

We thank the reviewers for careful reading and helpful comments that improve the quality of the manuscript. Reviewer comments have been copied followed by our responses in bold.

R2 (Anonymous Referee #1)

In this paper the authors describe results of environmental chamber experiments in which they investigate the formation of organic nitrates in aqueous aerosol from reaction of glyoxal with OH radicals under high NO_x conditions. Experiments were also conducted in the dark with O₃ and probably NO₃ radicals and in the absence of oxidants. Aerosol products were collected on filters and analyzed offline by electrospray mass spectrometry to obtain elemental formulas that were used to assign compound identity.

The experiments are well done and the discussion of results is very thorough and reasonable, although I have concerns about proposed product assignments and reaction mechanisms, as noted below. The results have the potential to be important, since organic nitrates are an important class of compounds. Determining the extent to which those present in the atmosphere are formed through aqueous chemistry matters because whereas gas phase formation from RO₂ + NO reactions sequester NO_x and radicals, aqueous phase formation from aldehydes/alcohols and nitric acid does not. I think the paper may be suitable for publication in ACP but have some significant comments that should first be addressed.

Specific Comments

R2C1) Page 4, lines 28-29: It is well known that sonication in water can form hydrogen peroxide and possibly other oxidants. What tests were conducted to ensure that this did not affect the composition of the samples?

Response) In our previous reaction vessel experiments, we used excess hydrogen peroxide as an OH radical source. Addition of hydrogen peroxide to standards verified that hydrogen peroxide does not react with glyoxal or oxalic acid. It does oxidize glyoxylic acid (Tan et al., 2009). However, in this smog chamber experiments, glyoxylic acid evaporates and becomes a major source of peroxy radicals during the irradiation (line 30, page 6). Therefore, a small amount of hydrogen peroxide formed during sonication is very unlikely to affect the sample composition. We add the following:

“Note that any possible hydrogen peroxide formed during sonication is not likely to affect aqueous-phase photooxidation. According to our previous reaction vessel experiments (Tan et al., 2009), hydrogen peroxide does not react with glyoxal or oxalic acid. It only oxidizes glyoxylic acid. But in this smog chamber experiments, glyoxylic acid evaporates.”

R2C2) Page 5, line 7: 150 ppm uncertainty in mass assignments seems large. I am used to values less than 5 ppm for accurate assignments of elemental formulas. Why is this, and how does this affect the assignment of elemental formulas? For example, in Tables 1-3 simple molecules like sulfuric acid and its dimer can be identified at the sub- 5 ppm level, but the proposed organic compounds cannot. This seems problematic. This issue should be discussed, and the authors should show what other possible products can be assigned with similar or better uncertainties. As it is, I do not have much confidence in these assignments, including the organic nitrates that are the focus of the paper.

Response) Unlike FTICR-MS, whose uncertainty is below 1 ppm, TOF-MS tends to have uncertainties. Actually this is not surprising because it is well known that uncertainties of TOF could be high (Smith et al., 2013). Note that throughout this work, if MIDAS provided more than one possible chemical formula, we selected the one with the lowest ppm difference. Regarding organonitrates, we also conducted an MS/MS analysis for m/z 147, which clearly indicated organonitrates by showing a nitrate fragment (m/z 62) (Fig. S2) and an ESI-MS analysis for a standard mixture solution of glyoxal and nitric acid, confirming m/z 147 and 226 were organonitrates (Fig. S3). Structures and mechanisms are proposed based on chemical

formula provided by MIDAS with the lowest ppm difference.

R2C3) Page 5, lines 32-33: It is difficult to believe that an alcohol would be converted to an organic nitrate in aqueous solution by a reversible reaction (the single arrow shown should be a double arrow for equilibrium). I would expect the water to shift the product distribution fully towards the alcohol. If such chemistry can occur it should be known for polyols or at least simple secondary alcohols, so literature should be cited and discussed to support these speculations. Although the mechanism provides an explanation for these particular products, it seems that one would expect many other organic nitrates from this mechanism as well. Why only these two out of many possibilities? This needs more discussion.

Response) We provided references for the formation of organonitrates (nitrate esters). As we all know, alcohols and sulfuric acid form organosulfates (sulfate esters). Esterification for organonitrate and organosulfate formation seems to be more favored than hydrolysis in the condensed phase (aerosol phase). Even in solutions we observed organosulfate formation (m/z-217), as shown in Table 3. Yes, organonitrate formation suggested in Scheme S1 is a proposed one. There could be other ways of forming organonitrates; however, the chemical formula provided is the one with the lowest ppm difference suggested by MIDAS.

We have provided references, and we now state:

“The proposed formation and molecular structures are illustrated in Scheme S1. Other organonitrates may form through this mechanism as well. However, the chemical formula provided herein has the smallest error compared to the measured mass.”

We replaced a single arrow by a double arrow.

R2C4) Page 7, line 33: Should “hydroxide” be “nitrate”? Where would one find ammonium hydroxide in aerosols?

Response) Ammonium hydroxide was used in our previous experiments (Ortiz-Montalvo et al., 2014; Tan et al., 2009). To clarify, we have modified this sentence:

“While sulfuric acid and ammonium hydroxide addition do not interfere the real-time formation of oxalic acid in dilute (cloud-relevant) photooxidation experiments...”

R2C5) Page 10, line 14: What is meant by “deprotonated acids”? Do you mean carboxylate ions? Ions do not evaporate from solutions.

Response) Page 10 should be page 9. We changed “deprotonated acids” to “undissociated acids.”

R2C6) Page 11, lines 5-11: Should be more specific in this paragraph. Do you mean total nitrates or inorganic nitrates or organic nitrates? Organic nitrates are not very soluble in water unless they are low molecular weight and multifunctional.

Response) We mean nitrates. They are major constituents, and form organonitrates in aerosols. They facilitate water uptakes. Alkyl nitrates (= organic nitrates or organonitrates) formed in the gas phase were already discussed in line 32-38, page 10. And we observed organonitrates formed in the aqueous phase and they are water soluble.

R2C7) It is well established that electrospray ionization is highly sensitive to compound structure and the sample matrix. How is it known that the signals assigned to organic nitrates are not just trace components that are not a significant portion of the aerosol mass? Some discussion of quantitation is warranted.

Response) A standard solution of glyoxal and nitric acid shows dominant organonitrate peaks at m/z 147 and 226. Therefore, m/z- 147 and 226 in the smog chamber samples cannot be “trace components.”

R2C8) Since the major conclusion of this paper appears to be that organic nitrates can be formed by mixing glyoxal and nitric acid in water in the absence of oxidants, the authors should better explain the point of the environmental chamber experiments. Showing that nitric acid can be formed under these photooxidation conditions seems unimportant, since it is readily formed in the atmosphere. How do the chamber results contribute to the conclusions?

**Response) We added the following in the conclusion section (line 32, page 10):
“Our main conclusion is that organonitrates can be formed in wet aerosols during the daytime in the presence of NO_x in humid areas. Hydrogen peroxide is an OH radical source, and its presence in wet aerosols can be expected when ~ppb is available in the gas phase. HNO₃ formation is facilitated by aqueous photooxidation: NO is effectively converted to NO₂ by volatile organic products (glyoxylic acids) during aqueous photooxidation; and OH generated in wet aerosols by photolysis of hydrogen peroxide evaporates and forms HNO₃ with NO₂. HNO₃ then forms organonitrates with aldehydes and alcohols, dominant water-soluble organic species in wet aerosols. This chemistry is inherently multiphase chemistry.”**

Technical Comments

R2C9) Page 1, line 27: “aerosols” should probably be “products”

Response) “Aerosols” are now changed to “products.”

R2C10) Page 2, line 36: “ethene” should be “acetylene”

Response) “Ethene” is now changed to “acetylene.”

R2C11) Page 3, line 8: “chromatography” should be “chromatograph”

Response) “Chromatography” is now changed to “chromatograph.”

R2C12) Page 5, line 26: “nitrate” should be “nitric”

Response) “Nitrate” is now corrected to “nitric.”

R2C13) Page 9, line 20: Should add “area” after “surface”

Response) “Surface” is now “surface area.”

R2C14) Page 9, line 38: “catalyzation” should be “catalysis”

Response) “Catalyzation” is now “catalysis.”

Reference

Smith, D. F., Kiss, A., Leach, F. E., Robinson, E. W., Paša-Tolić, L., and Heeren, R. M. A.: High mass accuracy and high mass resolving power FT-ICR secondary ion mass spectrometry for biological tissue imaging, *Anal. Bioanal. Chem.*, 405, 6069-6076, 10.1007/s00216-013-7048-1, 2013.