Point-by-point response to the reviewers' comments on the manuscript entitled "Speciated Measurement of Bicyclic Peroxy Radicals via Iodide-CIMS and its Implication on OH-Initiated Aromatic Oxidation"

We sincerely appreciate the professional and constructive feedback from the reviewers on our manuscript. We have meticulously addressed these insightful comments by the reviewers, leading to significant improvement in the manuscript. Our responses to each comment are presented in normal font, and any modifications or additions to the manuscript are given in blue for clarity.

Response to Reviewer #2

General comments

In this manuscript to authors describe an experimental study aimed at determining the branching ratio for the formation of products from bicyclic peroxy radicals (BPR) by making direct measurements of BPR using an iodide chemical ionization mass spectrometer. The measurement methods were optimized to detect BPR at concentrations of ~1 ppt, and various standards and reactions of toluene and xylene with OH radicals under variable NO and HO2 conditions were studied. The results were interpreted using a kinetic model to determine RO2 concentrations and then branching ratios for BPR formation are compared to those determined by others from product yield measurements.

The experiments were very well done, and the overall technical quality of the paper is excellent. The data analysis was also carefully conducted, and the interpretation of the results are reasonable. This is impressive work and opens the possibility for future studies of RO_2 *radicals that are key reactive intermediates in the atmospheric oxidation of volatile organic compounds. I recommend publication in ACP after the following minor comments are addressed.*

We are grateful for the valuable feedback provided by the reviewer. We will address each of comments individually below.

Comments：

1. *These reactions are known to form secondary organic aerosol (SOA), which is not discussed here. How could SOA affect the quantitation of* $[RO_2]$ *by removing gas phase molecular products and* RO_2 *radicals by gas-particle partitioning?*

Response:

Thanks for your question. We acknowledge that a certain fraction of aromatic oxidation products might contributed to SOA formation in our experiments conducted even in the absence of seed aerosol. However, we do not consider gas-particle partitioning to be a removing pathway of gas phase molecular products and RO_2 radicals here. The main reason is that the OH exposure in our experiments was relatively low. In the calibration reactor, the residence time was only 3–4 s, and in the flow tube experiment about 90 s, corresponding to OH exposures on the order of 10^9–10^{10} molecular cm^{-3} s. By contrast, in our previous smog-chamber study, oxidation proceeded for ~5 h, yielding OH exposures exceeding 10^{11} molecular cm^{-3} s. Even then, most early-generation products had reached steady state and the observed SOA molar yields still remained below 1% (He et al., 2023). This comparison highlights that, under the relatively modest OH exposures of the present experiments, gas–particle partitioning of early-generation products is expected to be negligible. Therefore, the gas-particle partitioning was not be considered in the quantitation of BPRs. A brief analysis of potential additional sinks of BPRs—beyond bimolecular reactions and physical losses, including the possible influence of SOA—has been added to the *Methods* section of the revised manuscript.

(Changes to the fourth paragraph in "BPRs calibration: system and quantitative method" section) "In contrast, the sinks of RO_2 are highly complex, including physical removal (e.g., wall loss), bimolecular reactions with NO, HO_2, and RO_2, as well as unimolecular reactions, gas-particle partitioning and other potentially unidentified pathways."

(Changes to the fourth paragraph in "BPRs calibration: system and quantitative method" section) "Other potential sinks were not included here, since under the high HO_2 conditions of our experiments, unimolecular reactions are not competitive with bimolecular reactions. In addition, previous studies have shown that SOA formation from early-generation aromatic products remains very low (less than 1%) without seed aerosol."

Comments:

2. *What are the lifetimes of initially formed cyclic peroxy radicals (CPR) with regards to ring closure and O_2 addition to form BPR and how does this compare to the experiment timescale? How do you know you are measuring all BPR that will be formed in the reaction, and if not, what are the consequences?*

Response:

We thank the reviewer for his insightful question. Under atmospheric conditions, cyclic peroxy radicals (CPRs) are rapidly formed from aromatic–OH adducts undergo O_2 addition and intramolecular cyclization, with reported cyclization rates on the order of 10^4–10^6 s^{-1} (Wu et al., 2014). As a result, CPR lifetimes are less than 10^{-4} s. This is several orders of magnitude shorter than the residence times in either the calibration reactor (3–4 s) or the OFR (~90 s).

With regard to the quantification of BPR yields, we have corrected the observed concentrations by accounting for its major sinks, including physical loss processes and bimolecular reactions with NO, HO_2, and RO_2, as described in Section 2.4. Following Galloway et al. (2011), the product yield was defined as the amount of product formed per unit of precursor consumed. In this study, the yield of a product R was calculated as (Xu et al., 2020):

$$Y_R = \frac{\Delta[R]^{corrected}}{\Delta[Precursor]} = \frac{F \cdot \Delta[R]}{\Delta[Precursor]}$$

where $\Delta[R]$ and $\Delta[R]^{corrected}$ represent the amount of R formed before and after correction for secondary loss, respectively. $\Delta[Precursor]$ represents the reacted amount of toluene or m-xylene. F is the correction factor for secondary loss of R which can be calculated by Eq.11. Therefore, though we could miss some BPR due to its physical and chemical losses in the reactor, these processes have been seriously considered and accounted during the BPR yield calculation.

Comments:

3. *This equation does not include losses by RO_2 + RO_2 reactions. Berndt et al. 2018 measured rate constants for self-reactions of BPR near the collision limit, and since [BPR] in Figure 5 are ~ 1 ppb, could these reactions also be sinks?*

Response:

Thanks for noticing this. $RO_2 + RO_2$ reactions are indeed important sinks. The main products of self- and cross-reactions of RO_2 radicals are either alkoxy radicals (RO), which subsequently undergo fragmentation to form ring-opening products, or alcohols (ROH) together with carbonyl compounds [R′(–H, =O)]. Such products were detected as ring-opening tracers, including bicyclic alcohols and carbonyls, for example $C_7H_8O_4$ and $C_7H_{10}O_4$ from toluene oxidation and $C_8H_{10}O_4$ and $C_8H_{12}O_4$ from *m*-xylene, as shown in Scheme S1 and S2. In our initial analysis, we indeed considered $RO_2 + RO_2$ reactions. By using the generic rate constant recommended by the MCM (8.8×10^{-13} cm^3 s^{-1}), their contribution was estimated to be less than 1%. We sincerely thank the reviewer for pointing out that this treatment may underestimate the importance of such reactions.

BPRs accounted for the majority of RO_2 in our system, so their self-reaction is undoubtedly the dominant $RO_2 + RO_2$ pathway in the calibration experiments, based on the box-model analysis in Section S4. However, there are only few studies reporting rate constants for this process. MCM approximates $RO_2 + RO_2$ reactions with a single generic rate constant of 8.8×10^{-13} molecular cm^3 s^{-1}, representing an average value across different RO_2 types. By contrast, a previous study reported self- and cross-reaction rate constants (~ 2×10^{-10} molecular cm^3 s^{-1}) for BPRs derived from trimethylbenzene approaching the collision limit (Berndt et al., 2018), much higher than the generic MCM value and also substantially higher than the rate constants reported by other studies (Jenkin et al., 2019) for functionalized RO_2, like alkyl RO_2 radicals.

To further evaluate this, we performed box-model simulations of the xylene calibration system. The models were initiated with the measured concentrations of m-xylene (10ppbv), NO (0.5ppbv) and HO_2 radicals (7.51×10^{11} molecules cm^{-3}) at the exit of the flow tube. The initial OH radical concentrations (4.5×10^9 molecules cm^{-3}) were tuned in order to match the OH exposure. Here, two scenarios were compared: M0, which used the MCM-recommended rate constant for RO_2 self reaction (8.8×10^{-13} molecular cm^3 s^{-1}), and M1, which differed only by replacing this value with the higher rate constant reported by Berndt et al. (2018) (2×10^{-10} cm^3 s^{-1}). As shown in Figure R2, the measured yields of $RO_2 + RO_2$ reaction products are much closer to the results from M1 than M0, supporting the use of the higher rate constant in our system. Accordingly, we adopted the Berndt et al. (2018) value as a reasonable approximation in this work. With this adjustment, the sensitivity of BPRs changed by ~20% and the calculated yields changed by 10–20% compared with our earlier results. We are grateful to the reviewer for highlighting this point, which has significantly improved the completeness and robustness of our analysis. All formulas related descriptions involving the $RO_2 + RO_2$ reactions and the changed results have been revised accordingly in the manuscript and SI.

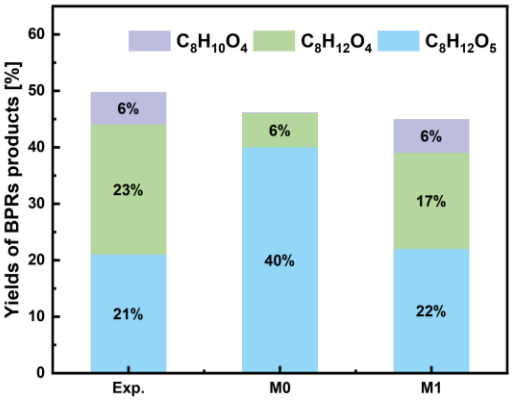

Figure R2. Effect of $RO_2 + RO_2$ rate constants on the simulated product yields of BPRs compared with experiment

(Changes to the fourth paragraph in "BPRs calibration: system and quantitative method" section) "As BPRs accounted for the majority of RO_2 in our system (~86% according to the box-model analysis in Section S4), their self-reaction represented the dominant $RO_2 + RO_2$ pathway. We therefore adopted the self-reaction rate constants of BPRs reported in recent studies and explicitly included this process in the quantification of BPRs."

(Changes to the third paragraph in "Quantification and Sensitivities of BPRs measurement" section) "The resulting sensitivities, calculated using Equation 8, are presented in Figure 5e, 5f, with sensitivities of 0.32 ± 0.04 and 0.61± 0.03 ncps/pptv for toluene-BPRs and m-xylene -BPRs, respectively, at a time resolution of 1 min."

(Changes to the last paragraph in "Mechanistic Analysis for Aromatics Oxidation Experiments" section) "Figure 6 also demonstrates the differences (filled with light grey) ranging from 4% to 9%, between the product-yield method and the direct measurement of BPRs method (outlined in red box)."

(Changes to the second paragraph in "Summary and conclusions" section) "Based on the direct measurement of BPRs, the other pathways of BPRs, which were not incorporated in current MCM, may account for approximately 4%-9% of the missing carbon flux during our oxidation experiments, as illustrated in Figure 6."

(Changes to the SI) The following kinetic reaction model analysis (including the following Figure) of the RO_2 fraction has been added to the SI as Section S4.

"Figure S9 shows the relative contributions of the two main RO_2 radicals, BPRs and MXYLO2 ($C_8H_9O_2$), in the calibration experiments. MXYLO is the first-generation RO_2 formed in the benzaldehyde pathway. As shown, BPRs dominate in the initial stage of the reaction, accounting for ~86% of the total RO_2."

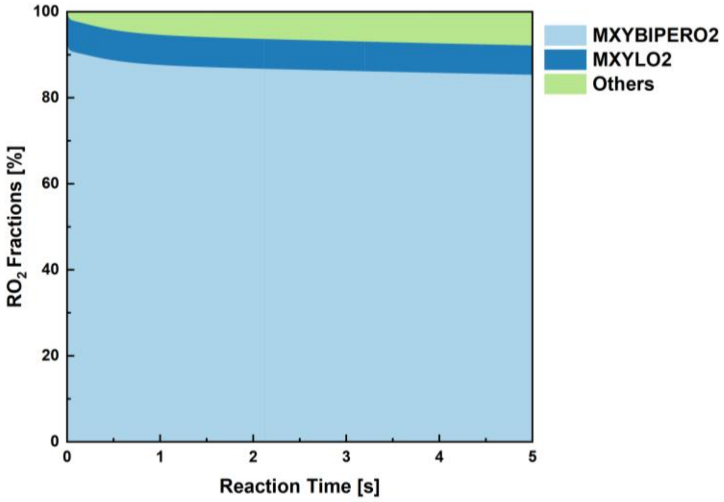

Figure S9 The fraction of RO_2 radicals according to the calibration flow tube kinetic model.

(Changes to Figure 5) The sensitivities results have been corrected in following figure.

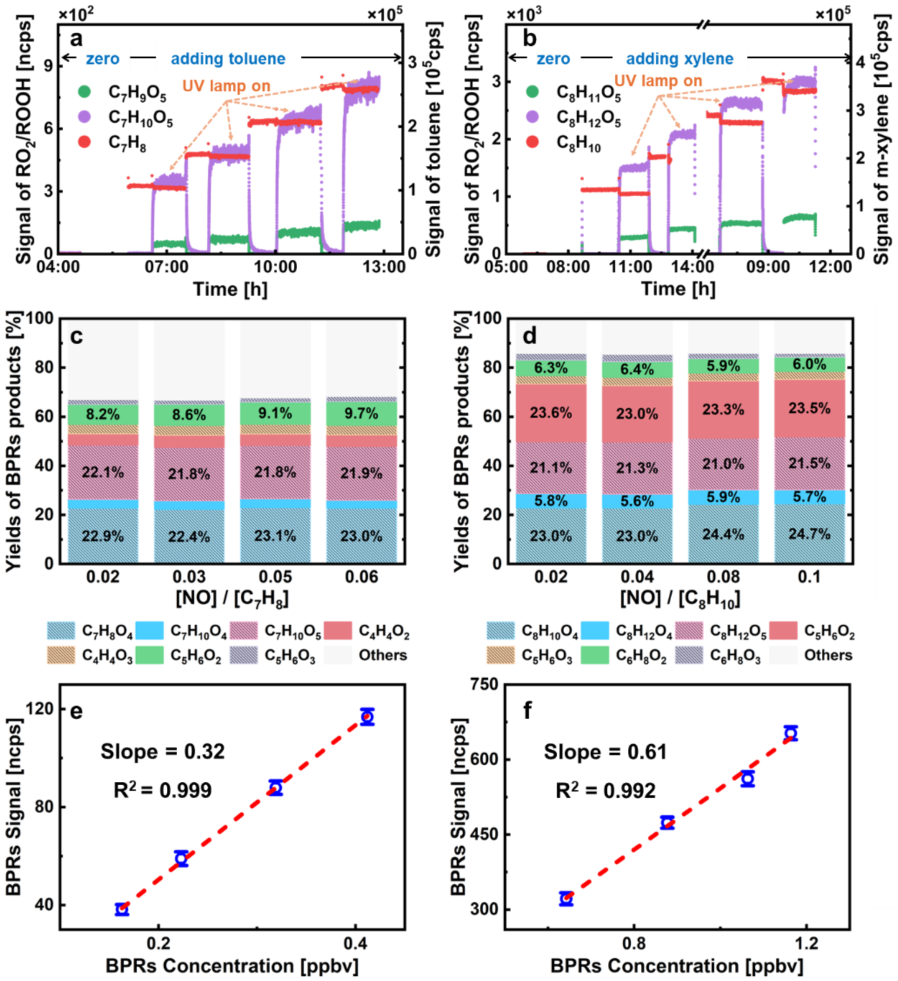

Figure 5. Time series and mechanistic analysis of toluene and m-xylene calibration experiments: temporal profiles of tol-BPRs (a) and xyl-BPRs (d) with their precursor and products, experimental branching ratios for peroxide-bicyclic pathways in the oxidation of toluene (b) and m-xylene (e), detection sensitivity of tol-BPRs (c) and xyl-BPRs (f) measured by Vocus AIM.

(Changes to the yield results in the manuscript and the SI) The yield results have been corrected in following figure (Figure 6 in the manuscript) and Table S8, S9 (in the SI).

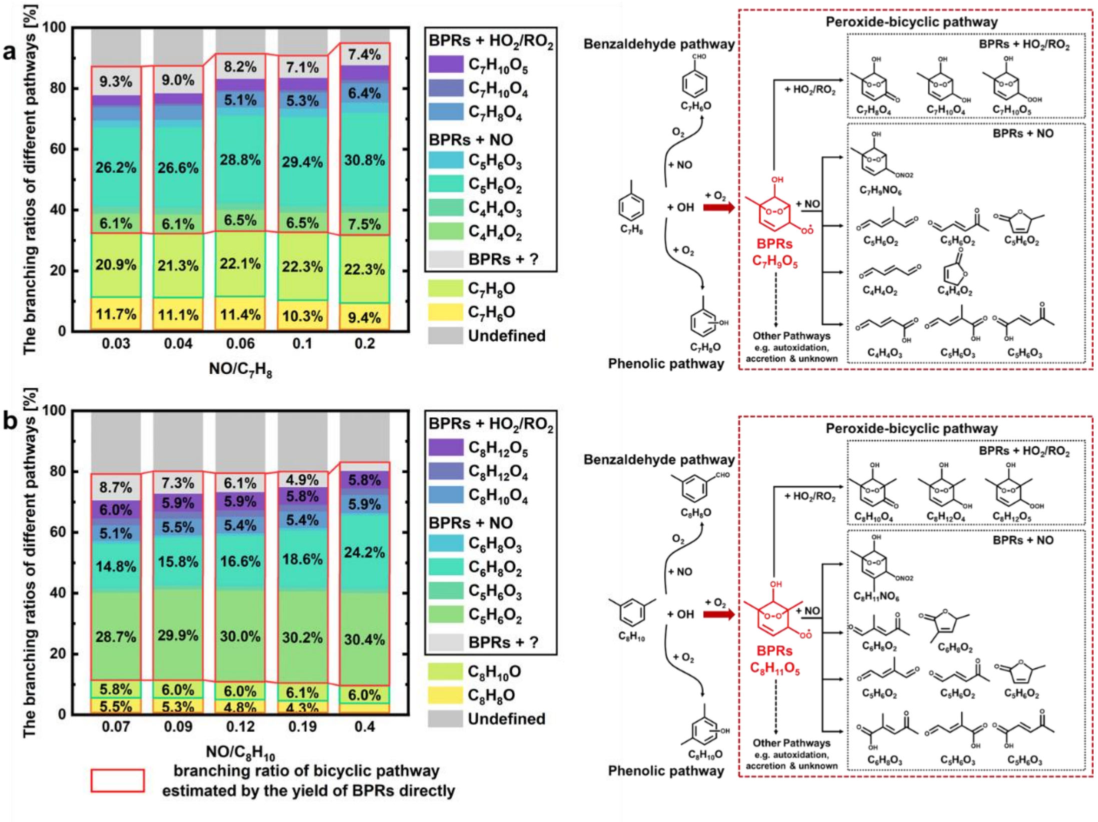

Figure 6. Experimental branching ratios for different pathways in the case of toluene and m-xylene, calculated by direct-measured method and product-yield method.

Comments:

4. *Figure 5: As I understand it, the values of [RO_2] in Figure 5 used for calibration were determined from Eq. 6 using literature rate constants; measured [X], [OH], [NO], and [HO_2]; and a branching ratio calculated from molecular product yields. Since this approach uses measured product yields, I am not sure it should be called a direct method and the other a product yield method.*

Response:

We appreciate this clarification and agree that precise terminology is important. Conventional approaches derive the yield of BPRs by summing product yields, without detecting the radicals themselves. By contrast, our approach directly detects BPRs with I^--CIMS and uses tracer product yields only to constrain the pathway branching ratio (α), we refer to this as a direct method. We stress that this terminology is adopted solely for clarity; the product-yield approach has been widely applied in earlier studies, and our use of “direct” versus “product-yield” is intended only to distinguish methodological differences.

Comments:

5. *How are the uncertainties in rate constants and branching ratios taken from the MCM incorporated into the calculated overall uncertainty?*

Response:

We sincerely thank the reviewer for highlighting this important point. To clarify, we did not adopt the branching ratios recommended by the MCM; instead, we calculated them by summing the tracer product yields, and the associated uncertainties in these yields have already been included in the overall uncertainty analysis. However, uncertainties in the rate constants were not explicitly incorporated into the sensitivity budget. In the revised manuscript, we address this by incorporating reported uncertainty ranges from the literature, including MCM recommendations and relevant kinetic studies.

(Changes to the first paragraph in "Uncertainty and Possible Interferences" section) "As previously mentioned, the quantification of RO_2 radicals relies primarily on Equation 2–9, with several main sources of uncertainty: (1) uncertainty in the measurement of precursors, oxidants, HO_2, and NO (Δ_{mea}), (2) uncertainty in flow tube loss, specifically related to the wall loss rate constants in the tube (Δ_{wl1}), (3) uncertainty in the branching ratio of the peroxide-bicyclic pathway (Δ_{α}) and (4) uncertainty for chemical reaction rate coefficients (Δ_k) , reported from previous reports."

(Changes to the Table 3 in "Uncertainty and Possible Interferences" section) The uncertainty analysis has included the uncertainty from reaction rates in Table 3.

Table 3. Contributions to the uncertainty of RO_2 sensitivities

Uncertainty Source		**Toluene-RO_2**	**m-Xylene-RO_2**
		Uncertainty	
Measurement	Precursor	4%	5%
	OH	5%	6%
	HO_2	8%[a]	8%[a]
	NO	5%	5%
Wall loss	k_w	15%[b]	15%[b]
Branching ratio	α	25%[c]	24%[c]
Reaction rates	$k_{Precursor+OH}$	10%[d]	12%[d]
	k_{RO_2+NO}	10%	10%
	$k_{RO_2+HO_2}$	10%	10%
	$k_{RO_2+RO_2}$	20%	20%
Overall		41%	41%

[a] estimated based on the method from Wang et al (2024a). [b] estimated by the approach from Zhang et al (2015). [c] details refer to Table S10, S11. [d] refers to evaluated literature data. [d] refers to evaluated literature data (Calvert and Calvert, 2002).

(Changes to the Table S10, S11 in the SI) The uncertainty of the branching ratios has included the uncertainty from reaction rates in Table S10 and Table S11.

Table S10. Measurement uncertainty contributions in tol-BPRs calibration.

NO	Formula	Compound	Measurement uncertainty	Loss uncertainty		Total uncertainty
			Sensitivity	Wall loss (Zhang et al., 2015)	OH reaction	
1	C_7H_8O	Cresol	9.50%	15%	10.0%[a]	20.38%
2	C_7H_6O	Benzaldehyde	7.60%	15%	5.8%[b]	17.79%
3	$C_7H_8O_4$	Bicyclic carbonyl	22%	15%	10%	28.44%
4	$C_7H_{10}O_4$	Bicyclic alcohol	22%	15%	10%	28.44%
5	$C_7H_{10}O_5$	Bicyclic hydroperoxide	22%	15%	10%	28.44%
6	$C_4H_4O_2$	Butene dial	20%	15%	4.9%[c]	25.48%
7	$C_4H_4O_2$	2(5H)-Furanone	18%	15%	10%	25.48%
8	$C_5H_6O_2$	2-Methylbutenedial	18%	15%	10%	25.48%
9	$C_5H_6O_2$	4-Oxo-2-pentenal	18%	15%	1.9%[e]	23.51%
10	$C_5H_6O_2$	5-Methyl-2(5H)-furanone	16%	15%	10%	24.10%
11	$C_5H_6O_2$	3-Methyl-2(5H)-furanone	7%	15%	10%	19.34%
12	$C_4H_4O_3$	Malealdehydic acid	21%	15%	10%	27.68%
13	$C_5H_6O_3$	4-Oxo-pent-2-enoic acid	21%	15%	10%	27.68%
14	$C_5H_6O_3$	2-Methyl-4-oxobut-2-enoic acid	21%	15%	10%	27.68%
15	The branching ratio of RO_2 pathway, α		-	-	-	24.87%

[a] **Refers to (Perry et al., 1977)**

[b] **Refers to (Sharma et al., 1997)**

[c] **Refers to (Martín et al., 2013)**

Table S11. Measurement uncertainty contributions in m-xyl-BPRs calibration.

NO	Formula	Compound	Measurement uncertainty	Loss uncertainty		Total uncertainty
			Sensitivity	Wall loss (Zhang et al., 2015)	OH reaction	
1	$C_8H_{10}O$	2,6-Dimethylphenol	10%	15%	5.1%[a]	18.74%
2	C_8H_8O	3-Mehtylbenzaldehyde	10%	15%	5.8%[b]	18.94%
3	$C_8H_{10}O_4$	Bicyclic carbonyl	20%	15%	10%	26.93%
4	$C_8H_{12}O_4$	Bicyclic alcohol	20%	15%	10%	26.93%
5	$C_8H_{12}O_5$	Bicyclic hydroperoxide	20%	15%	10%	26.93%
6	$C_5H_6O_2$	2-Methylbutenedial	18%	15%	10%	25.48%
7	$C_5H_6O_2$	4-Oxo-2-pentenal	18%	15%	1.9%[c]	23.51%
8	$C_5H_6O_2$	5-Methyl-2(5H)-furanone	16%	15%	10%	24.10%
9	$C_5H_6O_2$	3-Methyl-2(5H)-furanone	7%	15%	10%	19.34%
10	$C_6H_8O_2$	Methyl-4-oxo-2-pentenal	18%	15%	10%	25.48%
11	$C_6H_8O_2$	3,5-Dimethy-2(5H)-furanone	16%	15%	10%	24.10%
12	$C_5H_6O_3$	4-Oxo-pent-2-enoic acid	21%	15%	10%	27.68%
13	$C_5H_6O_3$	2-Methyl-4-oxobut-2-enoic acid	21%	15%	10%	27.68%
14	$C_6H_8O_3$	Acetyl methacrylic acid	21%	15%	10%	27.68%
15	The branching ratio of RO_2 pathway, α		-	-	-	24.42%

[a] Refers to (Perry et al., 1977)

[b] Refers to (Sharma et al., 1997)

[c] Refers to (Martín et al., 2013)

Comments：

6. *Line 404–412: Since the quoted uncertainty in RO_2 sensitivities is ~30%, might not all the differences discussed in this section be buried in the errors? Does the comparison between the results here and the product yield method include uncertainties in product yield measurements?*

Response:

We sincerely thank the reviewer for raising this important point. The quoted ~30% uncertainty reflects the error range of our method in reporting the absolute RO_2 concentration, i.e., the accuracy of measured values relative to the true concentration. In contrast, the differences observed between our CIMS-based approach and the product-yield method represent systematic deviations between two independent approaches. Such discrepancies are not expected to vanish within the ±30% margin, as this uncertainty mainly reflects common-mode calibration factors rather than random variability. Moreover, we conducted several repeated experiments of toluene-oxidation at the precursor levels of 6 ppbv, 12 ppbv and 18ppbv to evaluate the reproducibility of our results. A high level of consistency in the branching ratio of bicyclic pathway obtained from the direct-measured method and the products-yield method were both observed from these repeated experiment (as shown in Table S13). To further assess the difference between the two methods, we conducted statistical *t* tests. The results demonstrated that the branching ratios obtained from the direct-measurement method were significantly higher than those from the product-yield method. Comparable results are expected for the m-xylene system.

(“Section S5. Significant Tests on Branching ratios” added to the SI) “In this study, we conducted several repeated experiments of toluene oxidation at toluene levels of 6 ppbv, 12 ppbv and 18 ppbv to evaluate the reproducibility of our results. As we know, significance analysis typically requires repeated samples. A high level of consistency in the branching ratio of bicyclic pathway obtained from the direct-measured method and the products-yield method were both observed from these repeated experiment (as shown in Table S13). To further assess the difference between the two methods, we conducted statistical *t* tests. The results demonstrated that the branching ratios obtained from the direct-measurement method were significantly higher than those from the product-yield method. Comparable results are expected for the m-xylene system.”

(Changes to the SI) The following tables (Table S13) have been added in the revised SI.

Table S13. Significance test for the branching ratio of bicyclic pathway by the direct method and the product-yield method at different precursor concentration.

Toluene (ppbv)	**Method**	**Branching ratio (%)**				**Shapiro-Wilk test**	***t* test**
		Exp.1	**Exp.2**	**Exp.3**	**Mean**		
6	D[a]	63.3	60.4	60.6	61.4±1.3	p = 0.129 > 0.05	$H_0: \mu_D \le \mu_Y$ $H_A: \mu_D > \mu_Y$ p = 0.0036 < 0.05
	Y[b]	55.9	52.9	55.5	54.8±1.3	p = 0.218 > 0.05	
12	D	58.0	57.2	56.1	57.1±0.8	p = 0.749 > 0.05	$H_0: \mu_D \le \mu_Y$ $H_A: \mu_D > \mu_Y$ p = 0.0003 < 0.05
	Y	50.8	49.2	49.4	49.8±0.7	p = 0.253 > 0.05	
18	D	57.5	56.2	56.5	56.7±0.6	p = 0.562 > 0.05	$H_0: \mu_D \le \mu_Y$ $H_A: \mu_D > \mu_Y$ p = 0.002 < 0.05
	Y	49.3	49.4	48.7	49.1±0.3	p = 0.209 > 0.05	

Others Comments

1. *The equation should be* $k_{sinks}[RO_2] = \ldots$
2. *The second parenthesis should go after [OH].*

Response:

We thank the reviewer for pointing out these typographical errors and we have corrected these issues in the revise manuscript.

(Changes to the Equation 4)

"$k_{sinks} \approx k_{RO_2+NO}[NO] + k_{RO_2+HO_2}[HO_2] + k_{RO_2+RO_2}[RO_2] + k_w$"

(Changes to the Equation 13)

"$k_{RO_2,loss} = (k_{RO_2+NO}[NO] + k_{RO_2+HO_2}[HO_2] + k_{RO_2+RO_2}[RO_2] + k_w)/[OH]$"

References:

Berndt, T., Scholz, W., Mentler, B., Fischer, L., Herrmann, H., Kulmala, M., and Hansel, A.: Accretion Product Formation from Self- and Cross-Reactions of RO_2 Radicals in the Atmosphere, Angew Chem Int Edit, 57, 3820-3824, 10.1002/anie.201710989, 2018.

Calvert, J. G. and Calvert, J. G.: The mechanisms of atmospheric oxidation of aromatic hydrocarbons, Oxford University Press, Oxford ; New York, x, 556 pages : illustrations pp.2002.

He, S. Y., Liu, Y., Song, M. D., Li, X., Lu, S. H., Chen, T. Z., Mu, Y. J., Lou, S. R., Shi, X. D., Qiu, X. H., Zhu, T., and Zhang, Y. H.: Insights into the Peroxide-Bicyclic Intermediate Pathway of Aromatic Photooxidation: Experimental Yields and NO_X-Dependency of Ring-Opening and Ring-Retaining Products, Environ Sci Technol, 57, 20657-20668, 10.1021/acs.est.3c05304, 2023.

Jenkin, M. E., Valorso, R., Aumont, B., and Rickard, A. R.: Estimation of rate coefficients and branching ratios for reactions of organic peroxy radicals for use in automated mechanism construction, Atmos Chem Phys, 19, 7691-7717, 10.5194/acp-19-7691-2019, 2019.

Martín, P., Cabañas, B., Colmenar, I., Salgado, M. S., Villanueva, F., and Tapia, A.: Reactivity of E-butenedial with the major atmospheric oxidants, Atmos Environ, 70, 351-360, 10.1016/j.atmosenv.2013.01.041, 2013.

Perry, R. A., Atkinson, R., and Pitts, J. N.: Kinetics and Mechanism of Gas-Phase Reaction of Oh Radicals with Methoxybenzene and O-Cresol over Temperature-Range 299-435-K, J Phys Chem-Us, 81, 1607-1611, DOI 10.1021/j100532a001, 1977.

Sharma, S. B., Mudaliar, M., Rao, B. S. M., Mohan, H., and Mittal, J. P.: Radiation chemical oxidation of benzaldehyde, acetophenone, and benzophenone, J Phys Chem A, 101, 8402-8408, DOI 10.1021/jp9718717, 1997.

Wu, R. R., Pan, S. S., Li, Y., and Wang, L. M.: Atmospheric Oxidation Mechanism of Toluene, J Phys Chem A, 118, 4533-4547, 10.1021/jp500077f, 2014.

Zhang, X., Schwantes, R. H., McVay, R. C., Lignell, H., Coggon, M. M., Flagan, R. C., and Seinfeld, J. H.: Vapor wall deposition in Teflon chambers, Atmos Chem Phys, 15, 4197-4214, 10.5194/acp-15-4197-2015, 2015.