Author's Response to Referee #3

We greatly appreciate the time and effort that Referee #3 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 #3 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.

In this paper, Zhang et al. measure the reactivity in water of a specific class of aromatic organic compounds, namely benzothiazoles (BTs).

Since BTs are industrially produced, elucidating their multiphase fate in the atmosphere is important. They used the relative rate methodology to experimentally determine the reaction rates of BTs with OH. The rates they found are in line with the literature for BT, which gives trust in the new measurements for MBT and CBT They carried out product formation experiments (IC for inorganics, Orbitrap for organics, and NTA for nanoparticles) and measured optical properties (fluorescence spectrophotometry) to propose an OH-reaction mechanism of BTs. This last part is particularly interesting for understanding the contribution of organics aqueous phase chemistry to SOA formation for instance, and organics atmospheric aging in general.

Overall the paper is good and could be published in ACP after the authors address these comments as they deem appropriate.

Major comments

1. - Sect. 2.3: These types of experiments are often carried out in triplicates to account for systematic uncertainty. Maybe I missed the mention of it but if the experiments were not repeated, it would be important to explain why.

Response: We thank the reviewer for raising the point regarding the need for repeated kinetic experiments. We fully agree that performing the kinetic experiments in triplicate is essential to account for systematic uncertainties and to ensure reliable results. Our experiments were in fact carried out in triplicate. Sect. 2.3 already contains a statement indicating the experiments were repeated. "Kinetic experiments were performed three times at initial pH 2 and 10 with the adjustment of the concentration ratio of BTs and the reference compound for accurate determination of the rate constants for the reaction of BTs with OH radicals." As shown in Table 2, the rate constants for the reactions of BTs with each reference compound were determined based on three replicate runs. The ratio of initial concentrations of BTs to reference compounds were adjusted with 1:1, 1:2, and 2:1 (Table S2 in the Supplement).

However, we recognize that this detail might not have been sufficiently clear to the reader. To avoid any misunderstanding, we have slightly revised the wording of that sentence in Section 2.3 to explicitly highlight the triplicate nature of kinetic experiments as follows: "Kinetic experiments were performed in triplicate at initial pH 2 and 10, with the concentration ratio of BTs to the reference compounds adjusted to ensure accurate determination of the rate constants for the reactions of BTs with OH radicals." This update makes it unambiguous that all kinetic experiments were repeated three times, thus directly addressing the reviewer's concern about systematic uncertainty.

2. - l. 191: Is there an explanation why previous reported rate constants are significantly lower?

Response: We thank the reviewer for this observation. The discrepancy between our measured rate constant (~9×10^9 M^{-1} s^{-1}) and the lower values reported by Borowska et al. (2016) and Andreozzi et al. (2001) is indeed noteworthy. The differences likely due to varying experimental conditions, including the reaction temperatures, the reaction vessels, the type and the intensity of the light source, et al. The reaction temperature is maintained at 298 K in our study, but 293 K in the two previous studies (Borowska et al., 2016; Andreozzi et al., 2001). Lower temperature can generally lead to lower rate constant according to the Arrhenius equation. The reaction vessel used in our study is a quartz glass vessel, but ordinary glass vessels in the two previous study. Ordinary glass blocks more UV light than quartz glass. In addition, Borowska et al. (2016) employed a polychromatic mercury lamp while Andreozzi et al. (2001) used a low-pressure 254 nm UV lamp. Differences in material of the reaction vessels and irradiation source can lead to different OH radical production rates. The methodology used to determine the rate constants also differed. Prior studies measured BT degradation indirectly or at higher initial BT concentrations, which can underestimate the true second-order rate constant. In Borowska et al. (2016), the initial BT concentration was on the order of 10^{-4} M, significantly higher than ~10^{-6} M used in our study. Such high concentrations can cause increased competition for OH radicals, yielding lower measured rate constants. We added the following sentences in Section 3.1 of the revised manuscript for the explanation of the discrepancy, "The lower values from previous studies are potentially due to the differences in experimental conditions. The reaction temperatures in the previous studies were 293 K, lower than that in our study. In addition, the material of vessel employed in the previous studies is ordinary glass, but quartz glass in our study. The reduction in UV light caused by ordinary glass, together with the higher initial concentration of BT, limits the availability of OH radicals. These factors thus potentially yield lower measured rate constants."

3. - Conclusion: The lifetime evaluation is very useful and welcomed. However, the OH aqueous concentrations used here may be criticized. The literature referenced in Table 3 is quite old and does not reflect the high uncertainty surrounding the estimation of steady-state aqueous OH concentrations. The Arakaki et al. (2013) study did a nice job revisiting estimations of aqueous OH. For instance, OH is around 10^{-15} M in their maritime sample. The review of Bianco et al. (2020) also provides a more recent view on this question. I encourage the authors to revise their calculations and possibly their conclusions based on the range of reported aqueous OH concentrations.

Response: We thank the reviewer for their affirmation and suggestion for the lifetime evaluation. Initially, the evaluation of BTs lifetimes relied solely on a single reference and considered only the average steady-state aqueous OH concentrations. Taking the reviewer's advice, we have modified Table 3 along with its associated text and references. We have incorporated both the average steady-state aqueous OH concentrations and their large ranges reviewed and evaluated in Herrmann et al. (2010), Arakaki et al. (2013), and Bianco et al. (2020) for the BTs lifetime evaluation. The modified Table 3 in the revised manuscript 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).

The first paragraph of the Conclusion, corresponding to atmospheric lifetimes of BTs in the aqueous phases, has been modified in the revised manuscript as follows:

In Eq. (4), k_{BTs} is the rate constants of BT, MBT, and CBT reacted with OH radicals determined in this study, and [OH] represents the concentration of OH radicals in the atmosphere under various aqueous-phase conditions (Bianco et al., 2020; Arakaki et al., 2013; Herrmann et al., 2010). The aqueous-phase OH concentrations and the evaluated lifetimes of BT, MBT, and CBT are summarized in Table 3. Atmospheric aqueous phases are generally categorized into cloud droplets and deliquescent particles, and can be further classified by location as urban, remote, and maritime regions. Previous studies give the mean value of OH concentrations in various aqueous phases (Bianco et al., 2020; Hermann et al., 2010). The atmospheric lifetimes determined for BT, MBT, and CBT are in the range from 0.01 to 0.4 h in deliquescent particles, and 0.01 to 10.4 h in cloud particles. Previous studies also model varying ranges of OH concentrations in each aqueous phase, from 10^2 to 10^4 fold (Bianco et al., 2020; Arakaki et al., 2013; Hermann et al., 2010). For example, the OH concentrations are from 10^{-14} to 10^{-12} M in remote deliquescent particles and 10^{-16} to 10^{-12} M in urban deliquescent particles. The 10^2 to 10^4-fold ranges in aqueous-phase OH concentrations produce 10^2 to 10^4-fold spread in estimated BTs lifetimes based on Eq. (4). The large range of OH concentrations leads to large uncertainties of estimated BTs lifetimes. In urban regions, the OH concentrations are modeled to be from 10^{-16} to 10^{-12} M in both cloud droplets and deliquescent particles, which leads to considerably large ranges of BTs lifetimes, from several minutes to several days. In addition to this, in most cases, the BTs lifetimes can be limited to several minutes to several hours. In general, the selected BTs tend to be transformed by aqueous OH radicals, especially in the region of their emission sources, and in rare cases they are also probably more persistent in the aqueous phase.

The second paragraph of the Conclusion, corresponding to the comparison of atmospheric lifetimes between gas phase and aqueous phase, has been modified in the revised manuscript as follows:

The lifetimes of BTs estimated using mean OH concentrations in the gas phase are significantly longer than those estimated using mean OH concentrations in the aqueous phase, although in rare cases where aqueous-phase OH concentrations are on the order of 10^{-16} M, the estimated lifetimes in the aqueous phase can exceed those in the gas phase by several times. It reveals the high reactivity of BTs with OH radicals in the aqueous phase, suggesting that atmospheric aqueous-phase oxidation could be a significantly effective process to transform these contaminants in the atmosphere.

The corresponding references in the revised manuscript are added as follows:

Arakaki, T., Anastasio, C., Kuroki, Y., Nakajima, H., Okada, K., Kotani, Y., Handa, D., Azechi, S., Kimura, T., Tsuhako, A., Miyagi, Y.: A general scavenging rate constant for reaction of hydroxyl radical with organic carbon in atmospheric waters, Environ. Sci. Technol., 47, 8196-8203, 10.1021/es401927b, 2013.

Bianco, A., Passananti, M., Brigante, M., Mailhot, G.: Photochemistry of the cloud aqueous phase: A review, Molecules, 25, 423, 10.3390/molecules25020423, 2020.

Minor comments

1. - l. 56: BT gas-phase oxidation is introduced before the presentation of Fig. 1 which shows which molecule BT specifically is

Response: We thank the reviewer for this notification. The BT in Line 56 refers to benzothiazole. We have used “benzothiazole” to replace “BT” before the presentation of Fig. 1 in the revised manuscript for clarification.

2. - l. 60: the sentence is unusually formulated, it would be clearer to write something like "... could contribute to secondary organic aerosol after their oxidation into C3-8 organic compounds which also produces sulfuric acid"

Response: Taking the reviewer's advice, we have rewritten the sentence in the revised manuscript for clarification, "Simulation experiments of the gas-phase benzothiazole photooxidation with OH radicals indicated that benzothiazole could contribute to secondary organic aerosols after their oxidation into C_{3-8} organic compounds and could also lead to the production of sulfuric acid."

3. - l. 264: this sentence is confusing, please reword it because I can't understand its meaning.

Response: Taking the Reviewer's advice, we have rewritten this sentence at the end of the first paragraph of Section 3.4 to explicitly state our point about the potential contribution of BTs oxidation to sulfate aerosol formation by combining observations from both aqueous- and gas-phase oxidation. "Considering both aqueous- and gas-phase oxidation results, atmospheric BTs oxidation appears to be a potential source of sulfate aerosols, given the significant sulfate yields observed from the oxidation of sulfur-containing structures."

4. - Fig. 4a: the histograms may be better understood if they were transposed, i.e. number of carbon on the x-axis, number of assigned formulas on the y-axis. No obligation, it's only a matter of taste.

Response: We appreciate the reviewer's suggestion regarding the presentation style of Fig. 4a. While transposing the histograms (placing the number of carbon atoms on the x-axis and the number of assigned formulas on the y-axis) might indeed offer an alternative visualization, we have deliberately retained the current arrangement to maintain consistency and coherence between Fig. 4a and Fig. 4b. Specifically, the horizontal presentation of experiments from left to right in Fig. 4b naturally aligns with the existing structure of Fig. 4a, enhancing readability across the figure set. We therefore respectfully choose to keep the original presentation.

5. - l. 292: the sentence is confusing, please reword it. I guess it is supposed to mean that the CHONS fraction for BT and MBT is comparable to the CHONS+CHONSCl fraction for CBT?

Response: We thank the reviewer for highlighting the confusion in this sentence. The reviewer's interpretation accurately reflects our intended meaning. To improve clarity, we have rewritten the sentence in the third paragraph of Section 3.4 in the revised manuscript as follows: "In the CBT experiment, CHONS compounds alone account for only 30-40% of the total identified molecular formulas. However, when CHONSCl compounds are included, the combined proportion of CHONS and CHONSCl compounds becomes comparable to the fraction of CHONS compounds identified in the BT and MBT experiments."

References

Arakaki, Takemitsu, Cort Anastasio, Yukiko Kuroki, Hitomi Nakajima, Kouichirou Okada, Yuji Kotani, Daishi Handa, et al. 'A General Scavenging Rate Constant for Reaction of Hydroxyl Radical with Organic Carbon in Atmospheric Waters'. Environmental Science & Technology 47, no. 15 (6 August 2013): 8196–8203. https://doi.org/10.1021/es401927b.

Bianco, Angelica, Monica Passananti, Marcello Brigante, and Gilles Mailhot. 'Photochemistry of the Cloud Aqueous Phase: A Review'. Molecules 25, no. 2 (January 2020): 423. https://doi.org/10.3390/molecules25020423.

Response: We thank the reviewer for the suggestion to include additional references. These references have been added according to our response to the third major comment.