

Thanks very much for the comments on our paper “egosphere-2023-1649”. We appreciate the referee’s valuable suggestions, agree with the referee, and have addressed referee’s all issues and questions. We list below the corresponding changes and explanations we have added to the text, as requested by the referee.

Response to referee #1:

Referee's Comments to Author:

The manuscript entitled ‘Organosulfate produced from consumption of SO₃ speeds up sulfuric acid-dimethylamine atmospheric nucleation’ by Zhang et al. presents a detailed theory of the potential role of gas-phase glycolic acid (and its organosulfate derivatives) in new particle formation (NPF). The authors rely on quantum chemical calculations to define the most reasonable pathway and formation product of the reaction between glycolic acid and SO₃, leading to organosulfates. Also, kinetic modeling is used to understand the most efficient clustering with dimethyl amines. Their findings are backed up with atmospheric observations from Mt. Tai in China where intense NPF events have been observed. The authors also report observations from other locations around the world where the role of glycolic acid in NPF might be important but has been not evaluated earlier. First of all, I would like to acknowledge the authors for a very detailed, easy to follow manuscript. As mentioned by the authors, there are very few studies which tackle the role of organic acids in NPF, mainly due to the scarcity of their measurements. The results presented in this manuscript improve our understanding of the formation pathway of organosulfates from glycolic acid and sulfate and the role of the most stable organosulfate product in clustering with dimethyl amine and its role in NPF. The paper calls for an inclusion of organosulfate chemistry in global models when evaluating NPF and for more studies tackling hydroxyl acids in the gas phase from an observational and measurement point of view. The paper is well written and the finding are sound, I recommend publication after tackling the suggestions listed below.

General comments:

1. Could the authors comment on the role of relative humidity (availability of H₂O clusters) and how these affect the formation of GAS and GASA. Please see results by Tsona et al. (<https://doi.org/10.1016/j.atmosenv.2019.116921>)

Author reply:

Thanks for the referee’s question and suggestions. In order to comment the role of relative humidity (availability of H₂O clusters) and how these affect the formation of

GAS and GASA, we further explored hydration process of glycolic acid (GA) in the gas phase, according to the method reported by Tsona et al. (Tsona and Du, 2019) at tropospheric temperatures (258 K, 278 K, 298 K) and ambient pressure. The lowest-energy structure of clusters GA- n (H₂O) ($n = 0 - 3$) (Figure S2), equilibrium distribution of GA hydrates (Figure S3), thermodynamic data of the stepwise hydration of GA (Table S2), and relative equilibrium abundance of GA hydrates at different degrees of humidity (Table S3) were obtained and added to the revised supporting information of the manuscript. Following discussions were added to page S6 in our modified supporting information materials.

“As shown in Table S2, the first water addition to GA at 298 K, with a Gibbs free energy change of $-0.71 \text{ kcal mol}^{-1}$, are more favorable compared to the second and the third water additions, having free energy changes of 2.98 and $0.18 \text{ kcal mol}^{-1}$, respectively. Additionally, the energies decrease as the temperature decreases, and the energy of first water addition reaches to $-1.96 \text{ kcal mol}^{-1}$ at 258 K. Although the abundances of hydrated GA clusters, including mono-, di- and tri-hydrates, are slightly increased with increasing RH (relative humidity) (Figure S3 and Table S3), the hydration of GA is still weak at high RH. For example, the relative equilibrium abundance of GA hydrates is less than 7% at RH = 90% and 298 K. Therefore, the relative abundance of unhydrated GA is dominant at varying temperature and RH considered.”

Following sentences were also added to line 173 in page 6 in our modified manuscript.

“These results indicate that both reaction pathways for GA + SO₃ are favorable with the catalysis of H₂O to generate GAS and GASA, respectively. Therefore, as the relative humidity (RH) increases, it should be conducive to the formation of GAS and GASA. The abundances of hydrated GA clusters GA- n (H₂O) ($n = 0 - 3$) were also calculated at different RH (Figure S3 and Table S3). The relative equilibrium abundance of GA hydrates is less than 7% at RH = 90% and 298 K. Since the hydration

of GA is weak, the effect of the hydrated GA clusters to the formation of GAS and GASA is not further considered.”

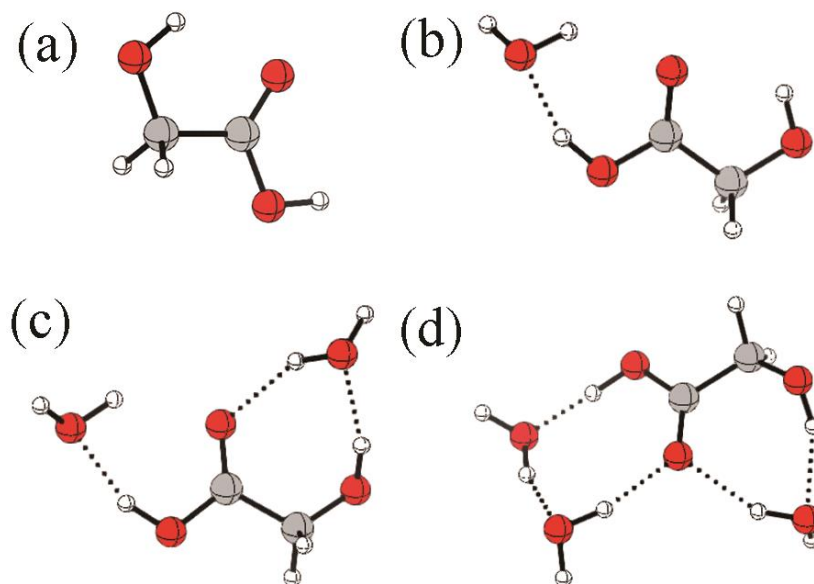


Figure S2 Lowest energy geometries of $(\text{GA})(\text{H}_2\text{O})_n$, optimized with the M06-2X/6-311++G(3df,3pd) method. The color coding is red for oxygen, grey for carbon, and white for hydrogen. The number of water molecules increases from (a) where $n = 0$ to (d) where $n = 3$.

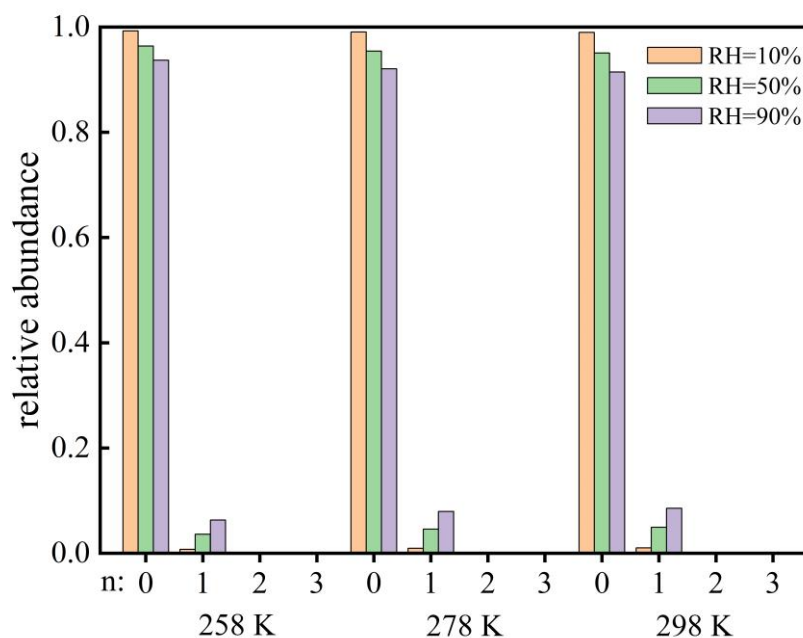


Figure S3 Equilibrium distribution of glycolic acid hydrates at different degrees of humidity (RH = 10%, 50% and 90%) and different temperatures (258 K, 278 K, and 298 K).

Table S2 Thermodynamic data (in kcal mol⁻¹) of the stepwise hydration of glycolic acid (GA) calculated by the M06-2X/6-311++G(3df,3pd) method.

n	ΔG		
	258 K	278 K	298 K
	$(GA)(H_2O)_{n-1} + H_2O \leftrightarrow (GA)(H_2O)_n$		
1	-1.96	-1.33	-0.71
2	1.77	2.38	2.98
3	-1.07	-0.44	0.17

Table S3 Relative equilibrium abundance of GA hydrates at different degrees of humidity (RH = 10%, 20%, 40%, 50%, 90% and 100%) and different temperatures (258 K, 278 K, and 298 K)

258 K

RH	10%	20%	40%	50%	90%	100%
n=0	0.98970000	0.97970000	0.96020000	0.95070000	0.91460000	0.90600000
n=1	0.01026766	0.02032661	0.03984325	0.04931278	0.08539284	0.09398853
n=2	0.00000006	0.00000025	0.00000098	0.00000151	0.00000472	0.00000577
n=3	0.00000002	0.00000018	0.00000139	0.00000268	0.00001504	0.00002044

278 K

RH	10%	20%	40%	50%	90%	100%
n=0	0.99050000	0.98120000	0.96310000	0.95430000	0.92070000	0.91260000
n=1	0.00948502	0.01879180	0.03689036	0.04569154	0.07934438	0.08738994
n=2	0.00000001	0.00000004	0.00000015	0.00000023	0.00000073	0.00000089
n=3	0.00000000	0.00000001	0.00000009	0.00000017	0.00000095	0.00000130

298 K

RH	10%	20%	40%	50%	90%	100%
n=0	0.99260000	0.98530000	0.97100000	0.96400000	0.93700000	0.93050000
n=1	0.00741927	0.01472926	0.02903091	0.03602716	0.06303219	0.06954867
n=2	0.00000000	0.00000000	0.00000001	0.00000002	0.00000006	0.00000008
n=3	0.00000000	0.00000000	0.00000000	0.00000000	0.00000002	0.00000003

Reference

Tsona, N. T., and Du, L.: Hydration of glycolic acid sulfate and lactic acid sulfate: Atmospheric implications, *Atmospheric Environment*, 216, 116921, <https://doi.org/10.1016/j.atmosenv.2019.116921>, 2019.

2. Could the authors comment on the role of coagulation sink? Eg. Line 134, it is a reasonable assumption to use the values from Hyytiälä for Mt. Tai for example?

Author reply:

Thanks for the referee's question. According to the reviewer's suggestion, the following detail descriptions about coagulation sink were clarified and modified in line 153 page 6 in our revised manuscript. "A constant coagulation sink of $2.6 \times 10^{-3} \text{ s}^{-1}$ was applied to account for scavenging by larger particles. The simulations were mainly run at 278 K, with additional runs at 258 K and 298 K to investigate the influence of temperature. These conditions correspond to a typical sink value and temperature in the boreal forest environment (Olenius et al., 2013; Maso et al., 2008)." A constant coagulation sink was applied in the cluster distribution dynamics simulations to account for scavenging by larger particles. The coagulation sink used in this work is the major loss by particles in the assumed atmospheric conditions. Mt. Tai is located in northern China, and its landscape is dominated by forests. Unfortunately, we did not find the measurement coagulation sink report in Mt. Tai. We chose a constant coagulation sink coefficient of $2.6 \times 10^{-3} \text{ s}^{-1}$, which is the median condensation sink coefficient of sulfuric acid vapor on pre-existing aerosol particles, based on measurements in the boreal forest environment in Hyytiälä, Finland (Maso et al., 2007). On the other hand, the cluster size dependent coagulation sink coefficient did not have a significant effect on the steady-state cluster concentrations, according to the parametrized formula from Kulmala et al. (Kulmala et al., 2001; Kulmala and Wagner, 2001). Additionally, this coagulation sink value is widely used for a typical sink for molecular sized clusters in continental background areas (Paasonen et al., 2012), and taking into account external losses of organic compound-sulfuric acid-dimethylamine cluster system (Li et al., 2017). Therefore, we think it is a reasonable assumption to use this coagulation sink value in this work.

Reference

Maso, M. D., Sogacheva, L., Aalto, P. P., Riipinen, I., Komppula, M., Tunved, P., Korhonen, L., Suur-Uski, V., Hirsikko, A., Kurtén, T., Kerminen, V.-M., Lihavainen, H., Viisanen, Y., Hansson, H.-C., and Kulmala, M.: Aerosol size distribution measurements at four Nordic field stations: identification, analysis and trajectory analysis of new particle formation bursts, 660 *Tellus B*, 59, 350-361, <https://doi.org/10.1111/j.1600-0889.2007.00267.x>, 2007.

Kulmala, M. and Wagner, P. E.: Mass accommodation and uptake coefficients – a quantitative

comparison, *J. Aerosol Sci.*, 32, 833–841, [https://doi.org/10.1016/S0021-8502\(00\)00116-6](https://doi.org/10.1016/S0021-8502(00)00116-6), 2001.

Kulmala, M., Maso, M. D., Mäkelä, J. M., Pirjola, L., Väkevä, M., Aalto, P., Miikkulainen, P., Hämeri, K., and O’Dowd, C. D.: On the formation, growth and composition of nucleation mode particles, *Tellus B*, 53, 479–490, <https://doi.org/10.1034/j.1600-0889.2001.530411.x>, 2001.

Li, H., Kupiainen-Määttä, O., Zhang, H., Zhang, X., and Ge, M.: A molecular-scale study on the role of lactic acid in new particle formation: Influence of relative humidity and temperature, *Atmospheric Environment*, 166, 479–487, <https://doi.org/10.1016/j.atmosenv.2017.07.039>, 2017.

Paasonen, P., Olenius, T., Kupiainen, O., Kurtén, T., Petäjä, T., Birmili, W., Hamed, A., Hu, M., Huey, L. G., Plass-Dueller, C., Smith, J. N., Wiedensohler, A., Loukonen, V., McGrath, M. J., Ortega, I. K., Laaksonen, A., Vehkamäki, H., Kerminen, V. M., and Kulmala, M.: On the formation of sulphuric acid - amine clusters in varying atmospheric conditions and its influence on atmospheric new particle formation, *Atmos. Chem. Phys.*, 12, 9113–9133, [10.5194/acp-12-9113-2012](https://doi.org/10.5194/acp-12-9113-2012), 2012.

3. The products GAS and GASA are better introduced in the main text. Could the authors move page S3 from the supplementary information to the main text in the methods section?

Author reply:

We appreciated the referee’s suggestion. According to the suggestion, we moved the page S3 to the methods section of main text in our revised manuscript.

4. References to studies who tackled the role of organosulfates and other similar organic acids in NPF are missing e.g. Katz et al. (<https://doi.org/10.5194/acp-23-5567-2023>) and Zhang et al. (<https://doi.org/10.5194/acp-22-2639-2022>)

Author reply:

Thanks for the referee’s comments. According to the suggestion, we have read articles, introducing the role of organosulfates and other similar organic acids in NPF by Katz et al. and Zhang et al. The following sentences and references were added to line 37 and line 51 page 2 in the Introduction part of the revised manuscript, respectively.

“Organosulfates have been identified as the most abundant class of organosulfur compounds, accounting for 5–30% of the organic mass fraction in atmospheric particles (Brüggemann et al., 2017; Tolocka and Turpin, 2012; Shakya and Peltier, 2015; Froyd et al., 2010; Mutzel et al., 2015; Glasius et al., 2018). Katz et al. measured the presence of organosulfates and identified its importance to new particle formation (Katz et al., 2023).”

“Organic acids, which are frequently observed in the atmosphere, have been expected to participate in the process of atmospheric nucleation, with a focus on the thermochemical properties of clusters between organic acids and common atmospheric nucleation precursors (Zhang et al., 2022).”

Reference

- Brüggemann, M., Poulain, L., Held, A., Stelzer, T., Zuth, C., Richters, S., Mutzel, A., van Pinxteren, D., Iinuma, Y., Katkevica, S., Rabe, R., Herrmann, H., and Hoffmann, T.: Real-time detection of highly oxidized organosulfates and BSOA marker compounds during the F-BEACH 2014 field study, *Atmos. Chem. Phys.*, 17, 1453-1469, <https://doi.org/10.5194/acp-17-1453-2017>, 2017.
- Tolocka, M. P., and Turpin, B.: Contribution of organosulfur compounds to organic aerosol mass, *Environ. Sci. Technol.*, 46, 7978-7983, <https://doi.org/10.1021/es300651v>, 2012.
- Shakya, K. M., and Peltier, R. E.: Non-sulfate sulfur in fine aerosols across the United States: Insight for organosulfate prevalence, *Atmos. Environ.*, 100, 159-166, <https://doi.org/10.1016/j.atmosenv.2014.10.058>, 2015.
- Froyd, K. D., Murphy, S. M., Murphy, D. M., de Gouw, J. A., Eddingsaas, N. C., and Wennberg, P. O.: Contribution of isoprene-derived organosulfates to free tropospheric aerosol mass, *Proc. Natl. Acad. Sci. U.S.A.*, 107, 21360, <https://doi.org/10.1073/pnas.1012561107>, 2010.
- Mutzel, A., Poulain, L., Berndt, T., Iinuma, Y., Rodigast, M., Böge, O., Richters, S., Spindler, G., Sipilä, M., Jokinen, T., Kulmala, M., and Herrmann, H.: Highly Oxidized Multifunctional Organic Compounds Observed in Tropospheric Particles: A Field and Laboratory Study, *Environ. Sci. Technol.*, 49, 7754-7761, <https://doi.org/10.1021/acs.est.5b00885>, 2015.
- Glasius, M., Hansen, A. M. K., Claeys, M., Henzing, J. S., Jedynska, A. D., Kasper-Giebl, A., Kistler, M., Kristensen, K., Martinsson, J., Maenhaut, W., Nøjgaard, J. K., Spindler, G., Stenström, K. E., Swietlicki, E., Szidat, S., Simpson, D., and Yttri, K. E.: Composition and sources of carbonaceous aerosols in Northern Europe during winter, *Atmos. Environ.*, 173, 127-141, <https://doi.org/10.1016/j.atmosenv.2017.11.005>, 2018.
- Katz, D. J., Abdelhamid, A., Stark, H., Canagaratna, M. R., Worsnop, D. R., and Browne, E. C.: Chemical identification of new particle formation and growth precursors through positive matrix factorization of ambient ion measurements, *Atmos. Chem. Phys.*, 23, 5567–5585, <https://doi.org/10.5194/acp-23-5567-2023>, 2023.
- Zhang, R., Shen, J., Xie, H. B., Chen, J., and Elm, J.: The Role of Organic Acids in New Particle Formation from Methanesulfonic Acid and Methylamine, *Atmos. Chem. Phys. Discuss.*, 2021, 1-18, <https://doi.org/10.5194/acp-2021-831>, 2022.

Technical comments:

1. In figure 3, could the authors write in the figure caption that the GA-SA-DMA lines are the same in a and b, but the y scale is different?

Author reply:

Thanks for the referee's suggestion. In our modified manuscript, we made a detailed description in the figure caption of Figure 3 that the GA-SA-DMA lines are same in a and b, but the Y-axis scale is different.

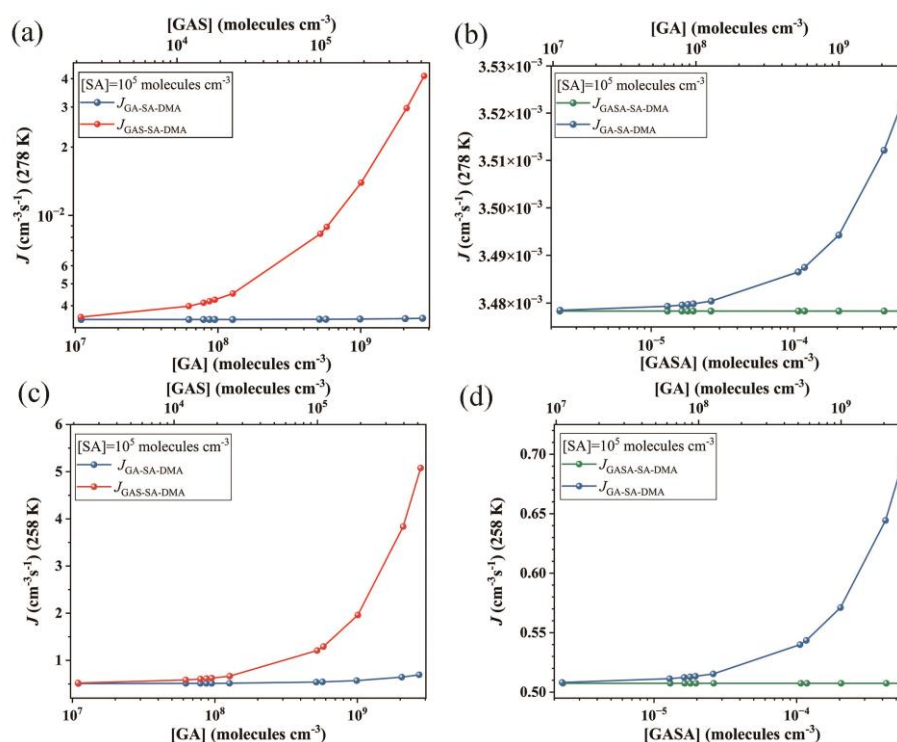


Figure 3. Simulated cluster formation rates J ($\text{cm}^{-3}\text{s}^{-1}$) as a function of monomer concentrations ($[\text{GA}]$, $[\text{GAS}]$, and $[\text{GASA}]$, respectively) at (a) (b) 278 K and (c) (d) 258 K under the condition of $[\text{DMA}] = 10^8$ molecules cm^{-3} and $[\text{SA}] = 10^5$ molecules cm^{-3} . Note that the simulated $J_{\text{GA-SA-DMA}}$ are the same data, but the Y-axis scale are different at (a) (b) and (c) (d), individually.

2. References format needs to be checked. In some cases, e.g. line 149, 150 the citation is starting the sentence.

Author reply:

Thanks for the referee's comment. According to the comment, we made an effort to check and correct all reference format in our modified manuscript. The sentence of line 149,150 "With high abundance ($\sim 10^{17}$ cm^{-3}) being detected in the troposphere,(Huang

et al., 2015) H₂O has been reported to effectively act as a catalyst in chemical reactions.(Liu et al., 2019)” was corrected to “With high abundance ($\sim 10^{17}$ cm⁻³) being detected in the troposphere (Huang et al., 2015), H₂O has been reported to effectively act as a catalyst in chemical reactions (Liu et al., 2019).” in line 169 page 6 of our revised manuscript.

3. Line 369, 'sight'. I guess the authors mean 'slight'?

Author reply:

Thanks for the referee’s suggestion. According to the suggestion, we corrected the above spelling error. The sentence of “Given the fact that GA has only a sight influence on the nucleation and growth processes of atmospheric clusters, the reaction between GA and SO₃ may provide a secondary source of the potential precursor since high concentrations of sulfur oxides being detected.” in line 394 page 15 was corrected to “Given the fact that GA has only a slight influence on the nucleation and growth processes of atmospheric clusters, the reaction between GA and SO₃ may provide a secondary source of the potential precursor since high concentrations of sulfur oxides being detected.” in our revised manuscript.