

## Reply to referee comments (RC) to manuscript egusphere-2024-4073

The authors are grateful to anonymous reviewer 1 for providing additional feedbacks to the manuscript.

Our detailed point-by-point response to their comments are reported below. We believe that these modifications improved the reading and the understanding of the manuscript, fostering its significance.

## Reply to Referee # 1 comments (RC) to manuscript egusphere-2024-4073

Dear authors, thanks for considering my comments. I have carefully reviewed the manuscript. This manuscript has been greatly improved. I recommend publication after addressing the points below.

We thank Referee #1 for the complete and thoughtful revision of our manuscript.

In the following the Referees' remarks and questions are in black and our replies are in light blue

1. Chemical Mechanisms and Oligomerization: The proposed reaction scheme (Fig 7, Page 27) is helpful but could be strengthened:

Suggestion: Explicitly discuss the role of the mineral surface in facilitating the proposed pathways (hydration, oxidation, oligomerization). Is it primarily providing an aqueous layer, acting as a catalyst (e.g., for acid-catalyzed oligomerization hinted at on Page 28), or participating directly in redox reactions? Link the observed product distribution (e.g., glycolic acid favored under light/O<sub>3</sub>) to potential surface-mediated reaction pathways. The detection of oligomers up to C<sub>10</sub> is interesting. Discuss how the confinement on a particle surface vs. bulk aqueous phase might favor higher-order oligomerization (Page 28). Are the identified oligomer formulas consistent with mechanisms proposed for glyoxal in aqueous aerosols or on other surfaces? The absence of formic acid detection is noted (Page 23). Discuss potential reasons (e.g., rapid further oxidation, partitioning) in light of its common observation in other glyoxal uptake studies.

Following the reviewer's suggestion we have now expanded the discussion on how the mineral surface could play a role in the observed reactivity of glyoxal. At page 29 of the revised version, from line 725: *"Concerning hydration reactions, Shen et al. (2016) showed that both glyoxal and water can accumulate onto dust particle surfaces (as evidenced by FTIR spectra) promoting hydration reactions through surface confinement of the reagents. Absorption of water on dust surfaces can also promote oligomerisation both directly (hydration is the first step of the oligomerisation reaction) as well as indirectly by enhancing particles' ability to absorb glyoxal."*

*Concerning oxidation, leading to organic acid formation, the dust surface could contribute directly to this mechanism by providing redox reactive sites (Shen et al., 2016). Redox reactions promoted the formation of glycolic, glyoxylic, and oxalic acids."*

Concerning formic acid, we hypothesize that we did not detect it in the particle phase due to the low amount of collected material on the filter which could mean that formic acid was below detection limit. In addition, the walls of the chamber provide a much larger surface compared to the dust which could make the partitioning of formic acid onto the dust less favourable. We have now amended the discussion at page 24, from line 605: *“Unlike previous studies (Galloway et al., 2009; Rubasinghege et al., 2013; Shen et al., 2016), formic acid was not detected on the particle phase despite high concentrations observed in the gas phase (Figure 2). It can be hypothesized that formic acid was not detected in the particle phase due to the low amount of organic material on the filter samples and the unsuitability of the method used (due to interferences at the retention time where formic acid is expected).”*

2. High Glyoxal Concentrations: The nominal initial glyoxal concentration (~1 ppmv) and measured peaks (370-1050 ppbv, Table 1) are significantly higher than typical ambient levels (ppt-ppbv). While the authors argue the first-order kinetics make  $\gamma$  transferable (Page 31), and Shen et al. showed decreasing  $\gamma$  with concentration, the potential for saturation effects or surface aging impacting the initial uptake kinetics observed here should be discussed. Suggestion: Explicitly discuss the potential impact of using such high concentrations on the measured initial uptake kinetics and product distribution. Can the results be confidently extrapolated to lower, atmospherically relevant concentrations? Consider citing Trainic et al. (2011) or similar regarding concentration effects on glyoxal uptake.

Referee is right about the possibility of surface saturation and this is what we observe and explicitly comment for figure 7. Trainic et al. (2011) compares the obtained mass growth rate and the ratio of final mass to seed mass (normalized by sulphate mass) and found them comparable to the previous results of Liggio et al. (2005) but higher than reported by Galloway et al (2009). Trainic et al. (2011) attribute these differences to differences in the initial seed sizes rather than in the initial glyoxal concentrations (which are a factor of 30 higher in Galloway et al. (2009)). Furthermore, we compared extensively the products of reactions, including for the control experiments with ammonium sulphate presented in the supplementary material (Text S5), and found in agreement with those studies.

Henceforth, in conclusion, we have now added an additional sentence in the conclusive remark section (lines 786-788) stating the following “After this time, the dust surface seems saturated, likely because of the excessive glyoxal concentrations injected in the chamber.”

3. Page 7, Line 203: Typo: "REI" should be "RIE" (Relative Ionization Efficiency).

This has been corrected, thank you

4. Page 18, Lines 482-483: "The presence of ozone appears uninfluential." This is an important observation given the complex chemistry possible. Briefly speculate why ozone might not significantly influence glyoxal uptake or product formation on this specific dust.

The observation that ozone is uninfluential to heterogeneous reactions on mineral dust is not new. Hanish and Crowley (2003a) investigated the combined uptake of  $O_3$  and  $HNO_3$  onto dust, and showed that the uptake of  $HNO_3$  on dust was not influenced by the presence of  $O_3$  (and conversely, the uptake of  $O_3$  was not influenced by the presence of  $HNO_3$ ). These authors attributed these observations to the fact that in their experiments,  $O_3$  concentrations were in excess by more than three orders of magnitude with respect to those of  $HNO_3$ , compensating for the fact that the uptake coefficients for  $O_3$  is approximately four orders of magnitude lower than for  $HNO_3$  (Hanish and Crowley 2003b; Chang et al., 2005). In these conditions, which are not generally met in the atmosphere, the presence of  $O_3$  could result in the modification of surface chemical characteristics, or to competition for adsorption sites of the two species. These considerations are applicable to our experiments, as the uptake coefficients of  $O_3$  and glyoxal are of comparable magnitudes and we use comparable concentrations. These considerations have been added to the main manuscript at line 485.

## References

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