Author’s Response to Referee #1

We greatly appreciate the time and effort that Referee #1 has devoted to reviewing our manuscript. The comments are thoughtful and helpful in improving the quality of our paper. Below we make a point-by-point response to these comments. The response to Referee #1 is structured in the following sequence: (1) comments from the referee in blue color, (2) our response in black color, and (3) our changes in the revised manuscript in red color.

This study investigates the aqueous-phase oxidation kinetics and oligomerization pathways of benzothiazoles (BTs), with notable atmospheric presence but poorly understood liquid-phase reactivity. By experimentally determining OH-radical reaction rate constants for BT, MBT, and CBT, the work provides quantitative data to constrain their atmospheric lifetimes in cloud droplets and aerosol liquid water, an underexplored aspect of BTs' environmental fate. The identification of oligomers via Orbitrap MS, coupled with nanoparticle formation observed through NTA, offers mechanistic evidence for BTs' contribution to secondary organic aerosols (SOA) through aqueous-phase processing. These findings complement existing knowledge on gas-phase BT oxidation and highlight the need to account for aqueous reactions in models predicting SOA formation in urban and industrial regions. The study advances the mechanistic understanding of heterocyclic SVOC transformations, particularly for sulfur- and nitrogen-containing species, and provides a foundation for future investigations into their role in brown carbon formation and regional haze events. These results can potentially be of interest to the ACP audiences. However, several minor issues remain in the present study and should be addressed with additional explanations and revisions. I suggest a minor revision for this manuscript.

1. In Sec. 1: The manuscript would benefit from a more narrative-driven introduction that sets up the central question: What are we missing in our current models of SOA formation? Rather than solely listing prior studies, characterizing BTs as a “missing piece” in the urban secondary aerosol puzzle could provide a sharper hook.

Response: We thank the reviewer for this thoughtful suggestion. A more narrative-driven introduction can help clarify the central motivation of the study. We have modified and revised a corresponding sentence in the third paragraph of the Introduction to emphasize the role of BTs as a potentially "missing piece" in current models of SOA formation, as the reviewer suggested. Our modification can better highlight the significance of investigating BTs in the context of urban secondary aerosols formation. Specifically, we now characterize BTs as a potentially important and previously underexplored contributor to secondary aerosols. The revised sentence is as follows: "Therefore, understanding the photooxidation reactions of BTs in the aqueous phase is significant not only for the integrated determination of the atmospheric fate of BTs, but also for assessing their potential contributions to both organic and inorganic components of secondary aerosols due to their nature as sulfur-containing organic compounds."

2. In Line 14: "aeras with heavy traffic" → Correct to "areas with heavy traffic."

Response: Taking the reviewer's advice, we have corrected this mistake.

3. In Line 24: The use of the term "illustration" in the abstract should be corrected. Also, the phrase "after illustration" in the Abstract is confusing – the rest of the paper implies it should be simply "after the reaction." Ensure that such terminology is consistent and clear across several sections.

Response: Taking the reviewer's advice, we have revised the terminology in the Abstract. "In addition, higher yields of sulfate are formed after the reactions."

4. In Line 145: The authors briefly introduce the calculation method of OH concentrations. I think it would be nice to include a bit more information on the method to estimate OH radical concentration (direct calculation from power output or using chemical actinometry?). Publications from Anastasio group (such as Atmos. Environ., 2015, 100, 230-237) can be referred for the estimation.

Response: We thank the reviewer for this suggestion. The steady-state OH was estimated in our study by the same method as in the Supplemental Material of the reference paper (Atmos. Environ., 2015, 100, 230-237). As shown in Figure R1, the VA loss (*k'*) in this system for pH 2 solutions containing 0.45 mM BT and 10 mM H_2O_2 was 1.03×10^{-4} s^{-1}.

$$k' = k_{BT+OH}\,[\mathrm{OH}]$$

From the BT loss (*k'*), we can determine the steady-state concentration of OH radicals by dividing it by the bimolecular rate constant for BT oxidation by OH that has been determined from our kinetic experiments ($k_{BT+OH} = 8.0 \times 10^{9}$ M^{-1} s^{-1}). Substituting the corresponding values, the average steady-state concentrations of OH ([OH]) in the BT-pH2 experiment was 1.28×10^{-14} M. Using this method, [OH] were estimated to be 0.64, 1.34, 0.58, 0.72, and 0.53×10^{-14} M for BT-pH10, MBT-pH2, MBT-pH10, CBT-pH2, and CBT-pH10, respectively.

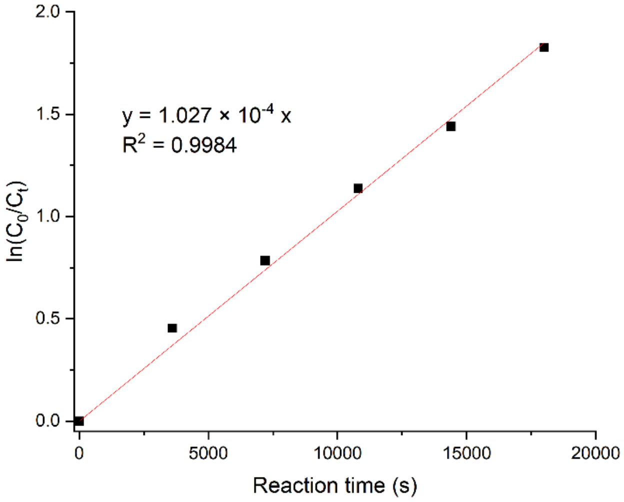

Figure R1. The BT loss in the aqueous phase under acidic conditions.

Thus, we have modified the related text at Section 2.4 in the revised manuscript as follows:

"The steady-state concentration of OH radicals can be estimated through dividing the BTs loss by the bimolecular rate constant of BTs with OH radicals (Eq. (2); George et al., 2015). Considering the different parent compounds and the rate constants at pH 2 and 10, the steady-state concentration of OH radicals was estimated to be approximately 10-14 M.

$$[\mathrm{OH}] = \frac{k\prime}{k_{\mathrm{BTs\,+\,OH}}} \qquad (2)$$

References

George, K. M.; Ruthenburg, T. C.; Smith, J.; Yu, L.; Zhang, Q.; Anastasio, C.; Dillner, A. M. FT-IR Quantification of the carbonyl functional group in aqueous-phase secondary organic Aerosol from phenols. Atmos. Environ., 100, 230-237 10.1016/j.atmosenv.2014.11.011, 2015."

5. In Line 193: "could be an significantly effective process" → Correct to "could be a significantly effective process"

Response: Taking the reviewer's advice, we have corrected this mistake.

6. LC-Orbitrap MS analysis identified hydroxylated products and oligomers. This piece of evidence is good, but rather qualitative. Did the authors perform LC-Orbitrap MS experiments at different time intervals, so that one can use peak areas of certain products to quantitatively/semi-quantitatively compare with the changes of long-wavelength absorption (e.g., at > 300 nm in Fig 3b)?

Response: We thank the reviewer for this suggestion. Time-resolved LC-Orbitrap MS analysis combined with UV-vis spectroscopic monitoring would offer a promising approach for quantitatively linking specific product formation with changes in chromophoric properties (e.g., long-wavelength absorption >300 nm). We did not perform LC-Orbitrap MS measurement at different time intervals under the present experimental condition and thus were unable to conduct quantitative or semi-quantitative analysis of product evolution based on peak area trends. We consider this a worthwhile direction for future investigation. Thus, we have explicitly acknowledged the limitation of quantification in the revised manuscript, which has been added in the third paragraph of Section 3.4. "It should be noted that in this study the LC-Orbitrap MS analysis provides more qualitative insights, as quantitative determination was limited and not conducted. It can be considered and developed for further characterization of the formation and evolution of organic products."

7. In Line 288: In this paragraph, the role of organosulfur and organonitrogen compounds deserves more attention. How might the CHONS products influence particle hygroscopicity, longevity, or climate-relevant properties? These aspects are hinted at but not explored in depth.

Response: We thank the reviewer for this valuable comment. The potential implications of CHONS compounds those account for the largest proportion of the overall molecular formula of identified compounds need to be explored in depth. Recent studies have demonstrated that CHONS compounds are important contributors to brown carbon, exhibiting strong light-absorbing capabilities. The presence of CHONS compounds has been positively correlated with increased mass absorption efficiency (MAE), particularly in aromatic-rich fractions. These optical characteristics suggest that CHONS species may influence aerosol radiative properties and thus potentially affect climate-relevant processes. In the revised manuscript, we have added a few sentences about discussion of optical properties following the description of CHONS compounds in the third paragraph of Sect. 3.4 and two corresponding references. "CHONS compounds have been shown to contribute significantly to particle light absorption, with higher mass absorption efficiencies observed in CHONS-rich fractions (Zhang et al., 2024; Bao et al., 2023). With the formation of abundant CHONS species, the aqueous-phase BTs oxidation may indicate a potential contribution to the climate-relevant properties of brown carbon through enhanced light absorption.

References

Bao, M., Zhang, Y.-L., Cao, F., Hong, Y., Lin, Y.-C., Yu, M., Jiang, H., Cheng, Z., Xu, R., and Yang, X.: Impact of fossil and non-fossil fuel sources on the molecular compositions of water-soluble humic-like substances in $PM_{2.5}$ at a suburban site of Yangtze River Delta, China, Atmos. Chem. Phys., 23, 8305-8324, 10.5194/acp-23-8305-2023, 2023.

Zhang, L., Li, J., Li, Y., Liu, X., Luo, Z., Shen, G., and Tao, S.: Comparison of water-soluble and water-insoluble organic compositions attributing to different light

absorption efficiency between residential coal and biomass burning emissions, Atmos. Chem. Phys., 24, 6323-6337, 10.5194/acp-24-6323-2024, 2024."

8. In Line 340: "BTs" in "kBTs" should be subscript and the Eq. (3) should be italic, consistent with other equations.

Response: Taking the reviewer's advice, we have corrected this mistake.

9. Table 3 is quite dense and might be better split or reorganized for readability.

Response: We thank the reviewer for this suggestion. The response to the third comment from Referee #3 involves a revision of the atmospheric lifetimes of BTs that are closely related to Table 3. We have reorganized and modified this table accordingly. The revised Table 3 is as follows:

Table 3. Atmospheric lifetimes of BT, MBT, and CBT initiated by OH radicals in various aqueous and gas phases.

	Ref.		[OH]^a	τ_{BT} in h^b		τ_{MBT} in h^b		τ_{CBT} in h^b	
Urban cloud droplets	Herrmann et al. (2010) & Bianco et al. (2020)	Mean	3.5×10^{-15}	9.9	8.2	10.4	8.1	10.4	8.4
		Max	1.6×10^{-14}	2.2	1.8	2.3	1.8	2.3	1.8
		Min	2.9×10^{-16}	119.7	98.7	126.0	97.7	126.0	101.9
	Arakaki et al. (2013)	Max	1.9×10^{-12}	0.02	0.02	0.02	0.01	0.02	0.02
		Min	1.0×10^{-14}	3.5	2.9	3.7	2.8	3.7	3.0
Remote cloud droplets	Herrmann et al. (2010) & Bianco et al. (2020)	Mean	2.2×10^{-14}	1.6	1.3	1.7	1.3	1.7	1.3
		Max	6.9×10^{-14}	0.5	0.4	0.5	0.4	0.5	0.4
		Min	4.8×10^{-15}	7.2	6.0	7.6	5.9	7.6	6.2
	Arakaki et al. (2013)	Max	2.4×10^{-12}	0.01	0.01	0.02	0.01	0.02	0.01
		Min	2.6×10^{-14}	1.3	1.1	1.4	1.1	1.4	1.1
Maritime cloud droplets	Herrmann et al. (2010) & Bianco et al. (2020)	Mean	2.0×10^{-12}	0.02	0.01	0.02	0.01	0.02	0.01
		Max	5.3×10^{-12}	0.01	0.01	0.01	0.01	0.01	0.01
		Min	3.8×10^{-14}	0.9	0.8	1.0	0.7	1.0	0.8
	Arakaki et al. (2013)	Max	2.0×10^{-12}	0.02	0.01	0.02	0.01	0.02	0.01
		Min	1.8×10^{-13}	0.2	0.2	0.2	0.2	0.2	0.2
Urban deliquescent particles	Herrmann et al. (2010)	Mean	4.4×10^{-13}	0.1	0.1	0.1	0.1	0.1	0.1
		Max	1.9×10^{-12}	0.02	0.02	0.02	0.01	0.02	0.02
		Min	1.4×10^{-16}	248.0	204.5	261.1	202.5	261.1	211.1

	Arakaki et al. (2013)		8.0×10^{-13}	0.04	0.04	0.05	0.04	0.05	0.04
Remote deliquescent particles	Herrmann et al. (2010)	Mean	3.0×10^{-12}	0.01	0.01	0.01	0.01	0.01	0.01
		Max	8.0×10^{-12}	0.004	0.004	0.005	0.004	0.005	0.004
		Min	5.5×10^{-14}	0.6	0.5	0.7	0.5	0.7	0.5
	Arakaki et al. (2013)		3.6×10^{-12}	0.01	0.01	0.01	0.01	0.01	0.01
Maritime deliquescent particles	Herrmann et al. (2010)	Mean	1.0×10^{-13}	0.3	0.3	0.4	0.3	0.4	0.3
		Max	3.3×10^{-12}	0.01	0.01	0.01	0.01	0.01	0.01
		Min	4.6×10^{-15}	7.5	6.2	7.9	6.2	7.9	6.4
	Arakaki et al. (2013)		4.0×10^{-16}	86.8	71.6	91.4	70.9	91.4	73.9
Gas phase	Prinn et al. (2001)	Mean	1.0×10^{6}	39.7[c]	132.3[d]	15.1[c]		56.4[c]	
	Finlayson-Pitts and Pitts Jr. (2000)	Mid-day	1.0×10^{7}	4.0[c]	13.2[d]	1.5[c]		5.6[c]	

[a] The units of OH concentrations are M and molecule cm^{-3} in the aqueous and gas phases, respectively.

[b] The two lifetimes in the aqueous phase are calculated by the rate constants at pH 2 and 10 obtained in this study.

[c] The lifetimes in the gas phase are calculated based on the rate constants from the Atmospheric Oxidation Program for Microsoft Windows (AOPWIN) model, which are 0.7, 1.8, and 0.5 × 10^{-11} cm^{3} molecule^{-1} s^{-1} for reactions of OH with BT, MBT, and CBT, respectively (USEPA, 2012).

[d] The lifetimes of BT in the gas phase are calculated by the rate constants determined by a relative rate method, which is $(2.1 \pm 0.1) \times 10^{-12}$ cm^{3} molecule^{-1} s^{-1} (Karimova et al., 2024).