Author's Response to Referee #4

We greatly appreciate the time and effort that Referee #4 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 #4 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 manuscript presents an investigation into the atmospheric transformations of benzothiazoles (BTs) via OH radical-initiated oxidation in the aqueous phase. BTs are increasingly recognized as emerging environmental contaminants due to their extensive use in industrial and consumer products, and their widespread presence in urban environment, especially in air. While their gas-phase reactions have been previously studied, the aqueous-phase chemistry of BTs remains largely unexplored, despite its relevance in cloud water, fog, and deliquescent aerosols. This study addresses this knowledge gap. The authors quantified the second-order rate constants for BTs + OH reactions, characterized the reaction products via LC-Orbitrap MS, and monitored the formations of nanoparticles and light-absorbing chromophores. Key findings include the identification of multifunctional oligomers and the observation of brown carbon-like optical features among the products. These results suggest that BTs could be a previously underappreciated source of both inorganic and organic secondary aerosols in polluted environments. The integration of kinetic, molecular, and particle-level data represents a notable advance in understanding the atmospheric fate of this class of compounds. The study's focus is within the scope of ACP and the paper is well written, and I recommend an overall minor revision with a few comments below.

Comments:

1. Both the Abstract and Conclusion highlight the formation of atmospheric brown carbon from BTs' aqueous reactions as a key finding. However, the Introduction does not mention brown carbon or aerosol optical properties at all. The concept does not

appear until the Results and Discussion section, leading to a minor narrative gap. To harmonize, the Introduction could include a brief mention that secondary aerosols can include light-absorbing organic matter (i.e., brown carbon) that affects climate.

Response: We thank the reviewer for the suggestion. Mentioning the concept of brown carbon/aerosol optical properties in the Introduction enhances logical consistency and highlights the importance of aqueous-phase reactions. The relevant sentence in the third paragraph of the Introduction has been revised to explicitly state that aqueous-phase processing can generate light-absorbing compounds in secondary aerosols, which may influence climate. "Based on laboratory, modeling, and field studies conducted over the past decades, there has been increasing evidence that aqueous-phase processing affects the formation of both organic and inorganic components of secondary aerosols and contributes to the production of light-absorbing matter, which has the potential to influence climate (Lv et al., 2025; Mei et al., 2025; Li et al., 2023b; Zhang et al., 2018b; Ervens, 2015; Herrmann et al., 2015; Laskin et al., 2015; McNeill, 2015; Zhang et al., 2020a; Meagher et al., 1990)."

2. The terms, "secondary aerosol" vs. "secondary organic aerosol", are used mostly consistently, though a slight variation in usage may cause confusion. The Introduction refers to secondary organic aerosols (SOA) when giving examples of compounds that undergo aqueous processing, whereas the Abstract and Conclusion use the more general term "secondary aerosols" (which include both organic and inorganic components). The authors' intention is to show BTs contribute to both organic and inorganic matters in aerosols. To avoid confusion, the terminology should be made consistent. The Introduction could mirror this phrasing when framing the knowledge gap. The Introduction might state that "BTs may contribute to secondary aerosol (both organic and inorganic) via aqueous-phase reactions" instead of focusing only on SOA. This would ensure the reader knows from the start that both organic and inorganic aspects are of interest.

Response: We thank the reviewer for the suggestion on terminology. Stating that BTs may contribute to both organic and inorganic components of secondary aerosols through aqueous-phase reactions is valuable, as it emphasizes the significance of investigating their aqueous-phase processing. In the revised manuscript, the sentence in the third paragraph of the Introduction now explicitly states that BTs may contribute to both organic and inorganic components of secondary aerosols through aqueous-phase reactions, due to their nature as sulfur-containing organic compounds. "Therefore, understanding the photooxidation reactions of BTs in the aqueous phase is significant not only for the integrated determination 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."

3. 3.2: The optical data are well-presented, but their implications could be tied more explicitly to the evolving definition of atmospheric brown carbon. In other words, the authors should more directly connect their observed optical changes to the characteristics of brown carbon reported in the literature.

Response: We thank the reviewer for this insightful suggestion. In response, we have clarified the link between our observed optical properties and the evolving understanding of atmospheric brown carbon. Specifically, we addressed both the mass absorption efficiency at 365 nm (MAE_{365}) and the excitation-emission matrix (EEM) fluorescence features, which are key indicators of brown carbon, and compared them to those found in brown carbon-related studies.

After 5 h of photooxidation, the reaction solutions exhibited visible yellow-brown coloration and distinct optical changes. MAE_{365} values reached 0.76 (Exp. BT-pH2), 0.74 (Exp. BT-pH10), 0.34 (Exp. MBT-pH2), 0.50 (Exp. MBT-pH10), 0.85 (Exp. CBT-pH2), and 1.02 $m^2\ g^{-1}$ (Exp. CBT-pH10). These values fall within or approach the range of MAE_{365} values for water-soluble brown carbon generated from biomass/coal combustion (0.21-3.1 $m^2\ g^{-1}$; Zhang et al., 2024) and are comparable to those formed in laboratory-generated secondary brown carbon via aqueous Maillard-like reactions from carbonyl compounds mixed with ammonium sulfate or amine (0.15-4.5 $m^2\ g^{-1}$; Tang et al., 2022b). These comparisons suggest that aqueous-phase oxidation of BTs can contribute to atmospherically relevant light-absorbing organic compounds.

EEM fluorescence spectra revealed clear red shifts in both excitation and emission wavelengths after 5 h of photooxidation. These spectral changes indicate an increase in molecular conjugation and complexity, which are characteristic of brown carbon chromophores. Notably, our results of EEM are quite close to the optical features of LO-HULIS (less-oxygenated humic-like substances), a subclass of atmospheric brown carbon identified in ambient aerosol studies (Jiang et al., 2022).

These combined findings support the classification of BT-derived products as atmospherically relevant brown carbon, both in terms of their absorption characteristics and molecular-level fluorescence signatures.

Thus, the results and discussions of MAE in Section 3.2 have been expanded and revised as follow: “The UV-vis absorption spectra were converted into mass absorption efficiency (MAE) using Eq. (3). After 5 h of photooxidation, the mass absorption efficiency at 365 nm (MAE_{365}) values of the light-absorbing substances derived from BTs reached 0.76, 0.74, 0.34, 0.50, 0.85, and 1.02 m^2 g^{-1} for Exps. BT-pH2, BT-pH10, MBT-pH2, MBT-pH10, CBT-pH2, and CBT-pH10, respectively (Fig. 3c and Fig. S4). Among them, the products from CBT exhibit the highest MAE_{365}, resulting from the higher electronegativity of the -Cl group in CBT. MAE_{365} values of the selected BTs-driven products are comparable to those reported for laboratory-generated brown carbon formed via Maillard-like aqueous-phase reactions from carbonyl compounds mixed with ammonium sulfate or amine, where MAE_{365} ranged from 0.15 to 4.50 m^2 g^{-1} depending on precursor combinations (Tang et al., 2022b). They are also within the MAE_{365} range observed in ambient brown carbon samples from biomass and coal combustion sources, which span from 0.21 to 3.10 m^2 g^{-1} (Zhang et al., 2024). It suggests that aqueous-phase oxidation of BTs can form light-absorbing organic products with optical properties relevant to atmospheric brown carbon.” The results and discussions of EEM fluorescence spectra have been expanded and the following sentences have been added at the end of Section 3.2. “Moreover, EEM fluorescence features of BTs-driven products are consistent with the LO-HULIS (less-oxygenated humic-like substances) group, a subclass of atmospheric brown carbon identified in studies of ambient aerosols (Jiang et al., 2022). LO-HULIS are less-oxygenated and nitrogen-containing aromatic compounds commonly observed in biomass burning aerosols. Given the spectral similarity, the aqueous-phase OH oxidation products of BTs in our study can be reasonably classified as LO-HULIS-type chromophores, further indicating a potential for contributing to the light absorption of aerosols.

References

Jiang, F., Song, J., Bauer, J., Gao, L., Vallon, M., Gebhardt, R., Leisner, T., Norra, S., and Saathoff, H.: Chromophores and chemical composition of brown carbon characterized at an urban kerbside by excitation–emission spectroscopy and mass spectrometry, Atmos. Chem. Phys., 22, 14971-14986, 10.5194/acp-22-14971-2022, 2022.

Tang, S., Li, F., Lv, J., Liu, L., Wu, G., Wang, Y., Yu, W., Wang, Y., and Jiang, G.: Unexpected molecular diversity of brown carbon formed by Maillard-like reactions in aqueous aerosols, Chem. Sci., 13, 8401-8411, 10.1039/d2sc02857c, 2022b.

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."

4. One goal of the study is to elucidate reaction mechanisms. In the Introduction it explicitly says that mechanisms would be proposed based on the products. The paper discusses these mechanisms in detail in the main text. However, the Conclusion section, while summarizing outcomes (products formed, etc.), does not explicitly summarize the mechanism that was proposed. It implies a mechanism, e.g., "suggesting radical–radical oligomerization is responsible for oligomers and brown carbon formation", but it doesn' t plainly state something like "a mechanism involving X, Y, Z steps was deduced." To fully close the loop, the authors could dedicate a sentence in the Conclusion to the mechanism. Including a high-level description of the reaction pathway would remind readers that the study achieved its aim of unraveling the

mechanism, not just finding the end products. This would tie back to the Introduction's promise of proposing a mechanism.

Response: We thank the reviewer for the suggestion. We have added a clear statement of the proposed reaction mechanism to the third paragraph of the Conclusion to ensure that the study's mechanistic insights are explicitly highlighted. This addition closes the loop between the Introduction's stated aim (to propose a mechanism) and the Conclusion, assuring the readers that we have indeed deduced a plausible reaction mechanism involving key steps. It reinforces that our study not only identified products but also elucidated how those products generate. "In this study, the formation of oxidized organic products with both higher and lower molecular weights was confirmed by LC-Orbitrap MS analysis, and a higher molar yield of sulfate was quantified by IC measurement. Based on these results, aqueous-phase oxidation mechanisms of BTs were proposed, in which OH radicals are assumed to initiate attack on the benzothiazole ring, forming radical intermediates that are subjected to radical-radical coupling, fragmentation, and further oxidation. It suggests that aqueous-phase BTs oxidation has the capacity to contribute to secondary aerosols, including both inorganic and organic components in the atmosphere. The contribution of secondary aerosols generated from BTs is considered non-negligible and can contribute to the fine particulate matters in some regions where BTs concentrations are comparable to common aromatic compounds."

5. The Abstract provides the exact rate constant values, highlighting the kinetic data, but it does not explicitly interpret what those mean in atmospheric terms. The Conclusion, on the other hand, emphasizes the implications of those kinetics by converting them to lifetimes and comparing aqueous vs. gas-phase transformation rates. While this is not a critical inconsistency (abstracts often omit detailed interpretation due to space), it is a difference in emphasis. Readers of the abstract see numbers but might not realize that corresponds to a very short lifetime. Abstract should include a brief interpretive phrase to complement the raw rate numbers. Similarly, the Introduction might also hint at expected fast kinetics by mentioning OH's known

reactivity. Currently, the Introduction imply this generally, and the conclusion confirms this quantitatively; making sure the abstract also reflects this would complete the chain of logic across all three sections.

Response: We agree with the reviewer's suggestion. For more consistency and clarity, we have revised the Abstract to include a brief interpretation that the reported rate constants are translated into lifetimes, immediately after listing the second-order rate constants for BT, MBT, and CBT. "Lifetimes ranging from several minutes to several hours were estimated under mean OH concentrations in various atmospheric aqueous phases, which are significantly shorter than those estimated under mean OH concentrations in the gas phase." This addition makes it clear that such rate constants imply rapid removal of BTs in the aqueous phase.

The Introduction already contains a general statement that aqueous-phase OH reactions can significantly shorten the lifetime of pollutants (Herrmann, 2003). With this revision, the Abstract, Introduction, and Conclusion are now aligned. The Introduction foreshadows OH's high reactivity, the Abstract presents the kinetic data along with its lifetime implication, and the Conclusion provides the quantitative comparison of aqueous- versus gas-phase lifetimes. This cohesive treatment across sections should help readers understand the atmospheric relevance of the kinetic findings.

6. The formation of sulfate is one of the major findings of this study, highlighted in both the Abstract and Conclusion, yet the Introduction does not mention sulfate at all. The Introduction should explicitly mention the possibility of sulfate generation from BTs during aqueous-phase oxidation. Establish a clearer rationale for investigating sulfate production, ensuring logical continuity from the Introduction's theoretical framework to the empirical results and their implications in the Conclusion.

Response: We thank the reviewer for the suggestion regarding explicitly mentioning sulfate formation in the Introduction. Clearly stating sulfate production potential significantly enhances the coherence and clarity of the manuscript. In the Introduction, we have noted that gas-phase BT reactions can lead to sulfate formation. In addition, when responding to the reviewer's second comment, we revised the description of the significance of studying BTs' aqueous-phase reactions in the Introduction 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." This sentence implicitly indicates that aqueous-phase oxidation of BTs can also generate sulfate.

7. L235-248: The authors state that nanoparticles formed after 5 hours of photooxidation, with sizes ranging from 50 to 400 nm and concentrations ~10^8 particles/mL. This is a striking observation, indicating significant particle formation from BT oxidation. However, this result is presented with minimal discussion. This section should be revised to include additional discussion that situates the observed nanoparticle formation within the broader literature.

Response: We thank the reviewer for highlighting the importance of this observation. The formation of nanoparticles (50-400 nm, ~10^8 particles/mL) after 5 h of aqueous-phase photooxidation of BTs is quite a notable finding. To date, many studies have observed the formation of oligomeric and polymeric products in atmospheric relevant aqueous-phase reactions using mass spectrometry and spectroscopy (Li et al., 2023a; Li et al., 2023b; Tang et al., 2022b). These studies consistently demonstrate the generation of compounds with higher molecular weight, often linked to brown carbon formation. However, direct detection of nanoparticles in such systems remain scarce in previous studies. Our findings suggest that the aqueous-phase oxidation of BTs facilitates formation of nanoparticles, potentially from aggregation of oligomeric species. This observation may represent an underexplored pathway for secondary aerosols formation in cloud or particle water. Thus, we have expanded the corresponding discussion in Sect. 3.3 of the revised manuscript. "While previous studies have reported the formation of oligomeric and polymeric products in atmospheric relevant aqueous-phase reactions (Li et al., 2023a; Li et al., 2023b; Tang et al., 2022b), direct detection of newly formed nanoparticles remains rare. The observed nanoparticles may originate from the aggregation of oligomeric products from aqueous-phase BTs oxidation, highlighting a potentially important but underrecognized route of secondary aerosols formation from aqueous-phase chemistry.

References

Li, F., Tang, S., Lv, J., He, A., Wang, Y., Liu, S., Cao, H., Zhao, L., Wang, Y., and Jiang, G.: Molecular-Scale Investigation on the Formation of Brown Carbon Aerosol via Iron-Phenolic Compound Reactions in the Dark, Environ. Sci. Technol., 57, 11173-11184, 10.1021/acs.est.3c04263, 2023a.

Li, F., Zhou, S., Du, L., Zhao, J., Hang, J., and Wang, X.: Aqueous-phase chemistry of atmospheric phenolic compounds: A critical review of laboratory studies, Sci. Total Environ., 856, 158895, 10.1016/j.scitotenv.2022.158895, 2023b.

Tang, S., Li, F., Lv, J., Liu, L., Wu, G., Wang, Y., Yu, W., Wang, Y., and Jiang, G.: Unexpected molecular diversity of brown carbon formed by Maillard-like reactions in aqueous aerosols, Chem. Sci., 13, 8401-8411, 10.1039/d2sc02857c, 2022.”

8. L200-235: UV-vis and EEM data show red shifts and increased MAE values. Though the red shift is described and linked to conjugation, there is limited discussion of (1) how these light-absorbing products compare to known brown carbon chromophores, and (2) any atmospheric implications of higher MAE (e.g., warming effects).

Response: We thank the reviewer for this valuable comment. As noted, this point closely overlaps with Comment 3, which also addressed the interpretation of UV-vis and EEM optical data in the context of brown carbon characteristics. In response, we have substantially revised Section 3.2 to clarify how both the observed red shifts in EEM fluorescence and the increased MAE values correspond to known brown carbon chromophores and their atmospheric implications. Specifically, we compared our MAE_{365} values with those reported for ambient and laboratory-generated brown carbon and discussed how the red-shifted EEM features resemble LO-HULIS-type chromophores. The potential for light absorption and radiative forcing was also discussed. These revisions are described in detail in our response to the third comment, and the corresponding modifications of the manuscript have been incorporated in Section 3.2.