

Interactive comment on “Photochemical Organonitrate Formation in Wet Aerosols” by Yong Bin Lim et al.

Anonymous Referee #1

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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 be-

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cause 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

1. 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?
2. 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.
3. 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.
4. Page 7, line 33: Should "hydroxide" be "nitrate"? Where would one find ammonium

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hydroxide in aerosols?

5. Page 10, line 14: What is meant by “deprotonated acids”? Do you mean carboxylate ions? Ions do not evaporate from solutions.
6. 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.
7. 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.
8. 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?

Technical Comments

1. Page 1, line 27: “aerosols” should probably be “products”
2. Page 2, line 36: “ethene” should be “acetylene”
3. Page 3, line 8: “chromatography” should be “chromatograph”
4. Page 5, line 26: “nitrate” should be “nitric”
5. Page 9, line 20: Should add “area” after “surface”
6. Page 9, line 38: “catalyzation” should be “catalysis”

