Author's Response to Referee #5

We greatly appreciate the time and effort that Referee #5 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 #5 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.

Zhang et al. investigated the aqueous-phase OH reaction of benzothiazoles. The reaction kinetics, transformation products, reaction mechanism, and optical properties were reported. The atmospheric fate of benzothiazoles is not well illustrated at this point, this study highlights that the aqueous-phase oxidation of BTs can contribute to the secondary aerosol mass in the atmosphere, and have the potential to change the optical properties of ambient particles. I recommend this paper to be published after some revisions.

1. The focus of this study is aqueous-phase reaction of benzothiazoles. The atmospheric significance of this process depends on the concentrations of benzothiazoles in atmospheric droplets. The authors mention that the highest concentration of benzothiazoles in PM2.5 is at the level of ng/m3. I wonder what is concentration in cloud water or aerosol liquid water? Not all benzothiazoles in PM2.5 will be present in aerosol liquid water, so the concentration in aqueous-phase is likely to be lower than ng/m3. If the concentration of benzothiazoles in aerosol liquid water is low, this will limit the potential for aqueous-phase reactions to change the optical properties of atmospheric particles. The authors need to further discuss this point in Implication section.

Response: We thank the reviewer for highlighting this critical issue regarding BTs concentrations in atmospheric droplets. Explicitly addressing BTs concentrations in cloud, fog, and aerosol liquid water is significant to better assess the atmospheric implications of their aqueous-phase oxidation. There are rarely reported data on BTs concentrations in cloud, fog, or aerosol liquid water samples to date. The available concentration of BT in atmospheric waters has been referenced in the Introduction of our manuscript. “BT is also present in urban rain, with a concentration as high as 70 ng L^{-1} (Ferrey et al., 2018).” Furthermore, Liao et al (2021), referred in our manuscript, has reported the BTs concentration in $PM_{2.5}$ samples from Guangzhou and Shanghai, where climate is humid. According to the sampling dates from this paper, we summarized the relative humidity data at that time from ERA5 (Hersbach et al., 2023) as shown in Table R1. ERA5 is a widely adopted global atmospheric reanalysis dataset that integrates a vast array of historical observations with advanced data assimilation techniques, which is developed by the European Centre for Medium-Range Weather Forecasts. For most sampling dates in Guangzhou and Shanghai, daily average relative humidity was above 70%, and in some cases, it can reach up to 93%. Under these humid conditions, atmospheric aerosol particles typically contain a certain amount of moisture and even exist in deliquescent states. To a certain extent, the measured BTs concentrations in $PM_{2.5}$ under such humid conditions can reflect BTs levels in aerosol liquid water. However, the explicit concentrations of BTs in aerosol liquid water remain unknown and require further investigation. This knowledge gap limits our current understanding of the atmospheric implications. Thus, we have revised the second last sentence of the Conclusion section to add this future research direction explicitly. “In the future, research should focus on the occurrence and distribution of BTs in atmospheric aqueous phases, with particular emphasis on integrating real-world BT concentrations and varying ambient conditions to advance the understanding of their atmospheric chemistry.”

Table R1. Basic information of the sampling sites (Liao, et al., 2021).

Sampling sites	No.	Sampling date	Temperature (°C)	Relative humidity (%)[a]
Guangzhou (Winter, n=8;	G1	2018/12/15	15.7	73.1
	G2	2018/12/05	22.9	78.1
	G3	2018/12/21	22.9	83.5

Summer, n=6)	G4	2019/01/13	18.2	78.8
	G5	2019/01/26	17.2	48.3
	G6	2019/01/03	12.1	78.5
	G7	2018/12/03	21.7	81.5
	G8	2018/11/25	18.1	77.1
	G9	2018/06/01	29.3	81.3
	G10	2018/06/06	25.8	92.33
	G11	2018/06/09	25.9	81.9
	G12	2018/06/20	30.2	86.0
	G13	2018/06/23	26.0	90.1
	G14	2018/07/17	30.0	77.8
Shanghai (Winter, n=8; Summer, n=6)	S1	2018/12/13	4.10	67.6
	S2	2018/12/14	6.20	75.1
	S3	2018/12/15	9.10	80.9
	S4	2018/12/16	7.20	79.7
	S5	2018/12/26	8.70	88.1
	S6	2018/12/27	5.60	67.3
	S7	2018/12/28	1.20	65.0
	S8	2018/12/31	2.90	81.1
	S9	2018/06/06	24.5	79.8
	S10	2018/06/08	23.6	88.1
	S11	2018/06/11	23.8	77.0
	S12	2018/06/15	24.9	74.8
	S13	2018/06/20	22.0	89.7
	S14	2018/06/23	21.8	82.5

[a] Relative humidity data are obtained from ERA5 (Hersbach et al., 2023).

References

Hersbach, H., Bell, B., Berrisford, P., Biavati, G., Horányi, A., Muñoz Sabater, J., Nicolas, J., Peubey, C., Radu, R., Rozum, I., Schepers, D., Simmons, A., Soci, C., Dee, D., Thépaut, J-N. (2023): ERA5 hourly data on single levels from 1940 to present. Copernicus Climate Change Service (C3S) Climate Data Store (CDS), DOI: 10.24381/cds.adbb2d47 (Accessed on 51-May-2025)

Liao, X., Zou, T., Chen, M., Song, Y., Yang, C., Qiu, B., Chen, Z.-F., Tsang, S. Y., Qi, Z., and Cai, Z.: Contamination profiles and health impact of benzothiazole and its derivatives in PM2.5 in typical Chinese cities, Sci. Total Environ., 755, 142617, 10.1016/j.scitotenv.2020.142617, 2021.

2. Experiments were conducted at two different pH conditions (pH 2 and pH 10). The authors need to provide the rationale for selecting these two pH to perform experiments. Are they relevant to atmospheric conditions?

Response: We thank the reviewer for raising this question about our rationale for selecting pH 2 and pH 10 as experimental conditions. Both pH levels chosen for our experiments (pH 2 and pH 10) are relevant to atmospheric aqueous-phase conditions. As noted in Section 2.3 of our manuscript, atmospheric liquid phases exhibit a wide pH range from highly acidic to slightly alkaline. Herrmann et al. (2015) have summarized the range of pH in various aqueous phases. Most atmospheric aqueous environments are typically acidic, ranging from strongly (pH -2.5) to slightly (pH < 7) acidic conditions. Therefore, pH 2 was selected as a representative scenario for acidic atmospheric aqueous conditions, well-supported by numerous previous aqueous-phase simulation studies (Li et al., 2023). Under certain conditions, like haze and marine aerosols, aqueous particles can reach mildly alkaline states, with reported pH values ranging from >7 to 10. This mild alkalinity (pH 9-10) has also been frequently used in laboratory simulations of atmospheric aqueous-phase reactions (Witkowski et al, 2022, Tang et al., 2020). Thus, we selected pH 10 to represent such weakly alkaline atmospheric conditions.

Reference

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Tang, S., Li, F., Tsona, N. T., Lu, C., Wang, X., and Du, L.: Aqueous-phase photooxidation of vanillic acid: A potential source of humic-like substances (HULIS), ACS Earth Space Chem., 4, 862-872, 10.1021/acsearthspacechem.0c00070, 2020.

Witkowski, B., Jain, P., and Gierczak, T.: Aqueous chemical bleaching of 4-nitrophenol brown carbon by hydroxyl radicals; products, mechanism, and light absorption, Atmos. Chem. Phys., 22, 5651-5663, 10.5194/acp-22-5651-2022, 2022.

3. Some reference compounds such as suberic acid and toluic acid are organic acids. Will the pH of solution be changed when adding these acids into the solution?

Response: In the experiments for determining rate constants, suberic acid and toluic acid were used as reference compounds. Their addition did not alter the measured pH of the solutions obtained by a pH meter (SevenCompact, Mettler Toledo). This observation can be explained by their low concentrations and pKa values. The concentration of these organic acids as reference compounds was only 1-2 nM. Taking suberic acid as an example, it is a dicarboxylic acid. Even assuming complete ionization, a 2 nM suberic acid solution would contribute only 4×10^{-9} M H^+. In comparison, the H^+ concentration is 10^{-2} M at pH 2, and the OH^- concentration is 10^{-4} M at pH 10. Thus, the effect of 4×10^{-9} M H^+ on the solution's pH is negligible and undetectable by the pH meter. Furthermore, suberic acid (pKa1 = 4.53, pKa2 = 5.52 at 25°C) and toluic acid (pKa = 4.37 at 25°C) are weak acids and do not fully dissociate in water. The actual H^+ concentration from their ionization is much lower than 4×10^{-9} M. Therefore, the addition of these acids does not change the pH of the solution.

4. L185, the authors state that the rate constants of selected BTs reacted with OH radicals under the highly acidic condition were slightly lower than those under the

weakly alkaline condition. Why the reaction rate constants at low pH are lower than those under high pH conditions? Please clarify.

Response: We appreciate the reviewer's comment regarding the pH dependence of the rate constants. The slightly lower rate constants observed under highly acidic conditions ($8.0 \pm 1.8 \times 10^9$ M^{-1} s^{-1}) compared to weakly alkaline conditions ($9.7 \pm 2.7 \times 10^9$ M^{-1} s^{-1}) are within experimental uncertainty, and the difference is not statistically significant. This is why we stated in the text that the values were "slightly lower" rather than definitively different. In addition, one of the focuses of this study was to demonstrate that BTs react rapidly with OH radicals under atmospherically relevant pH conditions, leading to relatively short atmospheric lifetimes. While subtle pH-dependent variations in rate constants may exist, these minor differences were not a central focus of our investigation, as they do not substantially affect our main conclusions about the atmospheric fate of BTs.

5. It is interesting that nanoparticles were formed after OH reactions. Did you observe different patterns for the formation of nanoparticles for different BTs. I would expect to see different patterns given that their structures are different and the product composition prolife in Figure 4 is also different.

Response: The formation of nanoparticles is indeed an interesting observation, which is proposed from the aggregation of oligomeric products (Fig. 4). However, based on the nanoparticle characterization data (Fig. 3f and Fig. S8), while the size distributions of nanoparticles formed from different BTs share some common features, such as close size ranges and number concentration magnitudes. Distinct patterns among them cannot be conclusively identified. This limitation primarily stems from the nanoparticle tracking analysis (NTA) method employed in this study. As noted in Section 3.3, NTA provides only an approximate estimation of nanoparticles within a size range of 10-2000 nm. Moreover, nanoparticles may undergo agglomeration, deagglomeration, or partial dissolution during sample transfer, which can significantly influence measured particle concentrations and size distributions. Thus, the reported size distributions may not precisely reflect the true state of the nanoparticles in the reaction solution. While this study focuses on demonstrating the potential for nanoparticle formation during the aqueous-phase reactions of BTs, a detailed comparison of nanoparticle patterns across different BTs was not a primary objective. Nevertheless, the reviewer's insightful suggestion highlights an important direction for future work. Further investigations employing more advanced characterization techniques would be valuable to elucidate whether structural differences among BTs lead to distinct nanoparticle formation patterns.

6. L274, The authors state that more products can be identified using ESI+ mode because organic products are rich in basic functionalities and slightly less rich in acidic functionalities. I am not sure this is correct for all organics or this is because BTs contain N, and N-containing compounds are more easily to be detected with ESI+ mode.

Response: We thank the reviewer for the comment regarding the interpretation of the +/-ESI results. The statement attributing the higher number of identified products in +ESI mode to the presence of basic functionalities may not be sufficiently rigorous. The causality should be softened to reflect a more nuanced interpretation. As observed by Tang et al. (2022), similar results were reported in Maillard-like reactions in atmospheric aqueous phases, where more compounds were identified in +ESI mode. They attributed the experimental result to the fact that products formed by Maillard reactions are rich in basic functional groups (e.g., amino) and poor in acidic functional groups (e.g., carboxyl), and are thus readily ionized in the +ESI mode. Lin et al. (2012) also showed that compounds detected in +ESI mode tend to contain reduced nitrogen functionalities like amines and alkaloids, which are basic in nature, whereas compounds identified in -ESI mode are often enriched in acidic groups such as carboxylic acids and organosulfates. Therefore, basic functionalities, especially organic compounds containing reductive nitrogen, generally tend to be detected in +ESI mode. As shown in Fig. 4b, although CHON species are more abundant in +ESI mode, the combined fraction of CHON and CHOSN species is comparable between modes, suggesting that the presence of nitrogen does not fully explain the observed differences between two modes either. Thus, the higher number of detected products in +ESI mode may result from the general tendency of basic functionalities (not limited to N-containing species) to ionize more efficiently in this mode. The corresponding sentences in the second paragraph of Section 3.4 have been rewritten in the revised manuscript. "Meanwhile, products contained more identified compounds in positive-ion (+ESI) mode than in negative-ion (-ESI) mode, which suggests a possible enrichment of basic functionalities in the product mixture, as such groups are generally more amenable to ionization in +ESI mode (Lin et al., 2012)."

References

Lin, P., Rincon, A. G., Kalberer, M., and Yu, J. Z.: Elemental composition of HULIS in the Pearl River Delta Region, China: Results inferred from positive and negative electrospray high resolution mass spectrometric data, Environ. Sci. Technol., 46, 7454-7462, 10.1021/es300285d, 2012.

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.

7. The proposed mechanism for BT reactions is convincing. I recommend the authors to describe the electron transfer process in Figure 5 such as ring-opening process, so that readers can better understand the chemical mechanism.

Response: We thank the reviewer for this helpful suggestion. The addition of the electron transfer process improves the clarity of the proposed mechanism. In the revised manuscript, we have modified Fig. 5 to include the electron transfer process at key steps, such as the ring-opening process, so that readers can better understand the chemical mechanism.

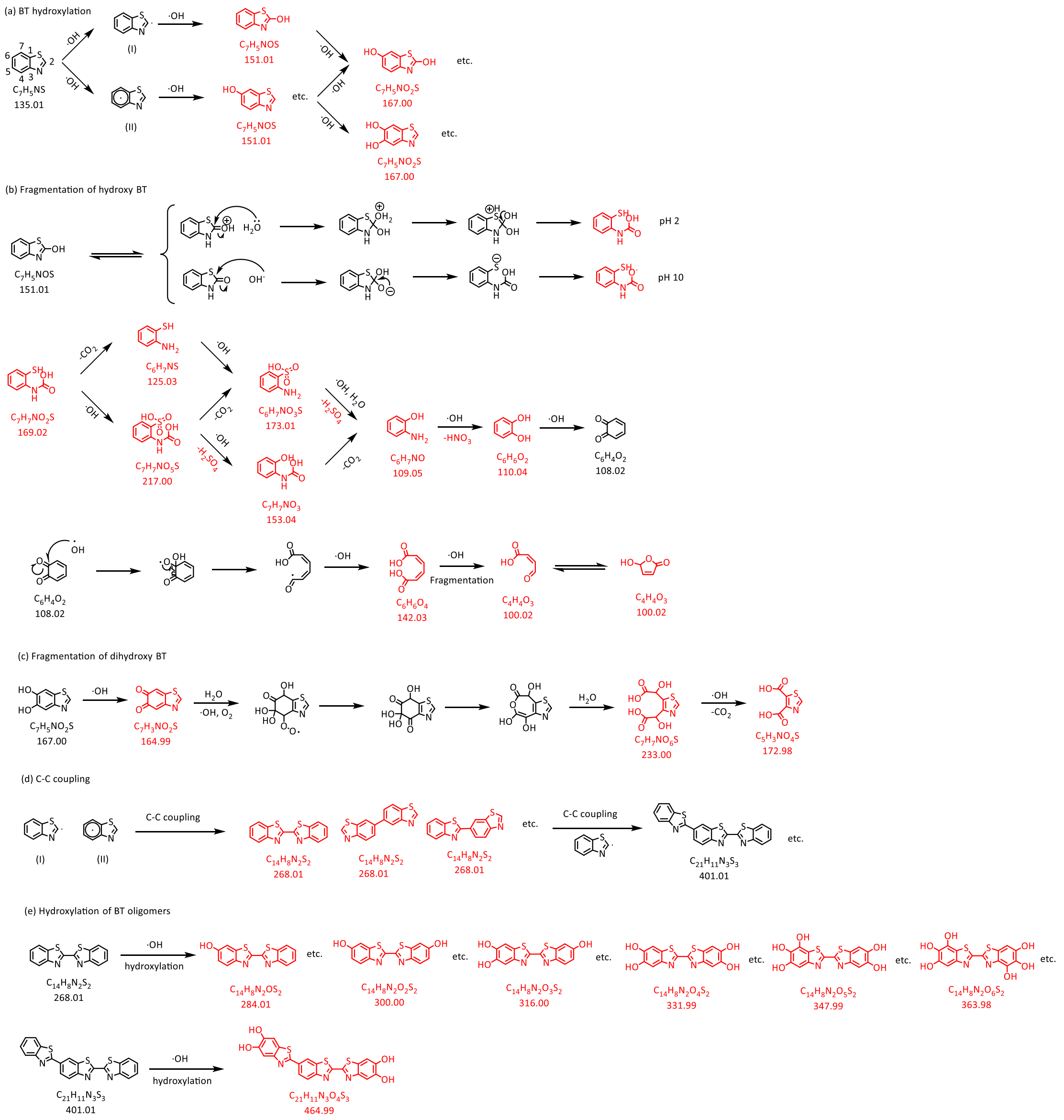

Figure 5. Proposed reaction mechanism and structures of partial products of BT oxidized by OH radicals in the aqueous phase. Red structures with formulas and molecular weight are the products assigned in Orbitrap mass spectra.

8. When discussing the atmospheric lifetime of BTs, the authors need to consider the impact of reaction conditions. The current calculation is based on an assumption that the pH of cloud droplets and deliquescent particles are similar to those using in the current experiments (pH 2 and pH 10). The authors need to point out the uncertainty associated with this assumption.

Response: We thank the reviewer for raising this important point. Estimation of BTs atmospheric lifetimes is influenced by rate constants and the aqueous-phase OH concentrations (Eq. (4)). First, we used pH 2 and pH 10 as representative conditions to explore the rate constants of BTs reacted with OH radical in the aqueous phase. Our experimental results indicate that the reaction rate constants under the two pH conditions did not differ significantly. Second, OH concentrations in cloud and particle water cannot be directly measured and are typically derived from model simulations. As noted in the third major comment from Referee #3 and supported by the studies of Herrmann et al. (2010), Arakaki et al. (2013), and Bianco et al. (2020), OH concentrations in different aqueous media can span 2-4 orders of magnitude, influenced by multiple factors, including the composition and reactivity of dissolved organic compounds, the efficiency of gas-water transfer, and the presence of metal ions catalyzing OH formation (Wolke et al., 2005; Herrmann et al., 2005; Herrmann et al., 2010). It leads to substantial uncertainty in lifetime calculations. We have revised Table 3 and the corresponding discussion to reflect this variability and have emphasized the impact of OH concentration uncertainty on lifetime estimates in the response to the third major comment from Referee #3. Besides, model studies show that pH influences aqueous-phase OH concentrations via dissociation equilibria, transition-metal catalysis, and radical reactivity (Wolke et al., 2005; Herrmann et al., 2005). Thus, pH may affect lifetime estimation through its effect on OH radical levels. Assuming the pH of atmospheric aqueous phases is comparable to the experimental conditions may introduce more uncertainty in aqueous-phase OH radical concentrations, and further in the estimation of atmospheric lifetimes. Thus, we have noted this point in the Conclusion section in the revised manuscript to acknowledge this limitation. “It should be noted that the pH conditions in this study may introduce additional uncertainty into the estimated atmospheric lifetimes of BTs, due to the pH-dependent variability in aqueous-phase OH radical concentrations (Wolke et al., 2005; Herrmann et al., 2005).”

References

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