

Reply to Interactive comment on “Effect of Inorganic-to-Organic Mass Ratio on the Heterogeneous OH Reaction Rates of Erythritol: Implications for Atmospheric Chemical Stability of 2-Methyltetrols” by Rongshuang Xu et al.

Anonymous Referee #2

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-981-RC2>, 2019

Xu et al. investigated the OH-initiated heterogeneous oxidation of erythritol particles and particles containing erythritol and ammonium sulfate (AS). Erythritol was used as a surrogate of 2-methyltetrols, one of the most important isoprene-derived SOA products. SOA chemical composition was retrieved using a soft atmospheric pressure ionization source (DART) coupled to an Orbitrap. The reactivity of erythritol was characterized as a function of inorganic-to-organic mass ratio. While the study is well constrained and clearly presents some interesting results, some aspects are not considered within the discussion (see comments below).

We would like to sincerely thank the reviewer for his/her thoughtful comments. The referee’s comments are below in italics followed by our responses.

Comment #1:

Page 2, lines 23-24: The authors stated that the reactivity of 2-methyltetrols has not been tested before. That’s not fully correct. Hu et al. (Jimenez’s group) investigated the aging of ambient isoprene-derived SOA and found that IEPOX-SOA (mainly producing 2-MT) are fairly unreactive. This study should be cited by the authors and further discuss.

Author Response:

We would like to thank the reviewer for bringing up this paper by Hu et al. (2016). This work investigated the heterogeneous reactivity of ambient IEPOX-SOA towards OH radical and reported reaction kinetics ($4.0 \pm 2.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $3.9 \pm 1.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for IEPOX-SOA collected in SE US and Amazon, respectively) based on the decay of $\text{C}_5\text{H}_6\text{O}^+$ ion (a tracer ion for IEPOX-SOA in ambient particles) in their AMS measurements. Based on these data, they calculated on average a more than 2-week (19 ± 9 days) atmospheric lifetime of IEPOX-SOA against OH radical oxidation based on rate constant of $4.0 \pm 2.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and averaged ambient OH concentration of $1.5 \times 10^6 \text{ molecule cm}^{-3}$. We would like to acknowledge that these measured values are for ambient IEPOX-SOA and not for pure 2-methyltetrols. To our best knowledge, the heterogeneous OH reactivity of pure 2-methyltetrols particles has been investigated.

We agree with the reviewer that 2-methyltetrols are important components of IEPOX-SOA in the atmosphere. For instance, 2-methyltetrols can account for 10 % – 20 % of IEPOX-SOA in an experimental study (Surratt et al., 2010) and ~ 24 % of ambient IEPOX-SOA in field studies in rural Alabama, southeastern US (Isaacman et al., 2014). As suggested by Hu et al. (2016), the rates derived in their study could be considered as a lower limit for individual molecular components of IEPOX-SOA (e.g. 2-methyltetrols), as it may take two or more OH reactions for their AMS spectrum to no

longer resemble that of IEPOX-SOA. We have added this information in the revised manuscript.

Page 3, Line 5: “Hu et al. (2016) have investigated the heterogeneous reactivity of ambient IEPOX-SOA (consisting of 2-methyltetrols, C5-alkene triols, organosulfate, etc.) towards gas-phase OH radicals in SE US and Amazon and reported the reaction kinetics for IEPOX-SOA based on the decay of $C_5H_6O^+$ ion (a tracer ion for IEPOX-SOA in ambient particles) in their AMS measurements. They calculated on average a more than 2-week (19 ± 9 days) atmospheric lifetime of IEPOX-SOA against heterogeneous OH oxidation based on rate constant of $4.0 \pm 2.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and averaged ambient OH concentration of $1.5 \times 10^6 \text{ molecule cm}^{-3}$. They also suggest that the observed rates may consider as a lower limit for individual molecular components of IEPOX-SOA (e.g. 2-methyltetrols) because it may take two or more OH reactions to make their AMS spectrum distinguishable from that of IEPOX-SOA after oxidation (Hu et al., 2016).”

Comment #2:

Page 3, lines 3-5: The authors should be careful here and do not overstate the impact of OH reactivity. A chemical lifetime of 2 weeks cannot be really classified as a "significant" reaction/loss.

Author Response:

We agree with the reviewer's comment. We have revised this sentence in the manuscript.

Page 3, Line 3: “Kessler et al. (2010) reported that heterogeneous oxidation of pure erythritol particles by gas-phase OH radicals with an effective OH uptake coefficient, γ_{eff} , of 0.77 ± 0.1 and a corresponding chemical lifetime of $\sim 13.8 \pm 1.4$ days at a relative humidity (RH) of 30 %.”

Comment #3:

Page 4, lines 26: The authors should provide more information regarding the experimental conditions: - What was the gas-phase concentration of erythritol? Is it possible that larger IOR lead to higher degassing (e.g., salting-out effect?) - Can the presence of gaseous erythritol decrease the concentration of OH radicals and further impact the heterogeneous reactivity? - Please provide the size, surface area and mass of particles for each condition.

Author Response:

Thanks for the comments. We have mentioned in the manuscript that control experiments had been carried out to investigate the volatilization of erythritol under our experimental conditions. The mass spectra were measured when erythritol particles and erythritol-AS particles were removed from the particle stream by filtration using a particle filter before entering the heater for DART analysis. No obvious peak was observed in mass spectra, suggesting that there is insignificant amount of erythritol present in the gas phase under our experimental conditions. We would also like to mention that the effective saturation vapor pressure, C^* of erythritol before oxidation for pure erythritol and erythritol-AS systems is estimated based on the framework by Zuend and Seinfeld (2012), using the saturation vapor pressure predicted by

EVAPORATION (Compernelle et al., 2011) and the activity coefficient derived from AIOMFAC. The C^* of erythritol is estimated to be $0.686 \mu\text{g m}^{-3}$, $0.792 \mu\text{g m}^{-3}$, $0.921 \mu\text{g m}^{-3}$, $1.60 \mu\text{g m}^{-3}$ at IOR = 0.0, 0.5, 1.0, 5.0, respectively (**Table 1** in the revised manuscript) and $\sim 99\%$ of erythritol would be expected to remain in particle phase in all experiments based on gas-particle partitioning model (Zuend and Seinfeld, 2012) with the particle mass loading of about $500 \mu\text{g m}^{-3}$ in our experiments. These results suggest that the volatilization and gas-phase reactivity of erythritol would not be significant in our work. We also acknowledge that the effects of the salt on the gas-particle partitioning of erythritol (in term of C^*) have been considered by calculating the activity coefficients of erythritols using AIOMFAC at different IORs.

The surface-weighted mean diameter of erythritol and erythritol-AS particles at all IORs have been given in **Table 1**. The mass loading under all experiments was around $500 \mu\text{g m}^{-3}$, and the surface area was $\sim 9 \times 10^9 \text{ nm}^2 \text{ cm}^{-3}$.

Comment #4:

Page 6, dart section: Please provide more information. Was it real-time evaporation or were the particles collected onto a filter prior vaporization?

Author Response:

Thanks for the comment. In our experiments, it was a real-time evaporation of the particles. The particle stream was directed into a stainless-steel tube, where the particles were fully vaporized in real time. The resultant gas-phase species were then delivered into an ionization region. The erythritol particles and erythritol-AS particles were confirmed to be fully vaporized at 300°C before introduced to the ionization region in separate experiments, thus yielding a mass spectrum representative of the entire particle (i.e., bulk composition). We have added this information in the manuscript.

Page 5, Line 22: “The remaining flow was directed to a stainless-steel tube heater, where the particles were fully vaporized in real time. The resultant gas-phase species were then delivered into an ionization region. The erythritol particles and erythritol-AS particles were confirmed to be fully vaporized at 300°C before introduced to the ionization region in separate experiments, thus yielding a mass spectrum representative of the entire particle (i.e., bulk composition).”

Comment #5:

Page 9: Recent studies have shown that isoprene-derived SOA, especially when formed in the presence of acidic aerosols are highly viscous, further impacting heterogeneous processes (e.e., Surratt’s group, Ault’s group, Thornton’s group). While the assumption that erythritol is well mixed is likely correct, the authors cannot ignore these recent studies and the last paragraph (i.e., atmospheric implications) should mention the impact of the phase and viscosity on the heterogeneous reactivity of isoprene derived SOA products. In other words, the rate constant/lifetimes proposed in this study are likely an upper limit suggesting that the OH oxidation of 2-methyltetrols is negligible.

Author Response:

We agree with the reviewer’s comment that the particle phase, morphology and viscosity can significantly affect the heterogeneous reactivity of isoprene derived SOA and their individual components (e.g. 2-methyltetrols). When the isoprene derived SOA

are highly viscous, this slows down the overall rate of reaction due to diffusion. In this study, the rate constants and lifetimes measured for well mixed erythritol particles and erythritol–AS particles at a high RH may consider as an upper limit. The OH oxidation of 2-methyltetrols in ambient particles could be slower than our reported values, depending on the formation pathways and composition of isoprene derived SOA and atmospheric conditions. We have added the following information in the conclusions.

Page 18, Line 22: “Recent studies have shown that the phase state and viscosity of the particles depending on the particle composition and environmental factors can significantly affect the diffusivity of organic molecules, water molecules and oxidants such as gas-phase OH radicals, which in turn the overall oxidation rate and formation of products (Chan et al., 2014; Slade and Knopf, 2014; Chim et al., 2017a; Marshall et al., 2016; 2018). Isoprene-derived SOA, especially when formed in the presence of acidic sulfate particles have been reported to be highly viscous (Shrivastava et al., 2017; Olson et al., 2019; Zhang et al., 2019). For instance, Riva et al. (2019) have shown that a viscous IEPOX-SOA coating was likely formed in the presence of acidic sulfate seed particles. The diffusion of organic molecules (e.g. 2-methyltetrols) from the bulk to the particle surface could slow down, lowering the overall heterogeneous reactivity.

To date, the effects of the complex interplay between particle phase, morphology and viscosity on the heterogeneous reactivity remains largely unexplored. We would like to acknowledge that in this study the rate constants and lifetimes measured for well mixed erythritol particles and erythritol–AS particles at a high RH may consider as an upper limit. The OH oxidation of 2-methyltetrols in ambient particles could be slower than our reported values, depending on the formation pathways and composition of IEPOX-SOA and atmospheric conditions (e.g. RH and temperature). All these results suggest that a single kinetic parameter may not be well described for the heterogeneous OH oxidation erythritols and 2-methyltetrols in atmosphere since the rates can vary significantly, depending on the particle composition, phase and morphology and environmental factors.”

Comment #6:

Page 9, lines 11-14: Did the particles shrink? Did the authors estimate a carbon closure?

Author Response:

As discussed in our response for **reviewer 1, comment #7**, we have observed slight changes in particle size upon oxidation for both erythritol and erythritol–AS particles (please see the **figure** below). The surface-weighted mean diameter changes from 276.1 nm to 255.8 nm (~ 7.3 %) for erythritol particles and decreases from 278.2 nm to 262.1 nm (~ 5.8 %), from 280.5 nm to 266.7 nm (~ 4.9 %), from 281.2 nm to 274.0 nm (~ 2.6 %) for erythritol–AS particles at IOR = 0.5, 1.0 and 5.0, respectively. The decrease in particle size could be explained by the formation and volatilization of some reaction products (i.e. C₄ hydroxyketone and hydroxyaldehyde (C₄H₈O₄), C₂ hydroxyketone (C₂H₄O₂) and C₃ hydroxyaldehyde (C₃H₆O₃)). We have added this information in the revised manuscript.

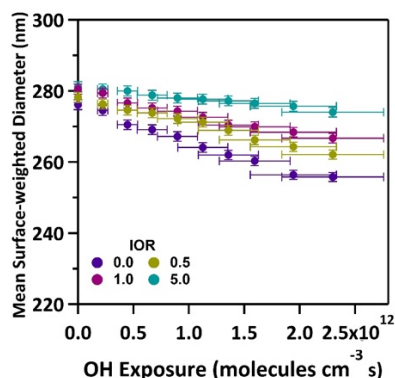


Figure S2. The change in surface-weighted mean diameter as a function of OH exposure for erythritol particles and erythritol-AS particles with different IORs.

Supporting material, we have added **Figure S2** in the *supporting material* to illustrate the change in particle diameter for erythritol particles and erythritol-AS particles upon oxidation.

Determining a carbon closure is a very good suggestion. However, we cannot estimate a carbon closure with a few reasons. One reason is that we may not be able to detect all reaction products with the DART-MS technique. Second, we cannot quantify the concentration of particle-phase products because the ionization efficiencies of the products are not known. At last, gas-phase products have not been measured in our experiments. However, we agree with the reviewer a carbon closure study should be considered and carried out in future study.

Comment #7:

Page 10, lines 9-10: That doesn't mean that thermal decomposition is not occurring for other types of compounds, e.g., carboxylic acid or other oxygenated species. As the authors did not report any concentrations it is not difficult to make such a statement; i.e., the observed compounds can be only a fraction of the quantity formed. In addition, the measured compounds can fragment into small ions: $< m/z$ 70. It is also unclear why the authors selected such a narrow mass range. To fully investigate the potential fragmentation the authors could have extended the mass range: i.e., 50-400. Please clarify.

Author Response:

Thanks for the comments. DART ion source is considered as a less energetic “soft” ionization technique, which applies less excess internal energy to the target molecule, resulting in minimal dissociation and yielding intact ions with minimal fragmentation. Previous studies (Cody et al., 2005; Nah et al., 2013) have shown that the dominant ions for their investigated organic compounds (M), including alkanes, alkenes, carboxylic acids, esters, and alcohols, in negative-ion mass spectra are observed in the form of $[M-H]^-$, or $[M]^-$. These results suggest that the thermal decomposition of these classes of organic compounds may not be significant. However, we agree with the reviewer that some potential reaction products (e.g. oligomers and peroxides) could be thermally decomposed in our experiments.

We agree with the reviewer about the concerns about the thermal decomposition and quantification of the reaction products in our particle-DART technique. Since the

ionization efficiency of erythritol and its reaction products are currently not well understood, we thus do not attempt to quantify their concentrations.

We chose this detected range because this gave the best overall performance when we optimized our systems. Thus, small ions which were less m/z 70 were not measured in our work. In this work, we primarily focus on the measurement of reaction products remained in the particle phase after oxidation. However, we agree with the reviewer that it would be important to measure these small ions, which are likely volatile fragmentation products present in the gas phase. The measurement of gas-phase products, together with the characterization of particle-phase products would provide better insight into heterogeneous reaction pathways.

Comment #8:

Page 10, lines 13-14: Here again the statement is not correct. The authors have to be quantitative in order to make such a statement. For example, did the authors try to generate SOA with one single compound (e.g., carboxylic, polyol,...) and determine if the mass measured with the DART corresponds to the mass measure with an SMPS?

Author Response:

On page 10, Line 21, we calculated the effective OH uptake coefficient for erythritol particles and erythritol-AS particles. We have not tried to generate SOA for the OH oxidation in this work.

As raised by the reviewer in his/her earlier comment, we do not attempt to quantify the particle mass measured with the DART and compare the results with that measured with an SMPS. One reason is that the ionization efficiencies of the reaction products are not known and not all reaction products were detected by the DART. While we cannot quantify the concentration of the reaction products, we can quantify the OH decay of the erythritol upon oxidation using their normalized signal before and after oxidation (Eqn.4 in the manuscript). This method does not require to know the mass concentration of the species.

Comment #9:

Page 10, line 17: What would be the expected fragment ions? Not all ions were identified in Fig 1 and some fragments ions were not present before the reaction. Please clarify.

Author Response:

Thanks for the comments. In terms of the expected fragment ion, we could not find the statement on Page 10, line 17 in the original manuscript. We think the reviewer may refer to Page 9, line 20: “but there was no indication of fragment ions expected from...”. As mentioned in our response for **comment #7**, in the literature, the thermal decomposition of alcohols and carboxylic acids has not been observed and reported using particle-DART technique (Nah et al., 2013). However, we acknowledge that at high temperature organic peroxides may break down with the cleavage of O-O bond, and oligomers may also thermally decompose during the analysis to yield smaller fragmentation products (Mukundan and Kishore, 1990). The fragment ions could be difficult to identify depending on their chemical structures. Further investigation on the

formation of these products during heterogeneous OH oxidation of organic compounds is desirable. We have revised our statement in the manuscript.

Page 10, Line 2: “However, we would like to note that some possible reaction products (e.g. organic peroxides and oligomers) could be formed from reactions between peroxy radicals (Stark et al., 2017). We do not rule out the formation of these products upon OH oxidation of erythritol as they may undergo thermal decomposition at high temperature with the cleavage of O-O bond (Mukundan and Kishore, 1990). Further investigation on the formation of organic peroxides and oligomers upon heterogeneous OH oxidation of organic compounds is desirable.”

We do not attempt to identify all ions in particle-DART mass spectra. One reason is that these ions were minor peaks with their relative abundances less than 2% (We could not rule out that their concentrations could be high since their chemical identities and ionization efficiencies are not known). Details about these ions are summarized in following table. We would like to acknowledge that $C_3H_3O_4^-$ ion ($m/z = 103$) was detected after oxidation at IOR = 0.0 but have been observed before oxidation at other IORs. Similarly, for $C_4H_3O_4^-$ ions ($m/z = 115$), it has been detected before oxidation at IOR = 1.0 and 5.0. We would also like to note that a minor ion at $m/z = 133$ ($C_4H_5O_4^-$) was only presented after oxidation. Based on the suggested chemical formula, it may be a second-generation reaction product. To avoid confusion and overstatement, these three minor peaks were not discussed in this work.

m/z	Chemical formula	Relative abundance
New ion after oxidation at IOR = 0.0		
103	$C_3H_3O_4^-$	1.97 %
115	$C_4H_3O_4^-$	1.87 %
133	$C_4H_5O_5^-$	1.68 %
New ion after oxidation at IOR = 0.5		
115	$C_4H_3O_4^-$	1.86 %
133	$C_4H_5O_5^-$	1.33 %
New ion after oxidation at IOR = 1.0		
133	$C_4H_5O_5^-$	1.01 %
New ion after oxidation at IOR = 5.0		
133	$C_4H_5O_5^-$	0.51 %

Comment #10:

Page 10, Fig 2: Please explain the meaning of the error bars. Is it from different experiments?

Author Response:

In Figure 2. (a), the x-error bar represents the calculated error in the OH exposure. The OH exposure, defined as the products of gas-phase OH concentration, [OH], and the particle residence time, t , was determined by measuring the decay of the hexane (Smith et al., 2009):

$$OH \text{ exposure} = -\frac{\ln([Hex]/[Hex]_0)}{k_{Hex}} = \int_0^t [OH] dt \text{ (Eqn.1)}$$

where $[Hex]$ is the hexane concentration leaving the reactor after oxidation, $[Hex]_0$ is the initial hexane concentration before oxidation, and k_{Hex} is the second-order rate constant of the gas-phase OH–hexane reaction).

Based on Eqn.1 and the error propagation rule, the uncertainty for OH exposure, $\sigma_{OH\ exp}$, was derived from Eqn.2:

$$\sigma_{exp} = 0.005 (OH\ exposure) \sqrt{\left(16 + \frac{2}{(OH\ exposure \times k_{Hex})^2}\right)} \quad (\text{Eqn.2})$$

where 0.005 is the precision of Hex measurement (0.5 % of the reading). The y-error is the error in parent decay index ($\frac{I}{I_0}$), where I is the signal intensity of erythritol at a given OH exposure, I_0 is the signal intensity before oxidation. The y-error was determined from the following equation when the uncertainty of signal intensity was assigned to be 0.1 %:

$$\sigma_{\frac{I}{I_0}} = \frac{I}{I_0} \times 0.1 \times \sqrt{2} \quad (\text{Eqn.3})$$

In Figure 2. (b), the y-error represents the uncertainty of derived effective OH uptake coefficient.

Comment #11:

Page 17, line 15: Is it possible to estimate any branching ratio? Is the DART technique more sensitive/selective for certain types of compounds?

Author Response:

Thanks for the suggestion. Since the ionization efficiencies of erythritol and reaction products are not known, the relative abundance of the products after oxidation cannot be well quantified. Furthermore, we are not able to detect all reaction products in both gas- and particle-phases. We thus do not attempt to estimate the branching ratios.

We agree with the reviewer that it is important to know whether the DART technique is more sensitive/selective for certain types of compounds. In the literature, the sensitivity and detection limits for some organic compounds has been reported to be dependent on the structure and functionality of investigated compounds (Cody et al., 2005; Nah et al., 2013; Chan et al., 2014; Chim et al., 2017a). For instance, Chan et al. (2014) have measured the ionization efficiency of oxalic acid, malonic acid, oxosuccinic acid, and tartaric acid relative to succinic acid and found these values can vary from 0.5 to 4.59 due to the change in carbon number (C_2 to C_4) and functional group (alcohol or ketone). To date, there are only limited classes of organic compounds were investigated. It remains largely unclear whether the particle-DART technique is more sensitive/selective for certain types of compounds. We would also like to note that the experimental configuration (Chan et al., 2013) and other factors (e.g. types of mass spectrometers) may have significant effects on the responses of organic compounds in the mass spectra (Nah et al., 2013). Cautions should be taken when we compare the results among different studies with various experimental configurations and conditions.

Comment #12:

page 5, line 5. Should molecule cm^{-3} s be molecule $cm^{-3} s^{-1}$

Author Response:

The reviewer may refer to the unit of OH exposure. The OH exposure, defined as the products of gas-phase OH concentration, $[OH]$, and the particle residence time, t , was determined by measuring the decay of the hexane (Smith et al., 2009):

$$OH\ exposure = -\frac{\ln([Hex]/[Hex]_0)}{k_{Hex}} = \int_0^t [OH] dt \quad (\text{Eqn.1})$$

where $[Hex]$ is the hexane concentration leaving the reactor after oxidation, $[Hex]_0$ is the initial hexane concentration before oxidation, and k_{Hex} is the second-order rate constant of the gas-phase OH–hexane reaction ($5.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Hence, the unit would be molecule $\text{cm}^{-3} \text{ s}$.

Comment #13:

page 6, line 7. It should be Orbitrap

Author Response:

We have revised the sentence.

Page 6, Line 1: “The gas-phase species leaving the heater were introduced into an atmospheric pressure ionization region, a narrow open space between the DART ionization source (IonSense: DART SVP), and the inlet orifice of the high-resolution mass spectrometer (Thermo Fisher, Q Exactive Orbitrap) for ionization and detection (Nah et al., 2013; Chan et al., 2013; 2014).”

Reference:

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