

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 #1

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2019-981-RC1>, 2019

This study examines the photochemical stability of pure erythritol particles and particles containing erythritol and ammonium sulfate (AS) against oxidation by OH radicals. Erythritol serves as a surrogate of 2-methyltetrols, a common compound of isoprene derived secondary organic aerosols. Reactive uptake of OH and subsequent degradation of erythritol in the particulate phase were determined as a function of inorganic-to-organic mass ratio (IOR). This was achieved using an aerosol flow reactor coupled to a soft atmospheric pressure ionization source (Direct Analysis in Real Time, DART) attached to a high-resolution mass spectrometer. It is found that the reactive uptake coefficient of OH decreases as the amount of AS increases. Furthermore, the results suggest that the reaction products due to OH oxidation are not significantly affected by the presence of AS. Since in the ambient methyltetrols are associated with AS, this study concludes that the chemical lifetime of methyltetrols is prolonged and may render methyltetrols stable against OH oxidation under humid conditions. The topic of this study fits well within the scope of ACP. I do not have major comments on this work, mostly minor ones and technical in nature. However, I suggest to carefully proofread the manuscript to improve the English language.

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:

P. 9, top paragraph: Just a comment to better understand the origin of HSO_4^- . As the particles are heated and vaporize (ammonia is gone), the SO_4^{2-} can abstract a hydrogen from the organic molecule? This leads to the detection of HSO_4^- ? Since HSO_4^- signal does not change significantly between non-oxidized and the oxidized case, reactivity of OH with SO_4^{2-} or HSO_4^- (and maybe NH_4^+) is not significant? A bit of rewording and better integration of previous studies would make this section easier to understand.

Author Response:

Thanks for the comments. We would argue that sulfate ion (SO_4^{2-}) is not an oxidant and cannot abstract a hydrogen atom from an organic molecule to form bisulfate ion (HSO_4^-). As discussed in the manuscript and in the literature, HSO_4^- likely originates from ammonium sulfate (AS). In our experiments, before introduced to the ionization region, erythritol–AS particles were fully vaporized under high temperature inside the particle heater and may thus thermally decompose into gas-phase ammonia (NH_3) and sulfuric acid (H_2SO_4) (Drewnick et al., 2015), which can be detected as HSO_4^- via direct ionization (Hajslova et al., 2011; Lam et al., 2019a, b; Kwong et al., 2018a, b).

George and Abbatt (2010) have revealed that dry $(\text{NH}_4)_2\text{SO}_4$ surface is highly unreactive toward gas-phase OH radicals. Furthermore, the surface reaction between dissolved SO_4^{2-} and gas-phase OH radicals is not efficient (Cooper and Abbatt, 1996;

Anastasio and Newberg, 2007). We have added this information in the revised manuscript.

Page 9, Line 12: “The HSO_4^- likely originated from AS. Before introduced to the ionization region, erythritol–AS particles were fully vaporized under high temperature and may thus thermally decompose into gas-phase NH_3 and H_2SO_4 (Drewnick et al., 2015), which can be detected as HSO_4^- via direct ionization (Hajslova et al., 2011; Lam et al., 2019a, b; Kwong et al., 2018a, b). The intensity of HSO_4^- before and after oxidation (Figure S1, *supplementary material*) showed no significant change, which is consistent with the argument in previous studies (Cooper and abbatt, 1996; Anastasio and Newberg, 2007) that the surface reaction between dissolved sulfate ions and gas-phase OH radicals is not efficient.”

Comment #2:

Derivation of the OH uptake coefficient necessitates the particle diameter. It appears that a polydisperse aerosol was applied. It would be helpful to plot the aerosol size distribution or give the corresponding distribution parameters. Did the authors measure the aerosol distribution before and after oxidation to assess potential volatilization of the particles upon oxidation?

Author Response:

Thanks for the comments. In our experiments, polydisperse particles were applied and the geometric standard deviation was 1.2–1.3. We acknowledge that the span of polydisperse particles could have effects on the determination of effective OH uptake coefficient, γ_{eff} . Further study which measures the γ_{eff} for both size-selected monodisperse and polydisperse particles is desired to better investigate the effect of particle size distribution on γ_{eff} calculation. As the spread of particle size in this work is small, we postulate that it would not significantly affect the determination of γ_{eff} .

We have observed slight changes in particle size upon oxidation for both erythritol and erythritol–AS particles (please see the **Figure S2** 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 proposed in the reaction scheme (i.e. C_4 hydroxyketone and hydroxyaldehyde ($\text{C}_4\text{H}_8\text{O}_4$), C_2 hydroxyketone ($\text{C}_2\text{H}_4\text{O}_2$) and C_3 hydroxyaldehyde ($\text{C}_3\text{H}_6\text{O}_3$)).

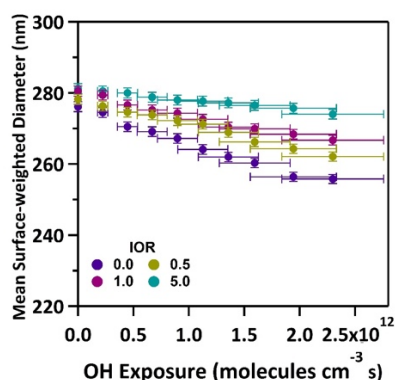


Figure S2. The change in surface-weighted mean diameter as a function of OH exposure for erythritol particles and erythritol-AS particles with different IORs.

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.

Page 10, Line 21: “Further, the initial effective OH uptake coefficient, γ_{eff} , defined as the fraction of OH collisions with erythritol molecule that result in a reaction, can be computed (Kessler et al., 2010; Davies and Wilson, 2015),”

Page 11, Line 2: “For erythritol particles, the initial mean surface-weighted particle diameter was 276.1 nm and decreased to 255.8 nm after oxidation ($\sim 7.3\%$).”

Page 11, Line 9: “For erythritol-AS particles, the particle diameters were measured to be 278.2–281.5 nm before oxidation (Table 1). Slight decreases in particle diameter ($\sim 5.8\%$, $\sim 4.9\%$, $\sim 2.6\%$ at IOR = 0.5, 1.0 and 5.0, respectively) were also observed (*Figure S2, supplementary material*).”

Page 11, Line 19: “The γ_{eff} is found to decrease from 0.45 ± 0.025 to 0.02 ± 0.001 when the IOR increases from 0.0 to 5.0. We acknowledge that the span of polydisperse particles could have effects on the determination of γ_{eff} . Further study which measures the γ_{eff} for size selected monodisperse and polydisperse particles is desired to better investigate the effect of particle size distribution on γ_{eff} calculation.”

Comment #3:

How is the uncertainty of presented uptake values derived? Likely the width of the aerosol size distribution and the uncertainty in AIOMFAC derived mfs values contribute to the overall uncertainty?

Author Response:

The uncertainty of effective OH uptake coefficient, γ_{eff} is calculated according to the error propagation rule:

$$\sigma_{\gamma} = \gamma_{\text{eff}} * \sqrt{\left(\frac{\sigma_k}{k}\right)^2 + \left(\frac{\sigma_{D0}}{D_0}\right)^2 + \left(\frac{\sigma_{\rho}}{\rho}\right)^2 + \left(\frac{\sigma_{\text{mfs}}}{\text{mfs}}\right)^2} \quad (\text{Eqn.1})$$

where γ_{eff} is the effective OH uptake coefficient, σ_{γ} is the uncertainty of effective OH uptake coefficient, k is the measured effective heterogeneous OH rate constant, σ_k is the uncertainty of effective heterogeneous OH rate constant, D_0 is the mean surface-weighted diameter, σ_{D0} is the uncertainty of the mean surface-weighted particle diameter ($\pm 0.5\%$ uncertainty), mfs is the mass fraction of solute, σ_{mfs} is the uncertainty of mass fraction of solute (± 0.02 for erythritol particles (Marsh et al., 2017), $\pm 5\%$ mfs for erythritol-AS particles predicted by AIOMFAC), ρ is the estimated particle density based on the volume additivity rule, σ_{ρ} is the uncertainty of particle density (determined based on following equation, Eqn.2)

$$\sigma_{\rho} = \rho^2 \frac{\text{IOR} * \rho_o * \rho_w + \rho_w * \rho_{\text{AS}} - (\text{IOR} + 1) * \rho_o * \rho_{\text{AS}}}{\rho_o * \rho_w * \rho_{\text{AS}}} * \sigma_{\text{mfs}} \quad (\text{Eqn.2})$$

where ρ_w is the water density (1.0 g cm⁻³), ρ_o is the erythritol density (1.451 g cm⁻³), ρ_{AS} is the density of AS (1.77 g cm⁻³), IOR is the inorganic-to-organic ratio. From the calculations, the uncertainty in particle diameter has minor effect on σ_v (less than 1 % at all IORs), while the uncertainty in mfs contributes about ~ 90 % at all IORs when determining σ_v .

Comment #4:

Addition of the MD simulation is a neat feature. However, its validity depends strongly on established parameters, applied fields, etc. It would have been nice to show that the simulated system or another test case behaves as expected. Here, things may get more complicated since NH_4^+ and SO_4^{2-} ions will be differently distributed within the particles? This could not be addressed as stated in text but could be discussed looking at previous studies (e.g., Tobias and Jungwirth groups).

Author Response:

Thanks for the comment. While the previous studies such as that by Tobias and Jungwirth (2001) suggest that the propensity of a species for the air-water interface can depend strongly on the MD force fields used, our explanation is based on two general physical observations that do not depend strongly on the model parameters. Our first observation is that the probability for an impinging OH radical to collide near an erythritol molecule decreases as the concentration of erythritol decreases when there is more water due to the hygroscopicity of a salt. A lower concentration of erythritol leading to a smaller collision probability should not be model-specific. The second observation is that the average distance between an OH radical and an erythritol molecule increases as their concentrations decrease because of more water. This again is a physical argument that does not depend strongly on the models used.

Comment #5:

P. 12., l. 10-13: Please be more specific. Do you expect salting in or salting out for the particle systems you investigated? Will it change for the different IOR?

Author Response:

To our best knowledge, the surface-bulk-partitioning behavior of erythritol when mixed with ammonium sulfate (AS) has not been experimentally measured. Ekström et al. (2009) have measured the surface tension using a FTÅ 125 tensiometer and have reported that when AS was added into 2-methylerythritol (with chemical structures similar to erythritol), the surface tension, σ was found to increase compared to that of 2-methylerythritol. For instance, for the system with 17 wt % of AS and 0.05 M of 2-methylerythritol, the surface tension was ~ 72.6 mN m⁻¹, which is larger than that for 2-methylerythritol/water system (σ (0.05 M) = ~ 69.7 mN m⁻¹). In their study, the surface tension increased from ~ 50.3 mN m⁻¹ to 72.6 mN m⁻¹ when IOR increased from ~ 0.8 to ~ 25.0 , suggesting a salting in effect.

Composition	Surface tension (mN m ⁻¹)	Molar concentration of 2-methylerythritol (M)
2-methylerythritol	$-14.3 \text{ c(M)} + 70.4$	0.02 – 1.87
2-methylerythritol + (17 % wt/wt) AS	$-15.1 \text{ c(M)} + 73.4$	0.05 – 1.53 ^a

^a the range of molar concentration of erythritol in our work is from 0.59 M at IOR=5.0 to 4.5 M at IOR=0.0. And the corresponding IOR for 2-methylerythritol/AS/water mixture ranges from ~0.8 to ~25.0.

On the other hand, Riva et al. (2019) have recently observed an interfacial tension depression using a biphasic microfluidic platform when AS is mixed with 2-methyltetrols (1.55 M of AS and 0.37 M of 2-methyltetrols (IOR = ~ 4.1)). This suggests a salting out effect. Based on these two results, the salt effect on the surface-bulk-partitioning behavior of 2-methyltetrols and likely erythritol remains unclear. Future investigations are needed to measure the surface tension for erythritol and erythritol–AS systems at different IORs in order to better understand the effect of salt on surface-bulk-partitioning behavior of erythritol within the particle and overall heterogeneous reactivity. We have added the following information in the revised manuscript.

Page 13, Line 4: “To our best knowledge, the surface-bulk-partitioning behavior of erythritol molecules in the presence of AS has not been experimentally measured. Ekström et al. (2009) have measured the surface tension using a FTÅ 125 tensiometer and have reported that when AS was mixed with 2-methylerythritol (with chemical structures similar to erythritol), the surface tension, σ was found to increase compared to that of 2-methylerythritol. For instance, for the system with 17 wt % of AS and 0.05 M of 2-methylerythritol, the surface tension was ~ 72.6 mN m⁻¹, which is larger than that for 2-methylerythritol/water system (σ (0.05 M) = ~69.7 mN m⁻¹). In their study, the surface tension increased from ~ 50.3 mN m⁻¹ to 72.6 mN m⁻¹ when IOR increased from ~0.8 to ~25.0, suggesting a salting in effect. On the other hand, Riva et al. (2019) have recently observed an interfacial tension depression using a biphasic microfluidic platform when AS was mixed with 2-methyltetrols (1.55 M of AS and 0.37 M of 2-methyltetrols (IOR = ~ 4.1)), suggesting a salting out effect. Based on these two results, the salt effect on the surface-bulk-partitioning behavior of 2-methyltetrols and likely erythritol remains unclear. Future investigations which can well represent the distribution of erythritol molecules at the particle surface are desirable to better understand how the presence of salts would alter the surface concentration of organic molecule and ultimately affect its heterogeneous reactivity.”

Comment #6:

Figure 2b: The legends using color bars are a bit confusing and maybe, I misunderstand those. Does the color coding of the experimental data has a relationship with the color coding of the ambient sulfate to 2-methyltetrol ratio? No ambient data is plotted and thus one wonders the meaning of that legend. The text already stated that the ambient ratio is much higher than the one probed in experiments. Same with the sulfate to erythritol ratio. There is no change in the color bar and the data are not plotted as a function of this ratio. This could be done by using a 3D plot. Also, the legends are not described in figure caption.

Author Response:

We are sorry for the confusion. We have modified the Figure 2 in the revised manuscript. The color scale represents the range of sulfate to erythritol mass ratio (0 – 3.7) at different IORs in this work, much smaller than that for ambient mass ratio of sulfate to 2-methyltetrols reported in field studies (~1.89 – ~250). Legends are described in the figure caption in the revised manuscript.

Page 36, Line 1: “

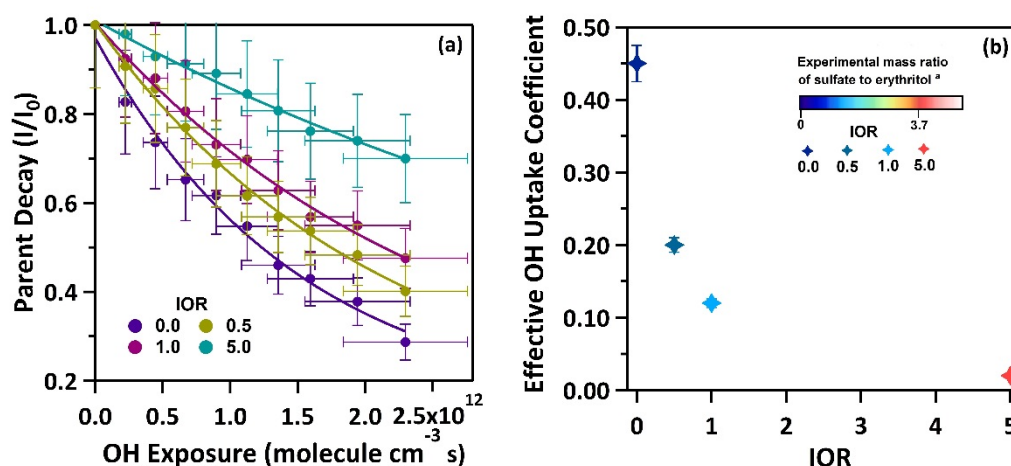


Figure 2. (a) The normalized decay of erythritol as a function of OH exposure during the heterogeneous OH oxidation of erythritol particles and erythritol-AS particles with different IORs. (b) The effective OH uptake coefficient, γ_{eff} . The data points represent γ_{eff} value at different IORs. The color scale represents the range of sulfate to erythritol mass ratio (0 – 3.7) at different IORs in this work, much smaller than that for ambient mass ratio of sulfate to 2-methyltetrols reported in field studies ($\sim 1.89 - \sim 250$).”

Comment #7:

p. 1, l. 26: ...inorganic salts often coexist in atmospheric...

Author Response:

We have changed this sentence in the revised manuscript.

Page 1, Line 25: “Additional uncertainty could raise since organic compounds and inorganic salts often coexist in atmospheric particles.”

Comment #8:

p. 9, l. 1: The HSO_4^- likely originated...

Author Response:

We have revised this sentence.

Page 9, Line 12: “The HSO_4^- likely originated from AS.”

Comment #9:

p. 9, l. 5: ...before and after oxidation (...) showed no significant change...

Author Response:

We have revised the sentence.

Page 9, Line 15: “The intensity of HSO_4^- before and after oxidation (Figure S1, supplementary material) showed no significant change,”

References:

- Anastasio, C. and Newberg, J. T.: Sources and sinks of hydroxyl radical in sea-salt particles, *J. Geophys. Res.: Atmos.*, 112, doi:10.1029/2006jd008061, 2007.
- Bethel, H. L., Atkinson, R. and Arey, J.: Hydroxycarbonyl products of the reactions of selected diols with the OH radical, *J. Phys. Chem. A*, 107, 6200–6205, doi:10.1021/jp027693l, 2003.
- Blanksby, S. J. and Ellison, G. B.: Bond Dissociation Energies of Organic Molecules, *ChemInform*, 34, doi:10.1002/chin.200324299, 2003.
- Block, E., Dane, A. J., Thomas, S., Cody, R. B.: Applications of Direct Analysis in Real Time Mass Spectrometry (DART-MS) in Allium Chemistry. 2-Propenesulfenic and 2-Propenesulfinic Acids, Diallyl Trisulfane S-Oxide, and Other Reactive Sulfur Compounds from Crushed Garlic and Other Alliums, *J. Agric. Food Chem.*, 58, 4617–4625, 2010.
- Cooper, P. L. and Abbatt, J. P. D.: Heterogeneous Interactions of OH and HO₂ Radicals with Surfaces Characteristic of Atmospheric Particulate Matter, *J. Phys. Chem.*, 100, 2249–2254, doi:10.1021/jp952142z, 1996.
- Davies, J. F. and Wilson, K. R.: Nanoscale interfacial gradients formed by the reactive uptake of OH radicals onto viscous aerosol surfaces, *Chem. Sci.*, 6, 7020–7027, doi:10.1039/c5sc02326b, 2015.
- Drewnick, F., Diesch, J.-M., Faber, P. and Borrmann, S.: Aerosol mass spectrometry: particle–vaporizer interactions and their consequences for the measurements, *Atmos. Meas. Tech.*, 8, 3811–3830, doi:10.5194/amt-8-3811-2015, 2015.
- Ekström, S., Nozière, B., and Hansson, H.: The cloud condensation nuclei (CCN) properties of 2-methyltetrols and C₃–C₆ polyols from osmolality and surface tension measurements. *Atmos. Chem. Phys.*, 9, 973–980. doi:10.5194/acp-9-973-2009, 2009.
- Hajslova, J., Cajka, T., and Vaclavik, L.: Challenging applications offered by direct analysis in real time (DART) in food-quality and safety analysis, *TrAC-Trend Anal. Chem.*, 30, 204–218, <https://doi.org/10.1016/j.trac.2010.11.001>, 2011.
- Kessler, S. H., Smith, J. D., Che, D. L., Worsnop, D. R., Wilson, K. R. and Kroll, J. H.: Chemical sinks of organic aerosol: kinetics and products of the heterogeneous

oxidation of erythritol and levoglucosan, *Environ. Sci. Technol.*, 44, 7005–7010, doi:10.1021/es101465m, 2010.

Kwong, K. C., Chim, M. M., Hoffmann, E. H., Tilgner, A., Herrmann, H., Davies, J. F., Wilson, K. R. and Chan, M. N.: Chemical transformation of methanesulfonic acid and sodium methanesulfonate through heterogeneous OH oxidation, *ACS Earth Space Chem.*, 2, 895–903, doi:10.1021/acsearthspacechem.8b00072, 2018a.

Kwong, K. C., Chim, M. M., Davies, J. F., Wilson, K. R. and Chan, M. N.: Importance of sulfate radical anion formation and chemistry in heterogeneous OH oxidation of sodium methyl sulfate, the smallest organosulfate, *Atmos. Chem. Phys.*, 18, 2809–2820, doi:10.5194/acp-18-2809-2018, 2018b.

Lam, H. K., Shum, S. M., Davies, J. F., Song, M., Zuend, A., and Chan, M. N.: Effects of inorganic salts on the heterogeneous OH oxidation of organic compounds: insights from methylglutaric acid–ammonium sulfate, *Atmos. Chem. Phys.*, 19, 9581–9593, <https://doi.org/10.5194/acp-19-9581-2019>, 2019a.

Marsh, A., Miles, R. E. H., Rovelli, G., Cowling, A. G., Nandy, L., Dutcher, C. S. and Reid, J. P.: Influence of organic compound functionality on aerosol hygroscopicity: dicarboxylic acids, alkyl-substituents, sugars and amino acids, *Atmos. Chem. Phys.*, 17, 5583–5599, doi:10.5194/acp-17-5583-2017, 2017.

Riva, M., Chen, Y., Zhang, Y., Lei, Z., Olson, N. E., Boyer, H. C., Narayan, S., Yee, L. D., Green, H. S., Cui, T., Zhang, Z., Baumann, K., Fort, M., Edgerton, E., Budisulistiorini, S. H., Rose, C. A., Ribeiro, I. O., Oliveira, R. L. E., Santos, E. O. D., Machado, C. M. D., Szopa, S., Zhao, Y., Alves, E. G., Sá, S. S. D., Hu, W., Knipping, E. M., Shaw, S. L., Junior, S. D., Souza, R. A. F. D., Palm, B. B., Jimenez, J.-L., Glasius, M., Goldstein, A. H., Pye, H. O. T., Gold, A., Turpin, B. J., Vizuete, W., Martin, S. T., Thornton, J. A., Dutcher, C. S., Ault, A. P. and Surratt, J. D.: Increasing Isoprene Epoxydiol-to-Inorganic Sulfate Aerosol Ratio Results in Extensive Conversion of Inorganic Sulfate to Organosulfur Forms: Implications for Aerosol Physicochemical Properties, *Environ. Sci. Technol.*, 53, 8682–8694, doi:10.1021/acs.est.9b01019, 2019.

Jungwirth, P. and Tobias, D. J.: Molecular Structure of Salt Solutions: A New View of the Interface with Implications for Heterogeneous Atmospheric Chemistry, *J. Phys. Chem. B*, 105, 10468–10472, doi:10.1021/jp012750g, 2001.