

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

Anonymous Referee #2

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General Comments

This paper presents evidence of formation of organonitrates, organosulfates, and mixed nitrate-sulfate organic compounds from glyoxal. Their formation is attributed to aqueous phase processing of glyoxal and its hydrated forms. While photochemistry of gas-phase species enhanced the formation of the organitrogen and organosulfur compounds, the authors present reasonable evidence that this was due to enhanced formation of HNO₃, which partitioned into aerosol and enhanced aqueous processing. Also, the products were formed during photochemical experiments were also formed without UV irradiation. An existing model of aqueous-aerosol glyoxal chemistry was modified to include some new reactions and partitioning of glyoxal. The formation of these interesting organitrogen and organosulfur compounds seems clear, supported by identification with mass spectrometry and a fairly straightforward experimental design.

The data to support conclusions regarding kinetics of these reactions and subsequent modeling is limited, and it is not clear if any strong conclusions can be made by comparison with a kinetics model. The main result of this work is the identification of the products, with the potential of their formation in atmospheric aerosol via the aqueous chemistry presented here. No attempt was made to track the total amount of oxidized forms of nitrogen (e.g. NO_x, organonitrates, HNO₃), and this should be done during revision. For example, can the observed changes in gas-phase NO_x levels be reasonably attributed to known sinks? The lack of detection of glyoxal or its hydrated forms in humidified ammonium sulfate aerosol, even at the beginning of the experiment, is somewhat puzzling and must be explained further. This work is significant in the identification of formation of organitrogen and organosulfur compounds from glyoxal chemistry. Therefore I recommend this work for publication, pending revisions. Fundamental points still need to be addressed, and a number of clarifications are required prior to publication, as detailed below.

Specific Comments

(2, 39) It should be noted that the low volatility of glyoxal results largely from the high level of hydration that occurs upon dissolution in water.

(4, 6) It has been shown that drying can induce chemistry in aqueous aerosols.(1-3) The aerosol in this study contained glyoxal prior to drying and addition to the chamber. Were there any indications that chemistry occurred during that drying process?

(4, 15) The humidifying process should be described in further detail. It is currently described as the chamber being filled with clean dry air and then humidified. It doesn't seem feasible that 90% RH can be reached with the chamber initially full of dry air.

(4, 12) Please elaborate on the relevance of your gas and particle phase concentrations to the atmosphere. Although the goal of this study is largely to show the potential source of these compounds and the link to aqueous processing, the relation to the atmospheric conditions should be addressed further.

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(4, 23) The use of E-AIM will also provide, as you note, the pH of the aerosol, yet pH is not reported here. pH will affect particle equilibria, partitioning, and may change the resulting chemistry. It is certainly an important environmental variable that should be reported for all experiments in Table S1. A general comment on pH and potential effects should be included in your updated discussion, particularly since acidity was a major aspect of your experiments (sulfuric acid seed vs. ammonium sulfate seed).

(5, 13-19) This section has the heading "... and 226", but no mention is made of m/z 226.

(6, 12-15) The authors observed that experiments that are similar, except for the presence of glyoxal (#2 and #7), had very different NO_x chemistry, but do not explain this. The sinks and consequences of gas-phase NO_x should be more clearly discussed, particularly in light of your observations. For example, if NO_x is converted to HNO₃ and partitions to aerosol, pH could be significantly altered.

(7, 9-11) Were NO₂⁺ to be formed in any significant amount, would this now be a potentially important reactive species (nucleophile) in your aerosol? Are there any indications that this is the case?

(8, 15) The authors state that no glyoxal peak was observed in mass spectra for the humid chamber AS aerosols, yet you do observe organonitrate products (Fig. 1). Does your model suggest complete and rapid conversion of glyoxal to products? Given the importance of ALW for partitioning of glyoxal, it is puzzling that AS aerosol under humid conditions does not contain glyoxal. This important point was dismissed by the authors.

(9, 32) The aerosols evaporate to maintain equilibrium at the RH conditions of the chamber, not due to surface area considerations. What comment about surface area was intended?

Technical Comments

(Page 1, Line 13) change to read "or sulfuric acid particles"

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(Page 1, Line 33) This sentence is awkward, but it makes an important point that SOA(aq) is likely to improve model predictions. Please make this sentence clearer, perhaps split into two.

(2, 12) Add references 4 and 5.

(2,18) Add reference 6.

(2, 20) change to read “..compounds, OH radicals, and water..”

(3, 6) The importance of more realistic aerosol composition should be noted here. Ambient aerosol will have a wide range of organic compounds in addition to those derived from glyoxal.(Refs 7,8) Recent work suggests that compounds like glyoxal will from condensation products (acetals, etc.) with these other aerosol constituents.(Ref 9) This could affect the chemistry studied in this work, by reducing the amount of glyoxal available for reaction and potentially changing the product distribution. The authors should address the effect of actual ambient aerosol composition.

(3, 23) remove the first word : “the”

(3, 35) change to read “.., liquid water, and ..”

(5, 30-31) change to read “. . .08C11) and not likely nitric acid adducts.”

(5, 37) change to read “..Cole, 2000), and MIDAS does not propose..”

(6, 12-13) change to read “Experiment #2) also shows significant..”

(6, 16) This is an interesting style of using an introductory question. It would be better to use a direct statement rather than giving the reader some suspense. Ambiguity impedes clarity. Please rephrase as a direct statement, such as “Aqueous phase chemistry and photochemistry may lead to volatile products that contribute to gas phase peroxy radicals”

(6, 37) and (7, 1) and throughout the manuscript, change to read “. . .after 3 hours of

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irradiation. . .”

(7, 3-5) While heterogeneous reactions are a possible source, do the authors consider OH + NO₂ a source of HNO₃? Is this included in the model?

(7, 12) change to read “Figure 2 suggests. . .”

(8, 3-4) change to read “During irradiation, oxalic acid was formed in the humid chamber, shown by UPLC-Q-TOF-MS detection of m/z- 89. . .”

(9,28) through (10, 29) The time-resolved data should be addressed within the context of other studies. Particularly for the reduced nitrogen species (imines, imidizoles, etc.) Studies have looked at this reaction under a wide range of conditions, which should allow comparison.(Refs 10-12)

(10, 18) change to read “. . . because aqueous phase reactions of glyoxal with ammonium form imines...”

(10, 22-23) change to read “. . .form oligomers and imines. In SA aerosols the formation. . .”

(11, 8) change to read “. . . during the daytime. Notably, nitrate concentrations. . .” Figures

Scheme S1. This should be placed into the main manuscript. You discuss extensively the formation of these organonitrates, so this should not be supplemental.

Figure 1. This figure should be a 4 panel grid, with the spectra for humid conditions on the top row, and dry conditions on the bottom row, with AS results on the left and SA results on the right. It is difficult to compare in a single column. Each figure (a-d) should have a label denoting the aerosol type and the humidity level.

Figure 3. The legends must be moved to the top right corner to avoid confusion between the data and the legend. R-squared should be reported to at most 3 decimal places (0.001). The linear fits do not need to fully displayed, only the time constants.

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The linear fit intercepts should all be 1.0. Instead of presenting the equations, you should label the plots with the effective lifetime or the half-life of the glyoxal.

Figure 4. The same 4-panel grid format as suggested for Figure 1 should be used.

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