3}, respectively."

(Line 521 – 524) as:

"as an example, [OH] = ~6.77×10^{8} molecule cm^{-3}, NO = ~4.73×10^{10} molecule cm^{-3}. NO$_2$ = ~1.67×10^{12} molecule cm^{-3}), low [OH] experiments (Exp. 2-7 as an example, [OH] = ~1.69×10^{7} molecule cm^{-3}, NO = ~3.19×10^{10} molecule cm^{-3}. NO$_2$ = ~2.70×10^{11} molecule cm^{-3}),"

and (Line 726 – 727) as:

"The averaged mass spectrometry of nitrate CIMS in the 4.41×10^{10} molecule cm^{-3} NO experiment and 1.18×10^{11} molecule cm^{-3} NO experiment …"

We have revised Table S1 in the supplement as:
"

Table S1. Summary of experimental conditions.

No.	Initial concentration of 1,3,5-TMB	O$_3$ concentration ($\times10^{12}$	NO concentration ($\times10^{10}$ molecule cm^{-3})	NO$_2$ concentration ($\times10^{11}$ molecule cm^{-3})	Estimated OH exposure based on the precursor

	($\times 10^{11}$ molecule cm^{-3})	molecule cm^{-3})*			consumption ($\times 10^9$ molecule cm^{-3} s)
1-1	13.4	11.0	0	0	18.5
1-2	14.4	11.1	0	0	11.2
1-3	15.4	11.4	0	0	5.2
1-4	9.4	10.6	0	0	44.0
1-5	9.8	10.8	0	0	40.9
1-6	10.1	10.9	0	0	34.8
1-7	10.3	11.1	0	0	28.7
1-8	10.7	11.3	0	0	21.9
1-9	11.2	11.5	0	0	13.3
1-10	11.5	11.7	0	0	6.3
1-11	11.7	11.8	0	0	5.9
1-12	11.8	11.8	0	0	44.9
1-13	11.9	10.5	0	0	39.8
1-14	11.7	10.6	0	0	35.9
1-15	11.7	10.9	0	0	31.5
1-16	12.0	11.0	0	0	26.8
1-17	12.1	11.2	0	0	18.9
1-18	12.2	11.4	0	0	11.3
1-19	12.3	11.8	0	0	5.3
1-20	7.1	10.5	0	0	48.7
1-21	7.7	10.5	0	0	48.1
1-22	8.0	10.5	0	0	44.1
1-23	8.2	10.8	0	0	38.1
1-24	8.3	11.0	0	0	32.5
1-25	8.4	11.1	0	0	23.8
1-26	8.5	11.4	0	0	16.1
1-27	12.2	10.4	0	0	41.9
1-28	12.4	10.6	0	0	37.8
1-29	12.3	10.8	0	0	34.3
1-30	12.4	11.0	0	0	29.7
1-31	12.6	11.2	0	0	24.4
1-32	12.6	11.4	0	0	17.8
1-33	12.9	11.7	0	0	10.6
1-34	11.4	10.5	0	0	43.5
1-35	11.6	10.7	0	0	38.5
1-36	11.7	10.8	0	0	35.2
1-37	12.0	11.0	0	0	30.1
1-38	12.3	11.3	0	0	25.6
1-39	12.4	11.4	0	0	18.1
1-40	12.6	11.7	0	0	11.6
1-41	7.3	21.2	4.9	14.7	31.1
1-42	9.1	21.0	4.5	15.7	28.9
1-43	10.9	20.9	4.6	16.4	27.3
1-44	12.8	20.9	4.3	16.7	25.7
1-45	14.6	21.0	4.2	17.2	24.1
1-46	16.6	21.0	4.0	17.4	22.6
1-47	6.6	21.1	4.8	15.9	31.9
1-48	7.7	21.4	4.7	16.7	30.9
1-49	9.7	21.4	4.5	17.2	28.6
1-50	11.4	21.5	4.3	17.6	27.0
1-51	13.5	21.6	4.2	17.9	25.3
1-52	15.9	21.6	4.0	18.1	23.6
1-53	18.0	21.2	3.9	18.4	21.9

1-54	20.6	21.6	3.9	19.1	20.6
1-55	7.2	17.5	11.8	25.5	39.8
1-56	8.7	17.2	11.8	27.2	37.7
1-57	4.1	17.0	13.0	26.7	41.8
1-58	5.6	17.1	12.8	27.4	41.4
1-59	7.3	17.1	12.0	28.7	38.4
1-60	8.8	1.71	11.5	29.2	36.2
1-61	10.1	1.71	11.1	29.9	34.3
1-62	11.4	16.9	11.3	31.4	33.1
1-63	12.8	17.0	11.0	31.9	31.8
1-64	6.1	16.5	13.4	30.6	38.9
1-65	7.6	16.7	13.0	31.1	36.8
1-66	9.0	16.9	12.3	32.1	34.7
1-67	10.4	16.9	12.0	32.3	33.3
1-68	11.9	16.9	11.4	32.8	32.2
2-1	7.6	3.6	0	0	5.5
2-2	7.6	3.7	0	0	2.4
2-3	7.6	3.7	0	0	1.0
2-4	7.6	3.7	0	0	0.6
2-5	8.5	3.0	17.4	9.3	3.1
2-6	8.5	3.4	7.6	5.2	2.0
2-7	8.5	3.5	3.2	2.7	0.9

"

and the figure caption of Figure S3 as:

"**Figure S3.** Average MS of HOMs detected by nitrate CIMS in the 1st-round experiments with NO_x, presented with the averaged normalized signals in 4.41×10^{10} molecule cm^{-3} NO + 1.72×10^{12} molecule cm^{-3} NO_2 and 1.18×10^{11} molecule cm^{-3} NO + 2.94×10^{12} molecule cm^{-3} NO_2 experiments. For comparison, the MSunder the low NO_x experiments is shown in opposite values.
"

(6) Figures and Tables must be introduced before they appear.

R6. We have moved the introduction of Figure 1 before its first appearance.

We have revised our manuscript (Line 433 – 444) as:

"We take Exp. 1-12 ([OH] = ~8.47×10^8 molecule cm^{-3} and NO_x = 0) and Exp. 2-3 ([OH] = ~1.64×10^7 molecule cm^{-3} and NO_x = 0) as representative examples and compare simulation results with those from the ambient atmosphere, since NO_x in the ambient is believed not to impact relative ratios for $R1 – R3$, $R5$, and $R6$. In the ambient atmosphere, the average [HO_2], [OH], and [RO_2] were 2.7×10^8, 8.0×10^6, and 1.4×10^9 molecule cm^{-3}, respectively, around summertime noon in urban Beijing (Whalley et al. 2021), and (4 – 28)×10^8, (0.8 – 2.4)×10^7, and 1.2×10^9 molecule cm^{-3} (modeled) at a suburban site in Yangtze River Delta (Ma et al. 2022). As shown in Figure 1a, for the most important RO_2, BPR, the fractions of monomeric termination reactions of $RO_2 + RO_2$ ($R1 – R3$), $RO_2 + HO_2$ ($R5$), and $RO_2 + OH$ ($R6$) were 6.2%, 29.3%, and 64.5%, respectively, in Exp.1-12. In contrast, the fractions were 32.5%, 31.8%, and 35.7%, respectively, in Exp. 2-3, whereas the values were 20.3%, 66.6%, and 13.2%, respectively, for summertime, urban Beijing."

We have also moved Scheme 1 before its first appearance (Line 679 – 684).

(7) Please explain the disappearance of dimers during NOx experiments, although the monomer signals are higher in this specific experiment.

R7. The dramatic decrease in the abundance of HOM dimers after the introduction of NO_x into the aromatic oxidation system have been reported in several previous studies (Garmash et al., 2020; Wang et al., 2020; Tsiligiannis et al., 2019), which might be a result from the competition of the NO_x channel. Our current understanding on the kinetics and mechanisms of the formation of HOM dimers is still incomplete, which limits us from obtaining an accurate estimation of the accretion reactions for every RO_2. We can only deduce that this disappearance came from the significant decrease of the signals of HOM dimers, which were below the detection limit of our instruments, as we discussed in the last reply.

We have revised our manuscript (Line 872 – 875) as:

"in the NO_x-present experiments in the 2nd-round experiments. Such a dramatic decrease in the abundance of HOM dimers after the introduction of NO_x into the aromatic oxidation system has been reported in several previous studies (Garmash et al., 2020; Wang et al., 2020b; Tsiligiannis et al., 2019)."

(8) It is apparent that the "tracked changes" version does not contain all the changes. For example, compare the lines 80-100 in this and the previous submission. Please address this issue.

R8. We are very sorry for this mistake. The formulas of BPR and its autoxidation product came with typos in the first version and were corrected by us in the last version.

We have revised our manuscript (Line 76 – 81) as:

"previous studies suggest that the main products of OH-initiated oxidation of alkylbenzenes (C_xH_{2x-6}, x=7, 8, or 9), i.e., bicyclic peroxy radicals (BPR, $C_xH_{2x-5}O_5\cdot$, x=7, 8, or 9) (Jenkin et al., 2003), can undergo an autoxidation reaction and form a new peroxy radical, $C_xH_{2x-5}O_7\cdot$ (x=7, 8, or 9) (Wang et al., 2017). The autoxidation of BPR could be fast if it has a favorable structure, as found in a previous study (Wang et al., 2017). On the other hand, the structure of resulting $C_xH_{2x-5}O_7\cdot$ is strongly different from that of BPR,"

(Line 86 – 87) as:

"atoms in stabilized first generation monomer and dimer products, respectively, formed from $C_xH_{2x-5}O_7\cdot$ (Molteni et al., 2018; Wang et al., 2020b; Mentel et al., 2015; Berndt et al., 2018b)."

We added Reactions No. 2 – No. 5 into Table S2 in the last reply, which have been included in the model but not listed in the first version.

We have revised Table S2 as:
"

No	Reactions	Reaction rate constants/photolysis rate (molecule^{-1} cm^3 s^{-1}/ s^{-1})
1	$HO_2 + h\nu$ ($\lambda = 254$ nm) $= OH + O(^1D)$	$2.63\times10^{-19}\times flux_{254}$
2	$O_3 + h\nu$ ($\lambda = 254$ nm) $= OH + O(^1D)$	$1.03\times10^{-17}\times flux_{254}$
3	$H_2O + O(^1D) = 2OH$	$1.63\times10^{-10}\times e^{60/T}$
4	$N_2 + O(^1D) = O(^3P)$	$2.15\times10^{-11}\times e^{110/T}$
5	$O_2 + O(^1D) = O(^3P)$	$3.30\times10^{-11}\times e^{55/T}$
6	$O_3 + O(^1D) = 2O_2$	1.20×10^{-10}

7    $O_3 + O(^1D) = O + O + O_2$ 1.20×10^{-10}
…"

We deleted the serial number in Table S5 in the last reply, but it cannot be shown in the "track changes" mode of Word.

We have checked the manuscript thoroughly and made sure all other changes have been included in the "tracked changes".

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