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.

R1 (Anonymous Referee #2)

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 organosulfar 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.

R1C1) No attempt was made to track the total amount of oxidized forms of nitrogen (e.g. NOx, organonitrates, HNO3), and this should be done during revision. For example, can the observed changes in gas-phase NOx levels be reasonably attributed to known sinks?

Response) We did not attempt to measure HNO_3 uptake quantitatively. A FACSIMILE model predicts ~500 μM of HNO_3 uptake in the aqueous phase after 3 hour irradiation when initial conditions are 10 ppb of NO, 0 ppb of NO_2, 10 ppb of O_3 and 500 ppb of an organic compound in the gas phase (glyoxylic acid). This concentration of HNO_3 is comparable to that of inorganic constituents in wet aerosols (200 μM of ammonium sulfate/sulfuric acid). We added this point at the end of section 3.3.

"We also estimate the concentration of HNO_3 taken up into wet aerosols by including chemistry of NO_x, HO_x, peroxy radical, HNO_3 partitioning into a FACSIMILE model. ~ 500 μM of HNO_3 uptake in the aqueous phase is predicted after 3 hours of irradiation when initial conditions are 10 ppb of NO, 0 ppb of NO_2, 10 ppb of O_3 and 500 ppb of an organic compound in the gas phase (glyoxylic acid). This concentration of HNO_3 is sufficient to form organonitrates with glyoxal and comparable to that of other inorganic constituents in wet aerosols (200 μM of ammonium sulfate/sulfuric acid)."

R1C2) 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.

Response) Thank you for pointing this out. We reinvestigated and found that m/z^+ 131 ([glyoxal + $2H_2O$ + Na]$^+$) was actually detected in 15 and 30 minute samples. But m/z^+ 131 that we detected in 0 minute sample was an imine (C4H7N2O3), which appeared to overlap the glyoxal peak. So, a decay plot cannot be constructed.

We changed the sentence in the paragraph (line 15, page 8) as follows:
"(glyoxal was also detected for AS aerosols in the humid chamber; however, since it was only detected in 15 and 30 minute samples, no decay plot was constructed)"

We also added the following in the text (line 12, page 8):

“131 (= $[M + H_2O + MeOH + Na]^+$)”

This work is significant in the identification of formation of organitrogen and organosulfur compounds from glyoxal chemsitry. 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
R1C3) (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.

Response) Clearly glyoxal undergoes hydration, but immediately hydrated glyoxal forms oligomers via acid catalysis and organic-inorganic complexes in the presence of inorganic constituents. These are likely to be SOA from glyoxal. And these points were already addressed in the previous paragraph (line 10-18, page 2).

We have modified that sentence to clarify the reviewer’s point:
“Water soluble organic compounds like glyoxal and methylglyoxal hydrate and form oligomers through hemiacetal formation and aldol condensation, especially in evaporating droplets.”

R1C4) (4, 6) It is 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?

Response) Yes. In Fig. S6, solutions and aerosols in the chamber at 0 minute were directly compared. Imines and acid-catalyzed oligomers were found in the aerosols. This is discussed in the text (line 13, page 10).

R1C5) (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.

Response) This humidifier was developed by modifying an existing commercial humidifier. Water spray and evaporation pan were specially designed to generate water steam rapidly. While adding water vapors into the smog chamber, we monitored SMPS to ensure that no water droplet was introduced. This device will be requested for patent in the future, so we cannot discuss more in details.

We added:
“This humidifier was developed by modifying an existing commercial humidifier. Water spray and evaporation pan were specially designed to generate water steam rapidly. While adding water vapors into the chamber, we monitored SMPS to ensure no water droplet was introduced.”

R1C6) (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.

Response) We added the following:
“Concentrations of NO_x, O_3, and particle mass in smog chamber can be related to a moderate haze condition in urban areas, particularly observed in Seoul or Beijing.”

R1C7) (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).

Response) We have added pH values in Table S1. It appears acidity affects oligomerization in SA aerosols, and this is discussed in line 22-29 on page 10.

R1C8) (5, 13-19) This section has the heading ": : : and 226", but no mention is made of m/z 226.

Response) We change the section title to:
"MS/MS analysis for m/z^- 147 and standard MS analysis for m/z^- 147 and 226"

R1C9) (6, 12-15) The authors observed that experiments that are similar, except for the presence of glyoxal (#2 and #7), had very different NOx chemistry, but do not explain this. The sinks and consequences of gas-phase NOx should be more clearly discussed, particularly in light of your observations. For example, if NOx is converted to HNO3 and partitions to aerosol, pH could be significantly altered.

Response) Please see our response for R1C1 regarding sinks of NOx to HNO3. NO2 is effectively formed by peroxy radical-NO reactions (#2), but is only slightly increased due to the lack of peroxy radicals when there is no glyoxal in the beginning (#7). This point is already discussed in line 10 on page 6. There was no evidence of enhanced oligomer formation by HNO3 uptake while more oligomers were observed in SA aerosols. We modified the text (line 3, page 10):

"However, acidity effects on oligomer formation requires further study because sulfuric acid in SA aerosols appears to enhance oligomerization while photochemically formed nitric acid does not."

R1C10) (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?

Response) We did not attempt to measure NO_2^+, so heterogeneous reactions of NO_2^+ is beyond the scope. In this paper, we focus on nitrates and organonitrates. We just mention this since no HNO_3 was observed in SA aerosols.

We have now added:
"If NO_2^+ were formed in a significant amount, it could be an important reactive species. However, measurement of NO_2^+ and investigation of its potential role is beyond the scope of this study."

R1C11) (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.

Response) See our response for R1C2.

R1C12) (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?

Response) This has been changed in the text to:
"When the solutions are atomized and introduced into the smog chamber, water evaporates to equilibrate to the chamber RH, and concentration of solutes increase."

Technical Comments
R1C13) (Page 1, Line 13) change to read "or sulfuric acid particles"

Response) It was already written as "or sulfuric acid particles."

(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.

Response) Now it reads:

"Including SOAaq is likely to improve model predictions, which currently underestimate the ambient concentration and oxidation state of organic aerosols. Water soluble organic compounds with a small carbon number (C2-C3) are not considered precursors to SOA formation through gas-phase chemistry and vapor pressure driven partitioning (Pankow, 1994) because of their high vapor pressure. However, they are potential SOAaq precursors."

R1C14) (2, 12) Add references 4 and 5.

Response) We add suggested references.

R1C15) (2,18) Add reference 6.

Response) We add suggested references.

R1C16) (2, 20) change to read "..compounds, OH radicals, and water.."

Response) Now it reads as the reviewer suggests.

R1C17) (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.

Response) Glyoxal is a surrogate of water soluble organic compounds in ambient wet aerosols. Radical and non-radical reactions of water soluble organic compounds in wet aerosols are expected to be seen in our glyoxal reactions. Glyoxal undergoes self-oligomerization through hemiacetal formation and aldol condensation leading to light absorbing products (Shapiro et al., 2009). Ammoniums, sulfates and nitrates are main inorganic constituents (Zhang et al., 2007), and glyoxal reacts with them. OH reactions of glyoxal produce dicarboxylic acids (e.g., oxalic acid), which are also expected to be the products of water soluble organic compounds.
These non-radical reactions compete with OH reactions. In our smog chamber experiments, non-radical reactions are more dominant than OH reactions in the condensed phase and we expect this is true for water soluble organic compounds in ambient wet aerosols.

We added the following in the sentence:
“Note that glyoxal is used, as a surrogate of water soluble organic compounds in ambient wet aerosols, to explore non-radical and radical reactions in the condensed phase leading to SOA.”

R1C18) (3, 23) remove the first word : “the”

Response) Now “the” is removed.

R1C19) (3, 35) change to read “.., liquid water, and : : :”

Response) We do not understand this request. Perhaps the page or line number the reviewer is referring to is incorrectly written??
It appears the reviewer indicates (3, 26). We insert the comma between “water” and “and.”

R1C20) (5, 30-31) change to read “: : :08C11) and not likely nitric acid adducts..”

Response) Now “and” is inserted

R1C21) (5, 37) change to read “..Cole, 2000), and MIDAS does not propose..”

Response) Now “while” is changed to “and.”

R1C22) (6, 12-13) change to read “Experiment #2) also shows significant..”

Response) Now “the” is removed, as suggested.

R1C23) (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”

Response) Now it reads as the review suggests:
“Photochemistry on wet aerosols may lead to volatile organic products that contribute to gas-phase peroxy radicals.”

R1C24) (6, 37) and (7, 1) and throughout the manuscript, change to read “: : :after 3 hours of irradiation: : :”

Response) Now we changed according to the reviewer’s suggestion.

R1C25) (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?

Response) We include this as an aqueous phase reaction. NO_2 concentration in the aqueous phase is determined by the Henry’s law constant. The contribution of this reaction to HNO_3 is, however, small.

R1C26) (7, 12) change to read “Figure 2 suggests: : :”

Response) We removed “also” to read as suggested.

R1C27) (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: : :"

Response) We changed according to the reviewer's suggestion.

R1C28) (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)

Response) We already discussed previous studies of nitrogen-containing organics (line 13-15, page 2). So we have added the suggested references (10 and 11) there. Ref 12 was already cited there.

R1C29) (10, 18) change to read ": : : because aqueous phase reactions of glyoxal with ammonium form imines..."

Response) Now we remove "in the" to read as suggested.

R1C30) (10, 22-23) change to read ": : :form oligomers and imines. In SA aerosols the formation: : :"

Response) We split the sentence into two as the reviewer suggests.

R1C31) (11, 8) change to read ": : : during the daytime. Notably, nitrate concentrations: : :" Figures

Response) Now we removed "And," as suggested

R1C32) Scheme S1. This should be placed into the main manuscript. You discuss extensively the formation of these organonitrates, so this should not be supplemental.

Response) We agree. Now Scheme S1 is Scheme 4. The previous Scheme 4 is now Scheme 5.

R1C33) 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.

Response) Figure 1 is now a 4 panel grid as the reviewer suggests.

R1C34) 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. 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.

Response) Legends are now placed on the top right corner. Y-intercept value (at t = 0) for A is now 1. Instead of the equations, the lifetimes, τ (min), are used. R-squared has now 3 decimal places. We modify the text (line 18-24, page 8) as follows:

"For SA aerosols, the lifetime of glyoxal in the dry chamber (51.3 min in Fig. 3A) is very similar to that in the humid chamber (54.1 min in Fig. 3B) due to high hygroscopicity of sulfuric acid (32% ALW in the dry chamber). Assuming no evaporation of ALW, the kinetic model (Details are discussed in the next section) predicts that the lifetime of glyoxal by OH reactions in the aqueous phase is 55.6 min, which is very similar to estimated values above. However, for AS

aerosols in the dry chamber, glyoxal peaks at m/z^+ 113, 117 and 131 decay sharply in 30 minutes and the estimated lifetime is 10.9 min (Fig. 3C), which is ~ 5 times shorter than the lifetime by OH reactions."

R1C35) Figure 4. The same 4-panel grid format as suggested for Figure 1 should be used.

Response) Figure 4 is now a 4 panel grid as the reviewer suggests.

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 NOx 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 NOx 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.

We added the following in the sentence:
"Note that unlike Fourier transform ion cyclotron mass spectrometry (FTICR-MS), whose uncertainty is below 1 ppm, TOF-MS tends to have uncertainties since it is well known that uncertainties of TOF could be high (Smith et al., 2013)."

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, other organonitrates could form through this mechanisms; 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. Alkylnitrates (= 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. HNO_3 formation is facilitated by aqueous photooxidation: NO is effectively converted to NO_2 by volatile organic products (glyoxylic acids) during aqueous photooxidation; and OH generated in wet aerosols by photolysis of hydrogen peroxide evaporates and forms HNO_3 with NO_2. HNO_3 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.

Photochemical Organonitrate Formation in Wet Aerosols

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Abstract. Water is the most abundant component of atmospheric fine aerosol. However, despite rapid progress, multiphase chemistry involving wet aerosols is still poorly understood. In this work, we report results from smog chamber photooxidation of glyoxal and OH – containing ammonium sulfate or sulfuric acid particles in the presence of NO_x and O_3 at high and low relative humidity. Particles were analyzed using ultra high performance liquid chromatography coupled to quadrupole time-of-flight mass spectrometry (UPLC-Q-TOF-MS).

During the 3 hour irradiation, OH oxidation products of glyoxal that are also produced in dilute aqueous solutions (e.g., oxalic acids and tartaric acids) were formed in both ammonium sulfate (AS) aerosols and sulfuric acid (SA) aerosols. However, the major products were organonitrogens (CHNO), organosulfates (CHOS), and organonitrogen-sulfates (CHNOS). These were also the dominant products formed in the dark chamber indicating non-radical formation. In the humid chamber (> 70 % RH), two main products for both AS and SA aerosols were organonitrates, which appeared at m/z^- 147 and 226. They were formed in the aqueous phase via non-radical reactions of glyoxal and nitric acid, and their formation was enhanced by photochemistry because of the photochemical formation of nitric acid via reactions of peroxy radicals, NO_x and OH during the irradiation.

1 Introduction

Atmospheric aerosols affect human health and climate (Seinfeld and Pandis, 1998), and a large fraction is secondary organic aerosol (SOA) (Zhang et al., 2007). SOA forms via partitioning of semi-volatile organic ~~aerosols~~ products from gas-phase oxidation of volatile organic compounds (VOCs) (Odum et al., 1996; Pankow, 1994), multiphase reactions involving aerosols (Jang et al., 2002; Kalberer et al., 2004), and aqueous-phase reactions in cloud/fog waters (Blando and Turpin, 2000). SOA formation via aqueous chemistry (SOA_{aq}) has been suggested by recent laboratory, field and modeling studies (El-Sayed et al., 2015; Ervens et al., 2011; Gong et al., 2011; Lee et al., 2012; Lee et al., 2011; Lin et al., 2012; Liu et al., 2012a; Liu et al., 2012b; McNeill et al., 2012; Myriokefalitakis et al., 2011; Ortiz-Montalvo et al., 2014; Ortiz-Montalvo et al., 2012; Tan et al., 2012; Zhou et al., 2011). ~~Considering~~ Including SOA_{aq} is likely to improve model predictions, which currently underestimate ambient measurements and ~~the~~ oxidation state of organic aerosols.~~, because w~~Water soluble organic compounds with a small carbon number (C2-C3)~~, which were~~ are not considered by the partitioning theory (Pankow, 1994)

~~due to~~because of their high vapor pressure.~~,~~ However, they are potential ~~precursors for~~ SOA$_{aq}$~~.~~ precursors. In addition, these water soluble organics and liquid water are abundant in the atmosphere (Blando and Turpin, 2000; Carlton and Turpin, 2013; Liao and Seinfeld, 2005).

SOA$_{aq}$ formation is expected in cloud/fog droplets and aerosol waters via radical and non-radical reactions (Lim et al., 2010; McNeill et al., 2012). Since OH radicals with the concentrations of 10^{-14}—10^{-12} M are available in the atmospheric aqueous phase (Arakaki et al., 2013; Ervens et al., 2014), water soluble organic compounds (e.g., glyoxal, methylglyoxal) undergo photooxidation forming dicarboxylic acids (e.g., oxalic acids) via peroxy radical reactions and oligomers via organic radical-radical reactions (Altieri et al., 2008; Lim et al., 2010; Lim et al., 2013; Tan et al., 2012; Tan et al., 2009). Even without OH radicals, the photolysis of pyruvic acid also forms oligomers in concentrated solutions (Guzman et al., 2006). Organic compounds form organosulfates with sulfuric acids via acid catalysis (i.e., with acidic sulfate) (Surratt et al., 2010; Surratt et al., 2008; Surratt et al., 2007a). Water soluble organic compounds like glyoxal and methylglyoxal hydrate and form oligomers through hemiacetal formation and aldol condensation, especially in evaporating droplets (Corrigan et al., 2008; Liggio et al., 2005; Loeffler et al., 2006; Noziere et al., 2009; Schwier et al., 2010). Ammonium ions, which are abundant in atmospheric aerosols (Zhang et al., 2007), form nitrogen-containing organics including imidazoles with water soluble organic compounds (Galloway et al., 2009; Kampf et al., 2012; Noziere and Cordova, 2008; Sareen et al., 2010; Yu et al., 2011), and also act as catalysts enhancing oligomer formation (Nguyen et al., 2014; Noziere et al., 2009). Water soluble carboxylic acids (Blando and Turpin, 2000; Chebbi and Carlier, 1996) and cations (e.g., Na$^+$, K$^+$, NH$_4^+$, protonated amines) form low volatility carboxylate salts (Drozd et al., 2014; Ortiz-Montalvo et al., 2014; Paciga et al., 2014; Smith et al., 2010).

Although these findings have significantly improved our understanding of aqueous chemistry, atmospheric processes like gas-wet particle partitioning of water soluble organic compounds, OH radicals, and water in aerosols are still poorly understood. Therefore, organic chemistry in the presence of wet aerosol warrants further study. Studies of wet aerosol chemistry to date have demonstrated that the chemistry in wet aerosols can be quite different than that under dilute (cloud-relevant) conditions. For example, in reaction vessel experiments for photooxidation of glyoxal or methylglyoxal in the dilute aqueous phase, sulfuric acid does not affect the formation of major products (e.g., oxalic acid) (Tan et al., 2009), while both smog chamber and field studies observe organosulfate formation in aerosols in the presence of sulfuric acid, which contributes both liquid water and acidity to condensed phase aerosol chemistry (Galloway et al., 2009; Surratt et al., 2007a; Surratt et al., 2007b; Tolocka and Turpin, 2012) . In fact, several key questions remain to be answered. For example, the major sink of nitrate radicals in the aqueous phase is the formation of HNO_3 (Kirkland et al., 2013). However, it should be noted that organonitrates are commonly observed in rain waters (Altieri et al., 2009), clouds (Boone et al., 2015) and wet aerosols (Hodas et al., 2014). Are organonitrates formed in the aqueous phase? Are they taken up into atmospheric waters after gas phase formation during the daytime ($ROO\cdot + NO \rightarrow RONO_2$) or the nighttime ($R + NO_3 \rightarrow RONO_2$)? Or are they formed via aqueous chemistry?

A smog chamber is ideal to explore condensed-phase chemistry to address these issues. Volkamer et al. (2009) conducted smog chamber experiments for aqueous chemistry of glyoxal in wet particles. In their experiments, glyoxal was photochemically produced from the ~~ethene~~acetylene-OH reaction in the gas phase, and partitioned into wet seed particles (e.g., ammonium sulfate, ammonium bisulfate, fulvic acid) with the RH range from ~ 20 %

to ~ 60 %. Clearly, glyoxal is volatile, not semivolatile. Nevertheless, it forms SOA due to the high water solubility. This provided evidence that SOA yields were correlated with the water content, not the organic mass portion in aerosols. Then, Galloway et al. (2009) studied glyoxal uptake by ammonium sulfate particles in a smog chamber, conducting dark and irradiated experiments at ~ 60 - 70 % RH. While Volkamer et al. focused on SOA yields, Galloway et al. characterized aerosol products from dark/irradiated reactions using a high resolution time-of-flight aerosol mass spectrometer, identifying imidazoles among other organic nitrogen products from dark reactions and glycolic acid sulfates (C2H3O6S1) among other organosulfate products from irradiated reactions (Note that Volkamer et al. conducted OH radical chemistry, but Galloway et al. had no OH source). Note that glyoxal is used as a surrogate of water soluble organic compounds in ambient wet aerosols, to explore non-radical and radical reactions in the condensed phase leading to SOA. Later, Kampf et al. (2012) studied further glyoxal-ammonium sulfate aerosols identifying various imidazoles and oligomers under dark reactions using a high performance liquid chromatograph~~y~~ coupled with a tandem mass spectrometer. Chamber studies for isoprene epoxides (IEPOX) in the aqueous phase have been also conducted. Surratt et al. (2010) observed in a dark chamber (~ 30 % RH) IEPOX taken up by acidic sulfate aerosols formed oligomers presumably in the aqueous phase since sulfuric acid takes up water even at low RH. Nguyen et al. (2014) observed that liquid water content strongly correlated with IEPOX uptake and oligomer formation by ammonium sulfate seed particles in the presence of aerosol liquid water.

There are still few smog chamber studies addressing condensed-phase chemistry explicitly in terms of radical reactions (irradiated reactions) and non-radical reactions (dark reactions); these two types of aqueous chemistry must be explored to understand SOA_{aq} formation in aerosols. One of the challenges in studies of SOA formation through wet aerosol chemistry is that the concentration of aerosol water, the medium of the aqueous-phase reactions, depends on the 1) hygroscopicity of aerosols, 2) concentration of aerosol particles and 3) RH. Furthermore, product formation also depends on 1) the gas-phase transport of water soluble organic compounds, 2) OH partitioning between the gas and aqueous phases, and 3) competition in the aqueous phase between photooxidation and dark (non-radical) reactions.

In this work, we conduct multiphase photochemical oxidation and dark reactions in the presence of wet aerosols: ~~the~~ glyoxal-H_2O_2-ammonium sulfate aerosols (AS aerosols) and glyoxal-H_2O_2-sulfuric acid aerosols (SA aerosols) in a smog chamber under low (< 5 % RH) and high (> 70 % RH) humidity conditions. Ammonium sulfate and sulfuric acid were used for seed particles to observe ammonium interactions, liquid water, and acidity effects. H_2O_2 provided a source of OH radicals in the wet aerosols during the irradiation. NO_x and O_3 were initially introduced into the chamber with modest concentrations ($[NO_x]_{initial}$ = 3—83 ppb, $[O_3]_{initial}$ = 0—12 ppb) to reflect chemistry under anthropogenic influences (Carlton and Turpin, 2013; Ervens et al., 2011). After chamber reactions wet aerosols were characterized by ultra-performance liquid chromatography quadrupole time-of-flight mass spectrometry (UPLC-Q-TOF-MS).

2 Experimental Section

2.1 Chemicals

The following chemicals were used in this study: glyoxal solution (Sigma-Aldrich) 40 % in H_2O (by weight), hydrogen peroxide (Kanto Chemical Co. Inc.) 30 % in H_2O (by weight), ammonium sulfate (Sigma-Aldrich) 99.999% (by weight), sulfuric acid (Junsei Chemical Co. Inc.) 95.0 % in H_2O (by volume), and nitric acid (Sigma Aldrich) 70% in H_2O (by weight).

2.2 Environmental Chamber Method

Photooxidation/dark experiments for AS aerosols and SA aerosols were conducted in a 5 m^3 PTFE environmental chamber at Korea Institute Science and Technology (KIST), Seoul, Republic of Korea. The chamber was initially filled with clean/dry air (< 0.5 ppb NMHC, < 5 % RH) at 20-25°C and atmospheric pressure. AS aerosols were made by atomizing the aqueous solution of 1 mM glyoxal, 200 µM H_2O_2, and 0.012 M $(NH_4)_2SO_4$ and SA aerosols were made by atomizing the aqueous solution of 1 mM glyoxal, 200 µM H_2O_2, and 0.012 M H_2SO_4. Note that atomized particles were passed through a diffusion dryer (3062-NC, TSI; residence time ~ 5 s) before introducing to the chamber to minimize the water content. 200 µM H_2O_2, previously used by Nguyen et al. (2013) in flow tube studies, was used here since this concentration generates ~10^{-14} M, an atmospheric aqueous OH concentration (Arakaki et al., 2013), during the reaction with 1 mM glyoxal according to the updated full kinetic model (Lim et al., 2010; Lim et al., 2013; Lim and Turpin, 2015) (Fig. S1; Model details are in Section 3.3). The smog chamber background levels were < 40 particles and ~10^{-2} µg/m^3. Atomized aerosols with mass concentrations of 70–180 µg/m^3 and a size of 70–90 nm (geometric mean diameter) were then introduced into the chamber for photooxidation and dark reactions. Concentrations of NO_x, O_3, and particle mass in the smog chamber can be related to a moderate haze condition in urban areas, particularly observed in Seoul or Beijing.

The photooxidation was initiated by turning on blacklights, which generate tropospheric UV light (340—400 nm) with a peak intensity at 359 nm. For humid condition experiments, the KIST humidifier was used to achieve up to ~ 90 % RH. RH and temperature were measured using a Kimo AMI 300 multi function meter. This humidifier was developed by modifying an existing commercial humidifier. Water spray and evaporation pan were specially designed to generate water steam rapidly. While adding water vapors into the chamber, we monitored SMPS to ensure no water droplet was introduced. All experiments were conducted in moderate O_3 and NO_x conditions ($[O_3]_{initial}$ = 0–13 ppb, $[NO]_{initial}$ = 2–81 ppb and $[NO_2]_{initial}$ = 0–5 ppb). NO and NO_x concentrations were measured using an NO-NO_2-NO_x Analyzer (Thermo Scientific Model 42i). Ozone concentrations were measured using an Ozone Analyzer (Thermo Scientific Model 49i). We conducted 14 experiments in an irradiated/dark chamber adjusting relative humidity from 5 % to 90 %. Table S1 summarizes experimental conditions. Fractions of aerosol liquid water (ALW) in aerosols were estimated using the extended aerosol inorganic model (E-AIM) (Wexler and Clegg, 2002) and also included in the table. For the ALW estimations, Model II (H^+, NH_4^+, SO_4^{2-}, NO_3^-, H_2O, and Organic Compound) was used and neither radical nor non-radical reactions in the condensed phase were considered.

2.3 Filter Extraction and Aerosol Analysis

At chamber reaction time of 0, 30, 60, 120, and 180 minutes, aerosols were collected on blank Teflon filters (25 mm, 1.0 µm, Pall Corporation) for 10 minutes at a sampling rate of 10 LPM (Only 0 and 180 minute samples were collected for dark reactions). These filter samples were extracted with 5 mL Milipore water (18.2 MΩ) for 20 minute sonication. 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.~~–~~ Ultra performance liquid chromatography coupled to quadrupole time-of-flight mass spectrometry (UPLC-Q-TOF-MS) (Waters, Synapt G2) was used to examine the elemental composition of aerosol samples. The capillary voltage and the capillary temperature were -2500 V and 350 °C, respectively for negative mode analyses. Positive mode analyses were conducted with the capillary voltage of 2500 V and the capillary temperature of 250 °C. The aerosol samples were diluted with methanol by 2 fold by volume (i.e., 50:50 water/methanol), then immediately introduced into the electrospray ionization source by direct infusion with a flow rate of 2.54 mL/hr. Since no column was used for separation, clusters could be formed during the ionization.

Two standard solutions, AS solution (1 mM glyoxal, 200 µM H_2O_2, and 0.012 M $(NH_4)_2SO_4$) and SA solutions (1 mM glyoxal, 200 µM H_2O_2, and 0.012 M H_2SO_4), were also analyzed by UPLC-Q-TOF-MS using the method described above.

Organic compounds (CHO), organonitrogens (CHNO), organosulfates (CHOS), and organosulfate-nitrogens (CHNOS) were analyzed both in the negative and positive modes. In the negative mode, ~~deprotonated~~ undissociated acid compounds (i.e., $[M-H]^-$) such as carboxylic acids, organonitrates and organosulfates, are detected. And some organonitrates are detected as Cl^- adducts. In the positive mode, glyoxal, glyoxal oligomers and reduced organonitrogen compounds (e.g., imines; note that imidazoles are imines) are detected via protonation ($[M + H]^+$) or as sodium adducts ($[M + Na]^+$). Elemental formulas were assigned by MIDAS Formula Calculator (version 1.2.3) within the uncertainty of 150 ppm based on the mass accuracy of measured nitrate peaks (m/z$^-$ 62). Note that unlike Fourier transform ion cyclotron mass spectrometry (FTICR-MS), whose uncertainty is below 1 ppm, TOF-MS tends to have uncertainties since it is well known that uncertainties of TOF could be higher (Smith et al., 2013). In addition to this, the elemental formulas for organosulfates (with 32S) were confirmed by the coexistence of the identical formula with the sulfur isotope (34S), present with a signal intensity reduced to ~ 100 times smaller in a mass spectrum (Note that natural abundance is 95 % 32S and 4 % 34S). Similarly, Cl^- adducts (35Cl) were confirmed by chlorine isotope (37Cl) adducts with an intensity reduced by ~ 20 times (Note that natural abundance is 75 % 35Cl and 25 % 37Cl).

2.4 MS/MS ~~A~~analysis for m/z$^-$ 147 and standard MS analysis of m/z$^-$ 147 and 226

The smog chamber product peak at m/z$^-$ 147 was further analyzed by a liquid chromatograph tandem mass spectrometer (LC-MS/MS; 6460 Agilent Triple Quadrupole). Again, the mobile phase was 50:50 water/methanol and the direct injection with a flow rate of 0.1 mL/min (no column) was used. The sample was analyzed in the negative mode. The capillary voltage and the capillary temperature were -3000 V and 350 °C, respectively. A standard solution prepared by mixing glyoxal (7.6 mM) and nitric acid (15 mM) was analyzed by UPLC-Q-TOF-MS with the method described above.

3 Results and Discussion

3.1 Photochemical Organonitrate Formation in Wet Aerosols

During the irradiation for both AS and SA aerosols in the humid chamber (> 70 % RH) the major products, organonitrates (m/z$^-$ 147 and 226) were likely formed by non-radical reactions of glyoxal with nitric acid in the aqueous phase of wet aerosols (Fig.1A and B), and nitric acid (m/z$^-$ 62) is formed via radical reactions in the gas-phase system of glyoxal-NO_x-OH. LC-MS/MS analysis was conducted for m/z$^-$ 147, and fragments were m/z$^-$ 62 and 103 (Fig. S2). m/z$^-$ 62 indicates nitrate acid and m/z$^-$ 103 is a loss of 44 (CO_2) suggesting that the parent molecule is a carboxylic acid. The standard solution of the glyoxal-HNO_3 mixture analyzed by UPLC-Q-TOF-MS showed the major peaks at m/z$^-$ 62, 147 and 226 (Fig. S3). This confirms that m/z$^-$ 147 and 226 can be formed via aqueous non-radical reactions of glyoxal and nitric acid without UV. According to the MIDAS molecular calculator, these two peaks are organonitrates (m/z$^-$ 147, C6H2N2O12 (z = 2); m/z$^-$ 226, C4H1N1O8Cl1), and not likely nitric acid adducts to glyoxal (clusters). The proposed formation and molecular structures are illustrated in ~~Scheme S1~~Scheme 4. Other organonitrates may form through this mechanism as well. However, the chemical formula provided herein has the smallest error compared to the measured mass. It appears that nitric acid undergoes nitrate ester formation (R-OH + HNO_3 ~~→~~ ⇄ R-ONO_2 + H_2O) (Boschan et al., 1955) and oxidizes some hydroxyl groups (Connelly et al., 2012). Therefore, m/z$^-$ 147 and 226 are organonitrates formed by the aqueous-phase reaction of glyoxal and nitric acid. m/z$^-$ 147 is likely to be doubly charged (z = 2) and this is supported by the coexistence of m/z$^-$ 147.5 ($\Delta z = 0.5$). On the other hand, m/z$^-$ 226 is likely to be a Cl^- adduct organonitrate. Cl^- adducts for organonitrates have been observed (Bouma and Jennings, 1981; Lawrence et al., 2001; Rajapakse et al., 2016; Zhu and Cole, 2000)~~ while~~, and MIDAS does not propose realistic organonitrates without Cl^-. The uncertainty for the mass of Cl adducts is reasonably low (~ 50 ppm). Cl^- adducts are confirmed by the coexistence of m/z$^-$ 228 ($\Delta z = 2$), organonitrates adducted by Cl^- isotope (37Cl) with the low mass uncertainty (10 – 30 ppm).

Despite the non-radical formation of organonitrates, nitric acid was photochemically formed during the irradiation (Scheme 1A). It is also possible that nitric acid is formed in the dark (Scheme 1B). Indeed, m/z$^-$ 62, 147 and 226 initially appeared for AS and SA aerosols in dark reactions (Fig. 2E and F). However, these peaks disappeared in 3 hours (Fig. S4). This suggests that photochemical formation of nitric acid is continuous during the irradiation. The chamber was initially filled with NO and little NO_2, but NO was converted to NO_2 as irradiation proceeded. Peroxy radicals are effective for the NO-NO_2 conversion (Atkinson and Arey, 2003) and our measured NO_x levels support this. During the irradiation of AS aerosols (Experiment #1, Table S1), the concentration of NO_2 increased from 4.0 ppb to 20.0 ppb ($\Delta[NO_2]$ = 16.0 ppb) while the concentration of NO was reduced from 24.0 ppb to 5.5 ppb ($\Delta[NO]$ = -18.5 ppb). Another photochemical experiment for AS aerosols (Experiment #2) also shows ~~the~~ significant increase of $[NO_2]$ ($\Delta[NO_2]$ = 10.0 ppb, $\Delta[NO]$ = -3.8 ppb). However, in the photochemical experiment for AS aerosols containing no glyoxal (Experiment #7), NO_2 only increased by 0.7 ppb while the initial [NO] was similar to Experiment #2. Notice that O_3 increased. This is due to photolysis of NO_2.

~~Then, which organic species became peroxy radicals in the gas phase?~~Photochemisry on wet aerosols may lead to volatile organic products that contribute to gas-phase peroxy radicals. Glyoxal is not likely to evaporate due to high water solubility (effective $H_{glyoxal}$ ~ 2e7) (Ervens and Volkamer, 2010). Among products of glyoxal-OH reactions glyoxylic acid and formic acid are not very water soluble ($H_{glyoxylic\ acid}$ = 9.12e3 M/atm; $H_{formic\ acid}$ = 5.50e3), so they could evaporate to the gas phase and undergo OH radical reactions forming peroxy radicals (Model simulations are discussed in Section 3.3). OH radicals produced via photolysis of H_2O_2 could evaporate while reacting with glyoxal in the aqueous phase (H_{OH} = 30 M/atm). Scheme 2 shows gas-phase OH reactions of glyoxylic acid and formic acid. In the gas phase, glyoxylic acid (HO(O)CC(O)H) reacts with OH and O_2 forming peroxy radicals (HO(O)CC(O)OO·), which convert NO to NO_2 (HO(O)CC(O)OO· + NO → HO(O)CC(O)O· + NO_2). Although there is no literature available for OH reactions of glyoxylic acid in the gas phase, these peroxy radicals (HO(O)CC(O)OO·) are not likely to produce organic nitrates since the similar structured peroxy radicals (H(O)CC(O)OO·), which are formed from OH reactions of glyoxal in the gas phase, are reported to produce neither alkyl nitrates (H(O)CC(O)OO· + NO → H(O)CC(O)ONO_2) nor alkyl peroxyacetylnitrates (H(O)CC(O)OO· + NO_2 → H(O)CC(O)$OONO_2$), and only convert NO to NO_2 (Orlando and Tyndall, 2001). OH radical reactions of formic acid lead to CO_2 without NO_x reactions (Scheme 2B) (Atkinson et al., 2004). Therefore, glyoxylic acid is likely to be the source of peroxy radicals that convert NO to NO_2, and organonitrates in this work are not from gas-phase formation. Since gas-phase OH reactions of glyoxylic acid and formic acid produce HO_2 (Scheme 2A and B), this HO_2 contributes to additional conversion from NO to NO_2 and recycles OH (i.e., HO_2 + NO → OH + NO_2) (Orlando and Tyndall, 2001). Lastly, NO_2 reacts with OH forming HNO_3 (Scheme 1A) (Finlayson-Pitts and Pitts Jr, 1999).

Subsequently, nitric acid is taken up into ALW. In the humid chamber, estimated ALW fractions in wet aerosols were 19.4—45.8 % for AS aerosols (Experiment #4, Table S1) and 53.1—74.2 % for SA aerosols (Experiment #12) throughout experiments, and after ~~the~~ 3 hours of irradiation the peaks at m/z^- 62 (nitric acid), 147 and 226 were prominent (Fig. 1A and B). However, in the dry chamber, ALW fractions were only ~ 1 % for AS aerosols (Experiment #1) and 26.5—32.4 % (Experiment #11) for SA aerosols. After ~~the~~ 3 hours of irradiation, only m/z^- 62 and 147 (m/z^- 226 was missing) appeared with smaller intensities for AS aerosols (Fig. 1C), and none of m/z^- 62, 147, and 226 appeared for SA aerosols (Fig. 1D). It is interesting that HNO_3 was found in AS aerosols in the dry chamber. Formation of HNO_3 by heterogeneous reactions of NO_2 on the surface of aerosols has been reported previously (Crowley et al., 2010). Note, the oxidation of NO (and NO_2) by O_2 in the gas phase is too slow (Atkinson et al., 2004), and NO and NO_2 are not very soluble for partitioning into the aqueous phase (H_{NO} = 0.019 M/atm, H_{NO2} = 0.007 M/atm). Therefore, heterogeneous reactions NO_2 on the dry surface of AS aerosols could form HNO_3. No nitric acid was observed in SA aerosols, which still contain 26.5—32.4 % ALW in the dry chamber. It is possible that in the presence of sulfuric acid nitric acid acts as a base forming NO_2^+ and HSO_4^- (i.e., $HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + 2HSO_4^- + H_3O^+$) (McQuarrie et al., 1991). If NO_2^+ were formed in a significant amount, it could be an important reactive species. However, measurement of NO_2^+ and investigation of its potential role is beyond the scope of this study. Further studies are required for HNO_3 uptake by AS and SA aerosols in the dry chamber.

Figure 2 ~~also~~ suggests gas phase photochemical production and uptake of HNO_3 into ALW. In Fig. 2A and B, both AS and SA solutions only show sulfuric acid peaks at m/z^- 97 (monomer) and m/z^- 195 (dimer), and an organosulfate peak at m/z^- 217 (C2H1O8S2), which is an ester product of a glyoxal and two sulfuric acids with the structure (A) and the formation (B) in Scheme 3. In the dry and dark chamber, neither nitric acid (m/z^- 62) nor organonitrates (m/z^- 147 and 226) were initially formed (Fig. 2C and D) suggesting little HNO_3 uptake in the dry chamber. Note that in the dry chamber ALW fractions are 1 % for AS aerosols (Fig. 2C; Experiment #8, Table S1) and 27 % for SA aerosols (Fig. 2D; Experiment #13). Again, in the humid and dark chamber m/z^- 62, 147 and 226 initially appeared for AS and SA aerosols (Fig. 2E and F) and this is due to HNO_3 uptake into sufficient ALW in both aerosols (ALW fraction for AS and SA aerosols are 54 %, 71 % respectively). But HNO_3 here is formed by dark reactions of O_3 and NO_x (Scheme 1B) and disappeared in the 3 hour dark reactions (Fig. S4).

3.2 Dilute Cloud-Relevant (Bulk) Chemistry vs. Multiphase Aerosol Photooxidation

The photochemistry of glyoxal in dilute aqueous solution vessel has been established (Lim et al., 2010; Tan et al., 2010). The OH reaction of glyoxal in the aqueous phase produces mostly oxalic acid with minor products like glyoxylic acid, formic acid and carbonic acid. When the glyoxal concentration is higher than cloud-relevant concentration, tartaric acid also becomes a major product formed via organic radical-radical reactions. The reaction mechanisms including concentration-dependent pathways were elucidated, and the aqueous photochemical kinetic model (Lim et al., 2010; Lim et al., 2013) was developed and validated by experimental results. Assuming adequate access to OH radicals, the model (Perri et al., 2010) predicts that oxalic acid, tartaric acid, and organosulfates will form via radical reactions in H_2SO_4-containing wet aerosols. However, multiphase modeling suggests depletion of OH radicals in wet aerosols may be substantial and predicts that non-radical chemical pathways will dominate, leading to the formation of organosulfates (McNeill et al., 2012).

While sulfuric acid and ammonium hydroxide addition do not interfere the real-time formation of oxalic acid in dilute (cloud-relevant) photooxidation experiments (bulk) (Ortiz-Montalvo et al., 2014; Tan et al., 2009), non-radical reactions with sulfate and ammonium ions dominate in AS and SA aerosols during the 3 hour irradiation in the humid/dry chamber. Mass spectral analyses in the negative mode (Fig. 1) suggest that the products are organic acids (CHO), organonitrates (CHNO), organosulfates (CHOS), and nitrooxy-organosulfates (CHNOS). Proposed chemical formula are listed in Table 1.

However, production of oxalic acid and tartaric acid provides evidence that OH reactions of glyoxal occurred in ALW. Note that oxalic acid cannot be formed in the gas phase since gas-phase photochemistry will decompose evaporated organic species (e.g., glyoxylic acid, formic acid) to CO_2 (Scheme 2). During ~~the~~ irradiation, oxalic acid~~s~~ ~~were~~was formed in the humid chamber, ~~since~~ shown by UPLC-Q-TOF-MS ~~detected~~detection of m/z^- 89 (oxalic acid) in AS aerosols (Fig. 1A) and m/z^- 187 (oxalic acid-sulfuric acid adduct) in SA aerosols (Fig. 1B). Sulfuric acid adducts to organic acid are commonly observed during aerosol nucleation and particle growth (Zhang et al., 2004). Even in the dry chamber oxalic acid (m/z^- 89), glycolic acid (m/z^- 173 as a sulfuric acid adduct) and tartaric acid (m/z^- 247 as a sulfuric acid adduct) were formed as in SA aerosols (Fig. 1D). This can be explained by the high hygroscopicity of sulfuric acid. In the dry chamber (7 % RH) SA aerosols still held 32 % ALW (Experiment #11, Table S1).

The decay of glyoxal provides additional evidence that glyoxal reacts with OH radicals in ALW. Glyoxal is detected in the positive mode of UPLC-Q-TOF-MS. A number of peaks at m/z^+ 59 (= $[M + H]^+$), 95 (= $[M + 2H_2O + H]^+$), 99 (= $[M + H_2O + Na]^+$), 113 (= $[M + MeOH + Na]^+$), 117 (= $[M + 2H_2O + Na]^+$), 131 (= $[M + H_2O + MeOH + Na]^+$, and 145 (= $[M + 2MeOH + Na]^+$) represent glyoxal in various hydrated forms and hemiacetal forms with water and methanol from the mobile phase (M = glyoxal $(CHO)_2$; MeOH = methanol). In Fig. 3, glyoxal peaks in AS aerosols and SA aerosols are plotted in a relative scale (~~no glyoxal peak was found for AS aerosols in the humid chamber~~glyoxal was also detected for AS aerosols in the humid chamber; however, since it was only detected in 15 and 30 minute samples, no decay plot was constructed). The relative intensity was obtained by normalizing the fraction of the raw signal intensity divided by the weight of the collected particles on the filter. These estimations are not based on real-time online analyses since extracted filters were collected for 10 minutes, but still qualitatively indicate the glyoxal decay in wet aerosols. For SA aerosols, the ~~decay rate~~ lifetime (τ) of glyoxal in the dry chamber (~~0.03~~51.3 min~~$^{-1}$~~ in Fig. 3A) is very similar to that in the humid chamber (~~0.02~~54.1 min~~$^{-1}$~~ in Fig. 3B) due to high hygroscopicity of sulfuric acid (32% ALW in the dry chamber). Assuming no evaporation of ALW, the kinetic model (Details are discussed in the next section) predicts that the ~~decay rate~~lifetime of glyoxal by OH reactions in the aqueous phase is ~~0.018~~55.6 min^{-1}, which is very similar to estimated values above. However, for AS aerosols in the dry chamber, glyoxal peaks at m/z^{+} 113, 117 and 131 decay sharply in 30 minutes and the estimated ~~decay rate~~lifetime is ~~~ 0.09~~10.9 min~~$^{-1}$~~ (Fig. 3C), which is ~ 5 times ~~faster~~ shorter than the ~~decay rate~~ lifetime by OH reactions. Since AS aerosols in the dry chamber hold only ~ 1 % ALW, this suggests that ALW evaporation affects glyoxal loss significantly. So it is possible that gas-phase glyoxal chemistry takes place during the irradiation of AS aerosols in the dry chamber since glyoxal could evaporate, too. However, gas-phase photochemistry of glyoxal produce neither oxalic acid nor organonitrates (PAN type compounds); it produces decomposed fragments (Scheme 2C) (Atkinson et al., 2006; Orlando and Tyndall, 2001).

Organonitrogens (CHNO), organosulfurs (CHOS), organonitrogen-sulfur (CHNOS) and organic compounds (CHO) were also detected in the positive mode of UPLC-Q-TOF-MS (Table 2 and Fig. 4). Imidazoles (m/z^{+} 69, 145, 149, and 203) observed by Kampf et al. were also observed here in AS aerosols in the humid and dry chamber.

Organosulfates were formed in both AS and SA aerosols and detected in the negative mode of UPLC-Q-TOF-MS. The organosulfate (m/z^{-} 155, C2H3O6S1) observed by Galloway et al. was also observed in AS aerosols in the humid chamber. Galloway et al. proposed two structures for m/z^{-} 155, a glyoxal-sulfate and a glycolic acid-sulfate ester and we argue that it is more likely to be the glycolic acid-sulfate ester. Since OH reactions of glyoxal produce glycolic acid in the presence of HO_2, which is commonly available during aqueous photochemistry (Lim and Turpin, 2015) (Scheme ~~4A~~5A), the glycolic-acid sulfate ester is formed by non-radical esterification between glycolic acid and sulfuric acid (Scheme ~~4B~~5B). The m/z^{-} 173 organosulfate (C2H5O7S1) formed in SA aerosols in the dry chamber (7 % RH, 32 % ALW) is likely to be a glycolic acid-sulfuric acid adduct (Scheme ~~4C~~5C). However, the m/z^{-} 171 (organosulfate, C2H3O7S1), which was formed via glycolic acid radical-sulfuric acid radical reactions (Perri et al., 2010), was not observed here. This suggests that in the condensed phase OH radicals mostly contribute to oxidation of organic compounds, making products that subsequently form organosulfates or organic acid-sulfuric acid adducts via non-radical reactions.

3.3 Model Simulations for Smog Chamber Photooxidation

In this work, aqueous glyoxal chemistry described in a previous kinetic model (Lim et al., 2010; Lim et al., 2013; Lim and Turpin, 2015) was expanded by including partitioning of radical oxidants (e.g., OH) and organic compounds (e.g., glyoxylic acid, formic acid) into the gas phase and the gas-phase OH reactions. Newly added reactions are listed in Table S3. The model was then applied to better understand the multiphase chemistry in the smog chamber experiments, including whether the proposed pathway for the production of NO_2 and subsequent organonitrate formation is plausible. It is assumed that carboxylates (e.g., formate, glyoxylate, and oxalate) do not evaporate since they are likely to form low volatility carboxylate salts in the atmosphere (Ortiz-Montalvo et al., 2012), so only ~~deprotonated~~ undissociated acids evaporate according to water solubility. The model is not well designed to simulate the dry conditions for AS aerosols in the chamber; since water evaporation is not allowed.

With the same initial concentrations of glyoxal (1 mM), H_2O_2 (200 µM) and $(NH_4)_2SO_4$ or H_2SO_4 (0.012 M), the model predicts that the dominant product is glyoxylic acid in both AS and SA aerosols in the presence of ALW (Fig. 5). In dilute (bulk) aqueous chemistry experiments designed to study chemistry in cloud water, the dominant product was found to be oxalic acid (Tan et al., 2009). But in the chamber, where aqueous chemistry takes place in concentrated non-ideal solutions in wet aerosols with large surface area to volume ratios, oxalic acid formation was suppressed by partitioning of glyoxylic acid to the gas phase, consistent with predictions elsewhere (Skog et al., submitted). The concentration of gas-phase glyoxylic acid produced through AS aerosol-phase chemistry reached up to ~ 200 ppb from AS aerosols (Fig. 6A) and ~ 800 ppb from SA aerosol-phase chemistry (Fig. 6B) in the presence of ALW. Note the predicted OH concentration in the gas phase was ~1e6 molecules/cm^3, which is atmospherically relevant (Fig. S5). Clearly, in the gas phase sufficient amounts of peroxy radicals would have been formed from aqueous aerosol photochemistry to convert NO to NO_2.

We also estimate the concentration of HNO3 taken up into wet aerosols by including chemistry of NO_x, HO_x, peroxy radical, HNO_3 partitioning (H = 1.6e5 M/atm) into a FACSIMILE model. ~ 500 µM of HNO_3 uptake in the aqueous phase is predicted after 3 hours of irradiation when initial conditions are 10 ppb of NO, 0 ppb of NO_2, 10 ppb of O_3 and 500 ppb of an organic compound in the gas phase (glyoxylic acid). This concentration of HNO_3 is sufficient to form organonitrates with glyoxal and comparable to that of other inorganic constituents in wet aerosols (200 µM of ammonium sulfate/sulfuric acid).

3.4 Dark Aerosol-Phase Reactions

AS and SA solutions, and AS and SA aerosols at t = 0 min in the dark chamber were analyzed by UPLC-Q-TOF-MS in the negative mode (Fig. 2). Solutions only show sulfuric acid and organosulfate (Fig. 2A and B), but atomized aerosols show many other peaks including organic acids (CHO), organosulfates (CHOS), nitric acids (HNO_3), organonitrogens (CHNO) and organonitrogen-sulfates (CHNOS) (Fig. 2C, D, E and F). When the solutions are atomized and introduced into the smog chamber, water evaporates ~~from aerosols due to the large increase of the surface area~~to equilibrate to the chamber RH, and concentrations of solutes increase. Water loss and concentration increase result in the formation of oligomers and inorganic products. Glyoxal forms oligomers via hemiacetal formation and aldol-condensation can lead organic acid products (Lim et al., 2010; Loeffler et al., 2006; Sareen et al., 2010). Generally, organic acid oligomers (CHO) were formed in the dry chamber, and inorganic compounds and oligomers (CHNO, CHNOS) in the humid chamber (Proposed molecular formula are listed in Table 3). It appears that acid ~~catalyzation~~ catalysis (aldol condensation and hemiacetal formation) leading to organic acid formation favors low ALW and high acidity because a hydrated glyoxal in the aqueous phase will be partially dehydrated to form an aldehyde group, and the dehydration can be maximized by the evaporation of ALW in the dry chamber (Lim et al., 2010). However, acidity effects on oligomer formation requires further study because sulfuric acid in SA aerosols appears to enhance oligomerization while photochemically formed nitric acid does not. As discussed in Section 3.1, the prominent peaks represent nitric acid (m/z^- 62) and organonitrates (m/z^- 147 and 226) for both AS and SA aerosols in the humid dark chamber (Fig. 2E and F). In the dark, nitric acid is formed by N_2O_5 uptake by water and the gas-phase reaction of NO_2 and NO_3 produces N_2O_5 (Scheme 1B) (Finlayson-Pitts and Pitts Jr, 1999). Dark experiments were conducted initially with NO and O_3 available, so NO_2 and NO_3 were probably formed by the O_3 oxidation of NO and NO_2, respectively (Scheme 1B).

After 1 hour of dark reactions, m/z$^-$ 62, 147 and 226 disappeared in AS and SA aerosols in the humid chamber (Fig. S4). NO_x and O_3 levels stayed almost the same indicating little HNO_3 formation in the dark. Instead, many other m/z$^-$ peaks appeared indicating that various non-radical reactions took place. Non-radical reactions also occurred in the dry chamber.

In the positive-mode mass spectra for the AS solution, imidazole (m/z$^+$ 69), glyoxal (m/z$^+$ 117), and imines (m/z$^+$ 133, 248, and 363) were detected (Fig. S6A) while high molecular weight organic compounds, which are presumably acid-catalyzed products from glyoxal, were detected in the SA solution (Fig. S6B). Many more peaks are found in the mass spectra of AS and SA aerosols (Fig. S6C, D, E and F) than the solutions. Proposed elemental compositions based on MIDAS are listed in Table S2. All organonitrogens in the positive mode for AS aerosols are expected to be imines because ~~in the~~ aqueous phase reactions of glyoxal with ammonium form imines (Galloway et al., 2009; Noziere et al., 2009; Yu et al., 2011). Organic compounds (CHO) are oligomers of glyoxal, which are mostly detected in SA aerosols while imines (CHNO) are prominent in AS aerosols.

After 1 hour dark reactions, oligomerization was evident in the positive mode mass spectra from dark experiments (Fig. S7). It appears that in AS aerosols ammonium ions form oligomers and imines. ~~, whereas i~~In SA aerosols the formation of oligomers and organosulfates are enhanced by sulfuric acid. This is consistent with the previous observation of oligomer formation for IEPOX (Nguyen et al., 2014). When ALW is sufficient (in AS aerosols in the humid chamber and SA aerosols in the humid/dry chamber), mass spectra are similar (Fig. S7A, B, and D), in which unidentified peaks at m/z$^+$ 99, 261, 299, 301, and 305 are dominant, indicating products of multiphase aerosol reactions are different from those of heterogeneous reactions on the dry aerosol surface (AS aerosols in the dry chamber, Fig. S7C). Further studies are required for surface and multiphase chemistry affected by hygroscopicity and acidity of aerosols and RH.

4 Conclusions and Atmospheric Implications

This work demonstrates HNO_3 uptake by wet aerosols and formation of organonitrates with water-soluble organic constituents via aqueous chemistry, which to our knowledge has not been reported previously. 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. HNO_3 formation is facilitated by aqueous photooxidation: NO is effectively converted to NO_2 by volatile organic products (glyoxylic acids) during aqueous photooxidation; and OH generated in wet aerosols by photolysis of hydrogen peroxide evaporates and forms HNO_3 with NO_2. HNO_3 then forms organonitrates with aldehydes and alcohols, dominant water-soluble organic species in wet aerosols. This chemistry is inherently multiphase chemistry. Organonitrates formed in aerosol waters are not likely alkylnitrates formed by peroxy radical reactions with NO in the gas phase, followed by gas-particle partitioning (Lee et al., 2016) because yields of alkylnitrates in alkane-OH-NO_x chamber experiments decreased in humid conditions due to hydrophobicity (Lim and Ziemann, 2009). In order to be hydrophilic, VOCs must contain a small number of carbons. This small size also facilitates uptake into wet aerosols. The reaction of peroxy radicals with NO favors alkoxy radical formation, and suppresses alkylnitrate formation (Arey et al., 2001). In our irradiated chamber, this organonitrate chemistry was facilitated by gas phase VOC-NO_x-O_3 photochemistry (Table S1) forming HNO_3. This represents typical anthropogenic photochemistry of VOC-NO_x-O_3 leading to HNO_3 formation as a sink

(Finlayson-Pitts and Pitts Jr, 1999). Note concentrations of glyoxal and hydrogen peroxide in atomized solutions are atmospherically-relevant (Guo et al., 2014; Lim et al., 2013).

Nitrates are major constituents in atmospheric aerosols (Zhang et al., 2007). They are very hygroscopic, facilitating water uptake into aerosols (Hennigan et al., 2008a; Hodas et al., 2014). ALW in turn facilitates aerosol partitioning of HNO_3. Field observations support HNO_3 uptake by aerosol waters during the daytime (Allen et al., 2015; Hodas et al., 2014). ~~And n~~Notably, nitrate concentrations are strongly correlated with water soluble organic compound concentrations (Hennigan et al., 2008b). This study suggests that small, highly oxidized organonitrates are formed in wet aerosols. An understanding of their contribution to overall atmospheric organonitrate particulate mass warrants further study.

5 Acknowledgements

This work was supported by Brainpool Fellowship from Ministry of Science, ICT and Future Planning, Republic of Korea (152S-5-2-1416) and Korea Institute of Science and Technology. The authors acknowledge Minsuk Oh and Hyunmi Park at Mass Spectrometry Division in KIST Chemical Analysis Center for UPLC-HR-Q-TOF-MS analysis. The authors thank Jino Kim for laboratory assistance. The authors also thank Frank N. Keutsch for helpful discussions. Barbara J. Turpin gratefully acknowledges support from the US National Science Foundation (#10526611).

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Table 1: Elemental compositions of organic-inorganic compounds at 180 minute irradiation time (UPLC-Q-TOF-MS negative mode analysis)

Aerosols (Conditions)	m/z$^-$	Elemental Composition	Compound	Error (ppm)
AS (Humid)	61.9907	N1O3	Nitric Acid	37.6
	88.9840	C2H1O4	Oxalic Acid	45.3
	96.9667	H1O4S1	Sulfuric Acid	68.0
	146.9669 (z = 2)	C6H2N2O12	Organonitrate	-95.5
	154.9581	C2H3O6S1	Glycolic acid-sulfate Ester*	-48.3
	197.9096	C2N1O8S1	Nitrooxy-organosulfate	-128.4
	225.9279 227.9426	C4H1N1O8Cl(35)1 C4H1N1O8Cl(37)1	Organonitrate	-51.9 26.0
SA (Humid)	61.9911	N1O3	Nitric Acid	44.1
	96.9603	H1O4S1	Sulfuric Acid	2.0
	146.9665 (z = 2)	C6H2N2O12	Organonitrate	-98.2
	181.9389	C2N1O7S1	Nitrooxy-organosulfate	-6.6
	186.9598	C2H3O8S1	Oxalic Acid-Sulfuric Acid	23.5
	197.9053	C2N1O8S1	Nitrooxy-organosulfate	-150.1
	225.9278 227.9404	C4H1N1O8Cl(35)1 C4H1N1O8Cl(37)1	Organonitrate	-52.3 16.4
	282.8897	C6H3O11S1	Organosulfate	-178.4
	288.8996	C8H1O10S1	Organosulfate	-103.8
AS (Dry)	61.9925	N1O3	Nitric Acid	66.7
	96.9614	H1O4S1	Sulfuric Acid	13.4
	146.9677 (z = 2)	C6H2N2O12	Organonitrate	-90.1
	171.0956	C6H11N4O2	Organonitrogen	40.0
	173.0084	C6H5O6	Organic Acid	-4.4
SA (Dry)	62.0241	N1O3	Nitric Acid	-10.5
	89.0389	C2H5N2O2	Organonitrogens	36.5
	96.9604	H1O4S1	Sulfuric Acid	3.1
	172.9572	C2H5O7S1	Glycolic Acid-Sulfuric Acid	109.5
	186.9687	C2H3O8S1	Oxalic Acid-Sulfuric Acid	71.1
	247.0045	C4H7O10S1	Tartaric Acid-Sulfuric Acid	113.2

*Glycolic acid-sulfate ester was detected by Galloway et al., 2009

Table 2: Elemental compositions of glyoxal and other organic-inorganic compounds at 180 minute irradiation time (UPLC-Q-TOF-MS positive mode analysis)

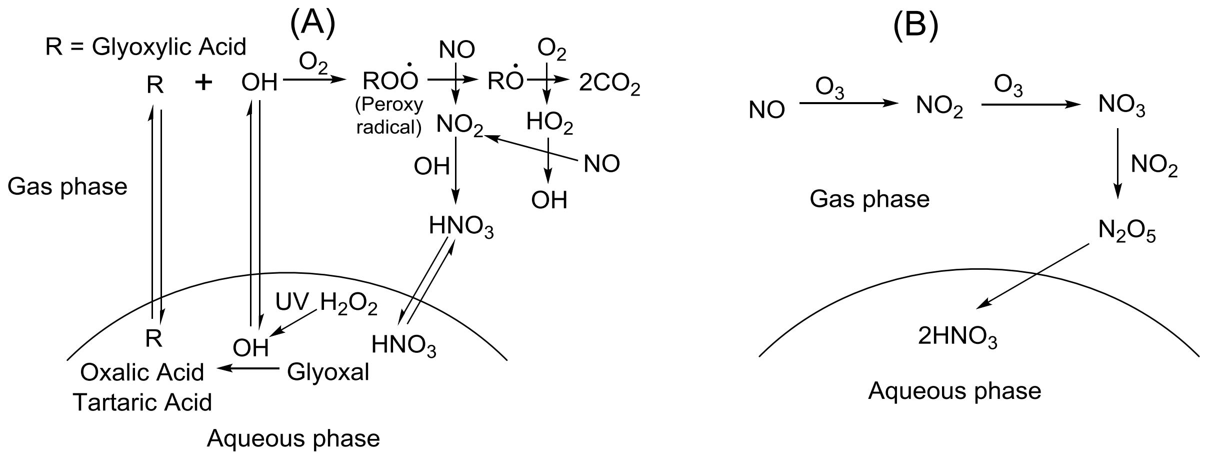
Aerosols (Conditions)	m/z^+	Elemental Composition	Compound	Error (ppm)
AS (Humid)	69.0491	C3H5N2	Imidazole*	63.4
	107.9732 (z = -2)	C4H1O9Na1	Organic Peroxide	-20.0
	109.0698	C4H10N2Na1	Imine	-35.0
	145.0652	C5H9N2O3	Imidazole*	30.5
	149.0299	C5H6N2O2Na1	Imidazole	-72.8
	203.1056	C7H12N6Na1	Imidazole	19.9
SA (Humid)	95.0307	C2H7O4	Glyoxal** (dihydrated)	33.5
	98.9911	C2H4O3Na1	Glyoxal** (monohydrated)	-143.1
	145.0499	C4H10O4Na1	Glyoxal (hydrated by 2 MeOHs)	19.1
	149.0294	C6H6O3Na1	Organic Compound	56.9
AS (Dry)	69.0528	C3H5N2	Imidazole*	116.9
	113.0274	C3H6O3Na1	Glyoxal (hydrated by 1 MeOH)	57.4
	117.0098	C2H4O6Na1	Glyoxal (dihydrated)	-51.5
	131.0348	C3H8O4Na1	Glyoxal (hydrated by 1 MeOH)	25.3
	149.0299	C5H6N2O2Na1	Imidazole	-33.9
	203.0614	C7H11N2O5	Imidazole*	23.9
SA (Dry)	95.0415	C2H7O4	Glyoxal** (dihydrated)	80.1
	98.9894	C2H4O3Na1	Glyoxal** (monohydrated)	-160.3
	131.0065	C3H8O4Na1	Glyoxal (hydrated by 1 MeOH)	-190.7
	149.0213	C6H6O3Na1	Organic Compound	2.6

*Imidazole detected by Kampf et al., 2012

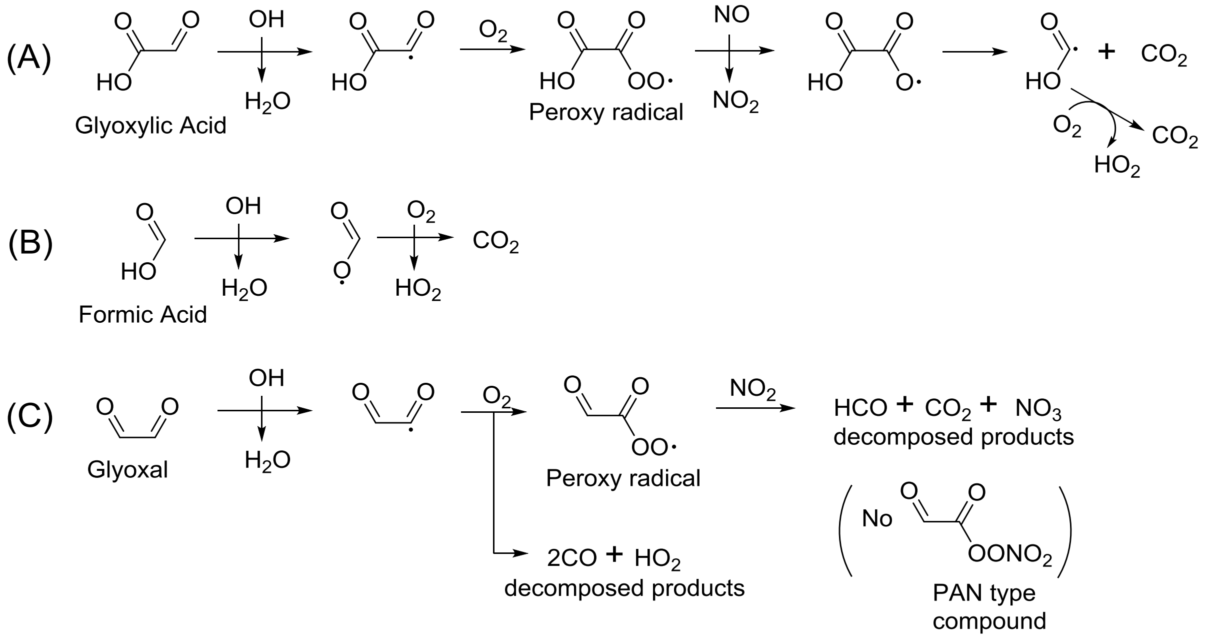
**Glyoxal appeared at t = 0 min, but disappeared during the irradiation

Table 3: Elemental compositions of organic-inorganic compounds in dark reactions (UPLC-HR-Q-TOF-MS negative mode analysis)

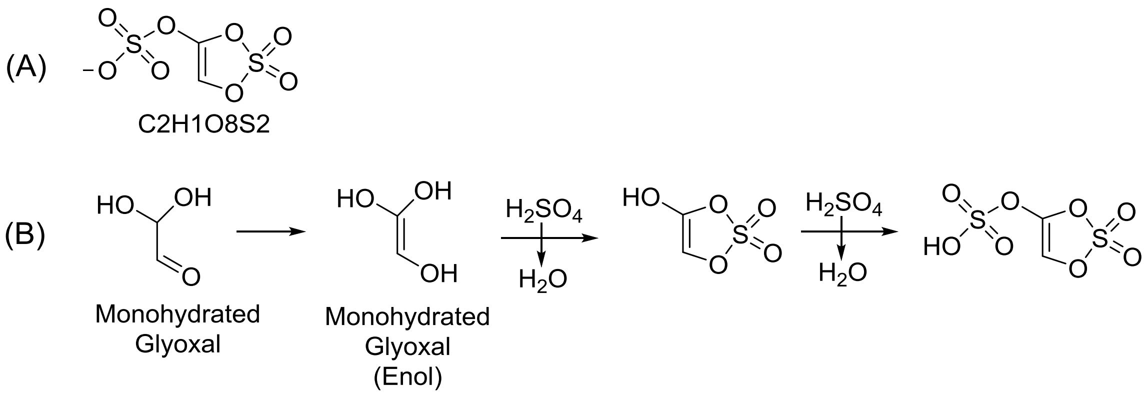
Aerosols (Conditions)	m/z^-	Elemental Composition	Compound	Error (ppm)
AS (Solution)	96.9596	H1O4S1	Sulfuric Acid	-5.2
	194.9268	H3O8S2	Sulfuric Acid Dimer	-3.5
	216.9095	C2H1O8S2	Organosulfate	-10.8
AS (Dry)	96.9608	H1O4S1	Sulfuric Acid	7.2
	216.9142	C2H1O8S2	Organosulfate	10.9
	275.1671	C13H23O6	Organic Acid Oligomer	62.1
	311.1689	C13H27O8	Organic Acid Oligomer	-7.2
	339.1974	C15H31O8	Organic Acid Oligomer	-14.9
	397.0972	C14H21O13	Organic Acid Oligomer	-3.9
AS (Humid)	61.9862	N1O3	Nitric Acid	-35.0
	96.9603	H1O4S1	Sulfuric Acid	2.0
	146.9671 (z = 2)	C6H2N2O12	Organonitrate	-94.1
	181.9377	C2N1O7S1	Nitrooxy-Organosulfate	-13.2
	197.9200	C2N1O8S1	Nitrooxy-Organosulfate	-75.8
	209.9507	C3N1O8S1	Nitrooxy-Organosulfate	14.8
	225.9276	C4H1N1O8Cl1	Organonitrate	-52.7
	243.9025	C3O9S2	Organosulfate	14.7
	288.9074	C4H1O13S1	Organosulfate	24.0
	373.8744	C6N1O14S2	Nitrooxy-Organosulfate	-5.8
	401.9027	C6N3O16S1	Nitrooxy-Organosulfate	5.5
	486.8823	C10H3N2O17S2	Nitrooxy-Organosulfate	-11.1
SA (Solution)	96.9614	H1O4S1	Sulfuric Acid	13.4
	194.9283	H3O8S2	Sulfuric Acid Dimer	4.2
	216.9104	C2H1O8S2	Organosulfate	-6.6
SA (Dry)	96.9611	H1O4S1	Sulfuric Acid	10.3
	275.1615	C13H23O6	Organic Acid Oligomer	41.7
	293.1608	C13H25O7	Organic Acid Oligomer	0.8
	311.1589	C13H27O8	Organic Acid Oligomer	-39.3
	339.1808	C13H27O9	Organic Acid Oligomer	-43.5
SA (Humid)	61.9908	N1O3	Nitric Acid	39.3
	96.9622	H1O4S1	Sulfuric Acid	21.6
	146.9669 (z = 2)	C6H2N2O12	Organonitrate	-95.5
	209.9499	C10N2O15S1	Nirooxy-Organosulfate	-7.7
	225.9277	C4H1N1O8Cl1	Organonitrate	-52.7
	243.9090	C6O18S4	Organonitrate	41.3
	288.9016	C4H1O11S2	Organosulfate	17.4
	311.1672	C10H23N4O7	Organonitrate	32.1
	339.1943	C12H27N4O7	Organonitrate	17.0
	373.8829	C6N1O14S2	Nitrooxy-organosulfate	16.9
	401.9040	C6N3O16S1	Nitrooxy-organosulfate	8.8
	486.8861	C8H7O18S3	Nitrooxy-organosulfate	12.5



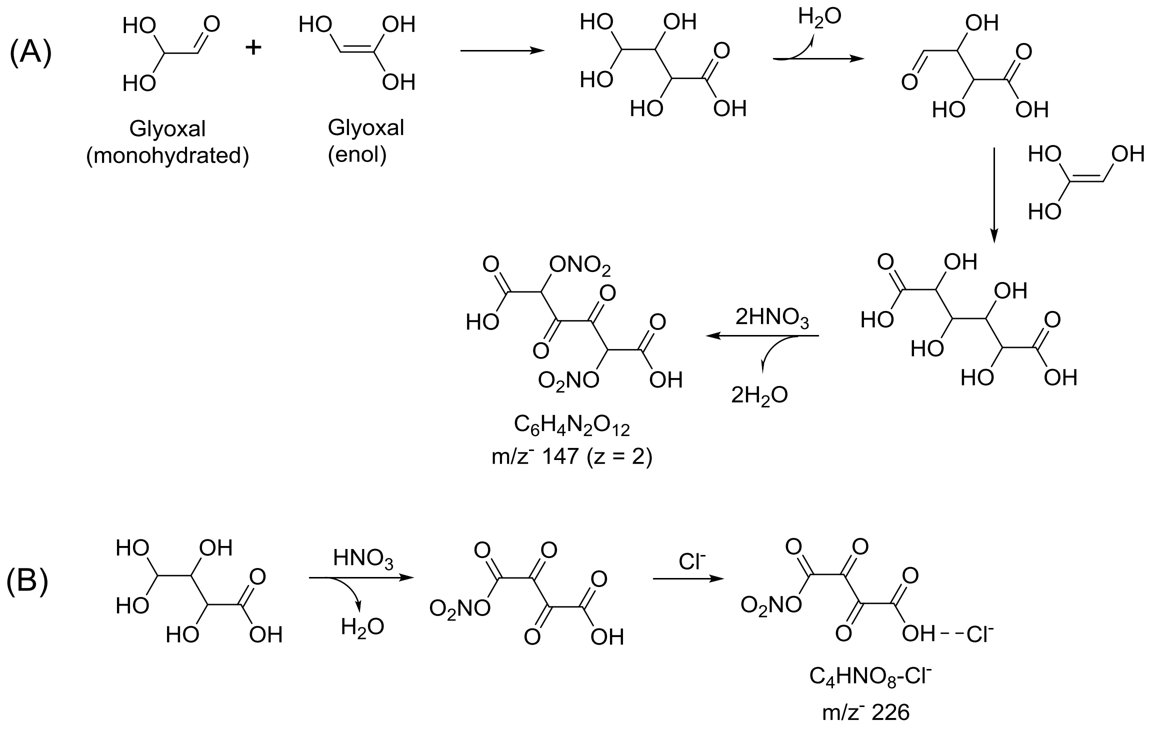
Scheme 1: Nitric acid formation in the UV (A) and in the dark (B)



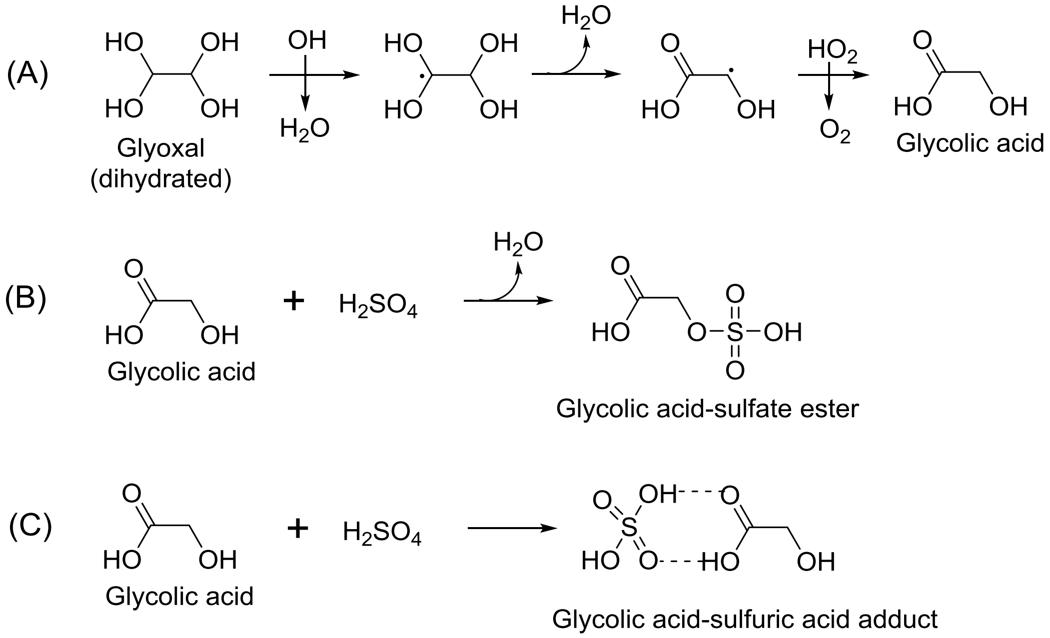
Scheme 2: Mechanisms of gas-phase OH reactions in the presence of NO_x for glyoxylic acid (A) formic acid (B) and glyoxal (C)



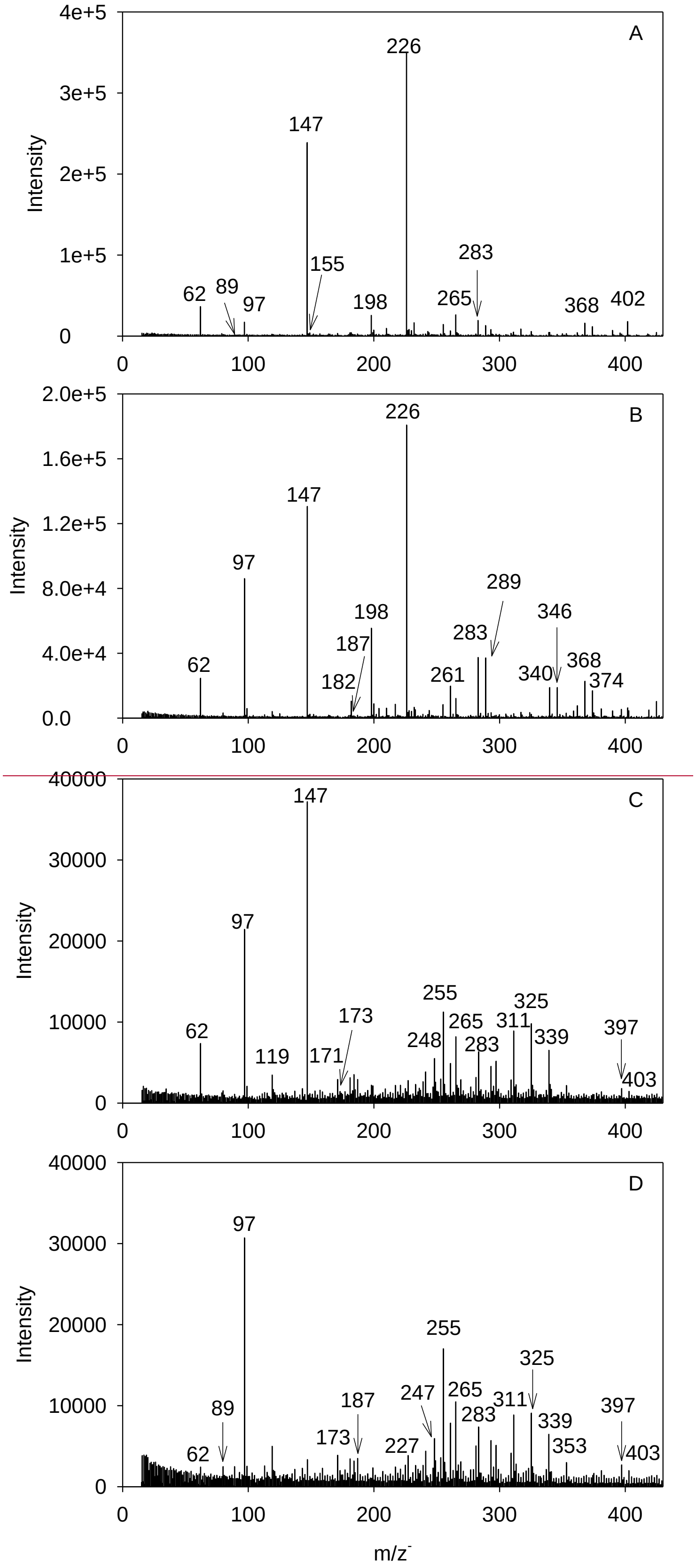
Scheme 3: The structure of C2H1O8S2 (A) and its formation from glyoxal and sulfuric acids (B)



Scheme 4: Proposed formation of two organonitrates, m/z⁻ 147 (A) and m/z⁻ 226 (B)



~~Scheme 4~~Scheme 5: Proposed glycolic acid formation from OH reaction of glyoxal in the aqueous phase (A), glycolic acid-sulfate ester formation from non-radical reactions of glycolic acid with sulfuric acid (B), and glycolic acid-sulfuric acid adduct formation (C)


A
Intensity
4e+5
3e+5
2e+5
1e+5
0
226
147
155
283
62
89
97
198
265
368
402
0
100
200
300
400
B
Intensity
2.0e+5
1.6e+5
1.2e+5
8.0e+4
4.0e+4
0.0
226
147
97
289
198
346
283
187
62
368
340
261
182
374
C
Intensity
40000
30000
20000
10000
147
97
255
325
173
265
311
397
62
248
339
283
119
171
403
D
Intensity
97
255
325
187
247
265
311
397
89
283
339
173
227
353
62
403
m/z-

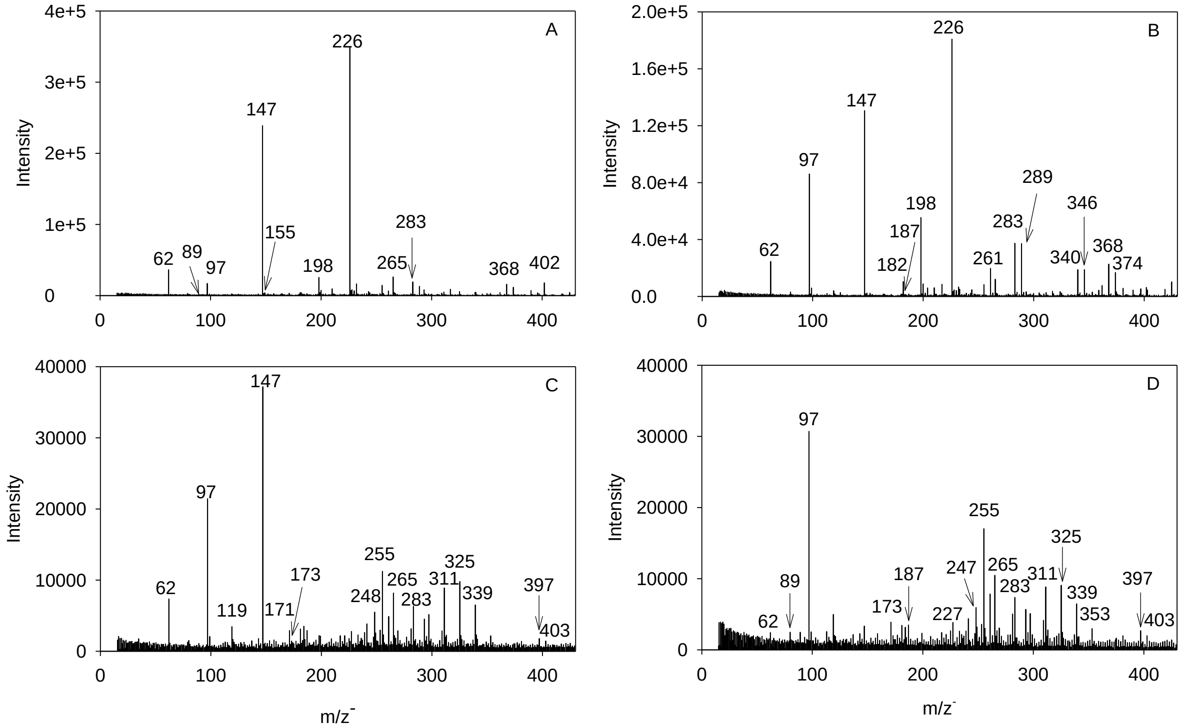


Figure 1: Negative-mode mass spectra for 3 hour-irradiated AS aerosols (A) and SA aerosols (B) in the humid chamber, and AS aerosols (C) and SA aerosols (D) in the dry chamber

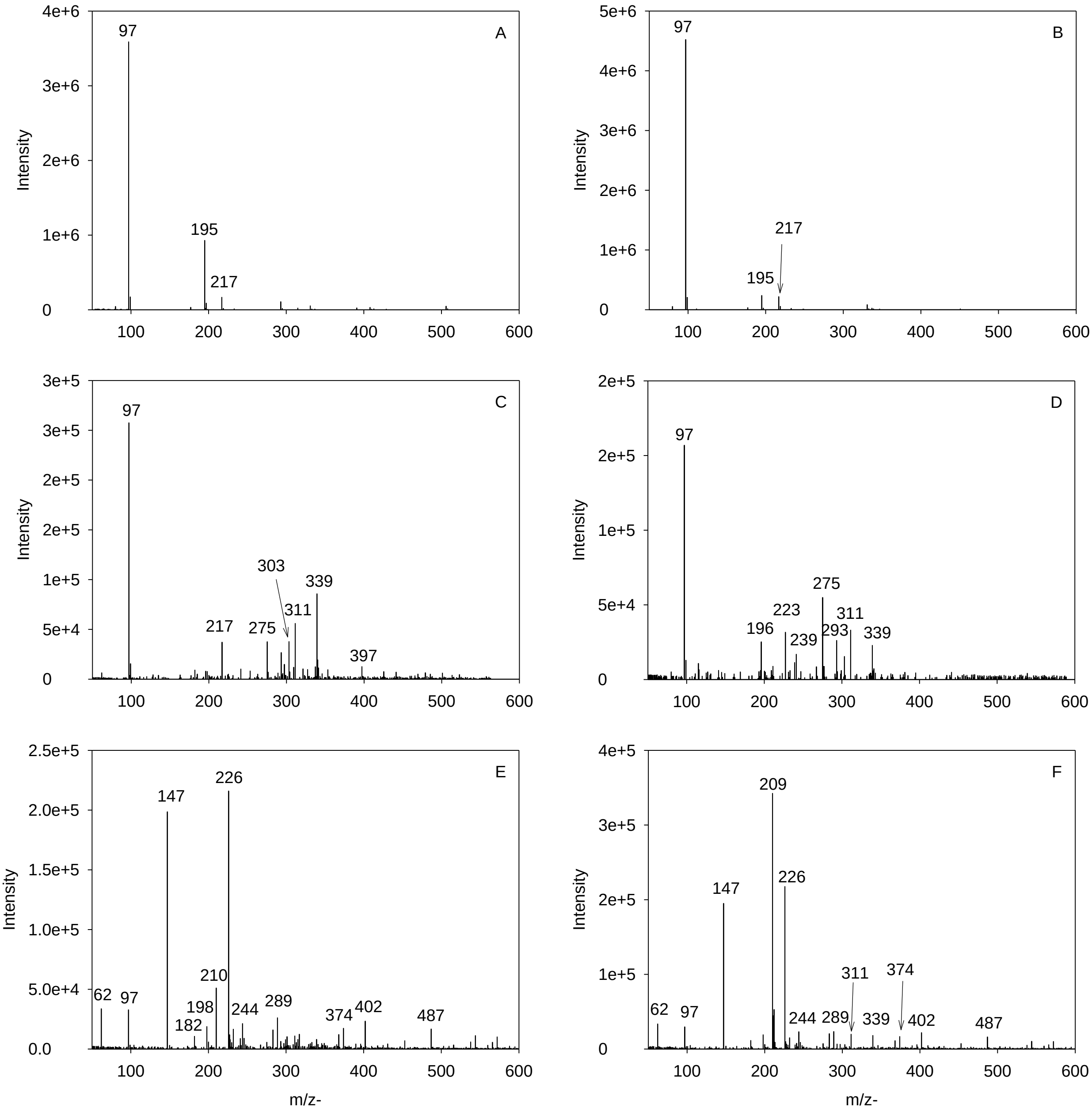
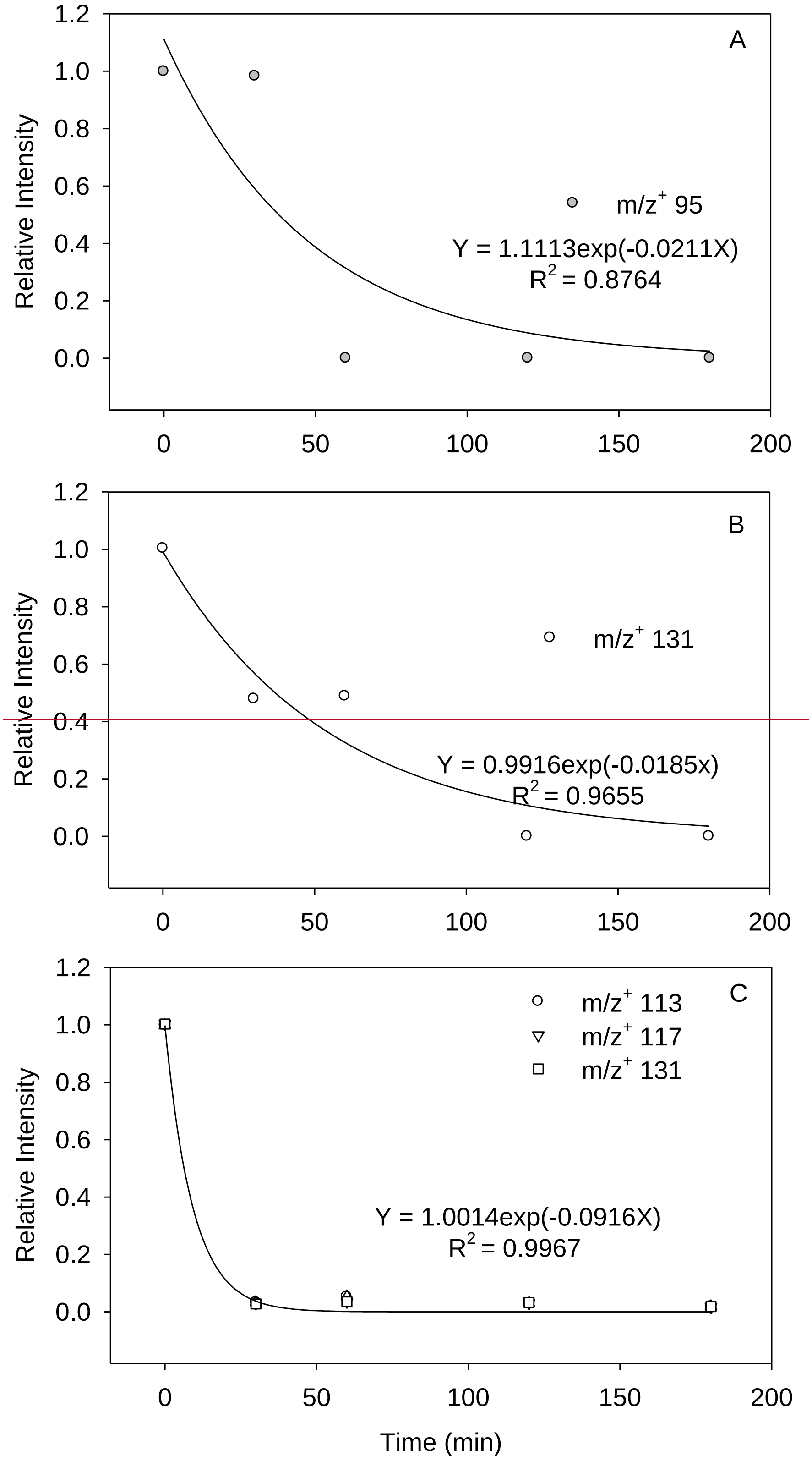


Figure 2: Negative-mode mass spectra for dark reactions of glyoxal-H_2O_2-$(NH_4)_2SO_4$ (A, C and E) and glyoxal-H_2O_2-H_2SO_4 (B, D and F). (A) and (B) are solutions. (C) and (D) are aerosols in the dry chamber, and (E) and (F) are aerosols in the humid chamber at dark reaction time = 0 min


A
m/z+ 95
Y = 1.1113exp(-0.0211X)
R2 = 0.8764
B
m/z+ 131
Y = 0.9916exp(-0.0185x)
R2 = 0.9655
C
m/z+ 113
m/z+ 117
m/z+ 131
Y = 1.0014exp(-0.0916X)
R2 = 0.9967
Relative Intensity
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
Time (min)

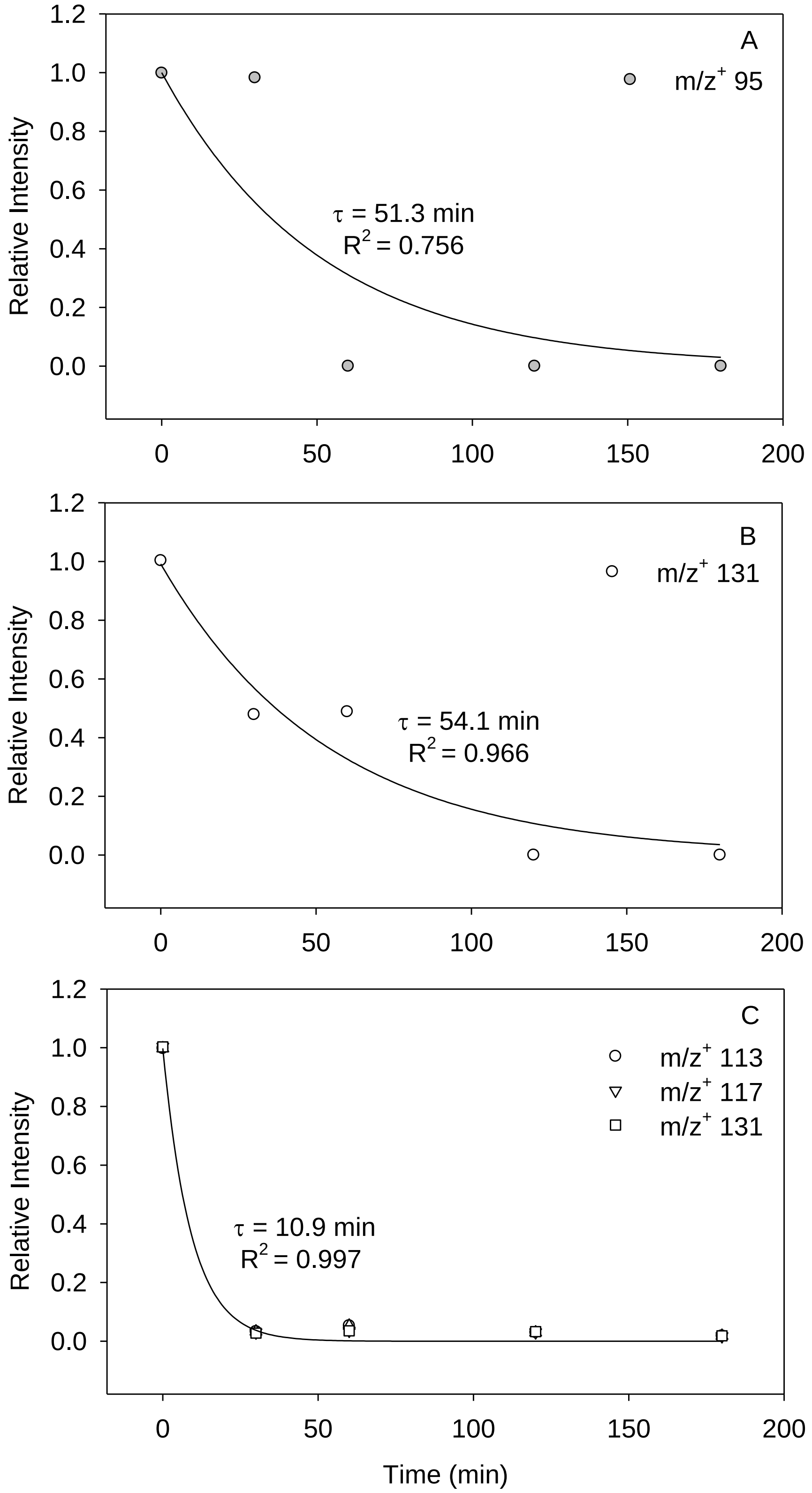
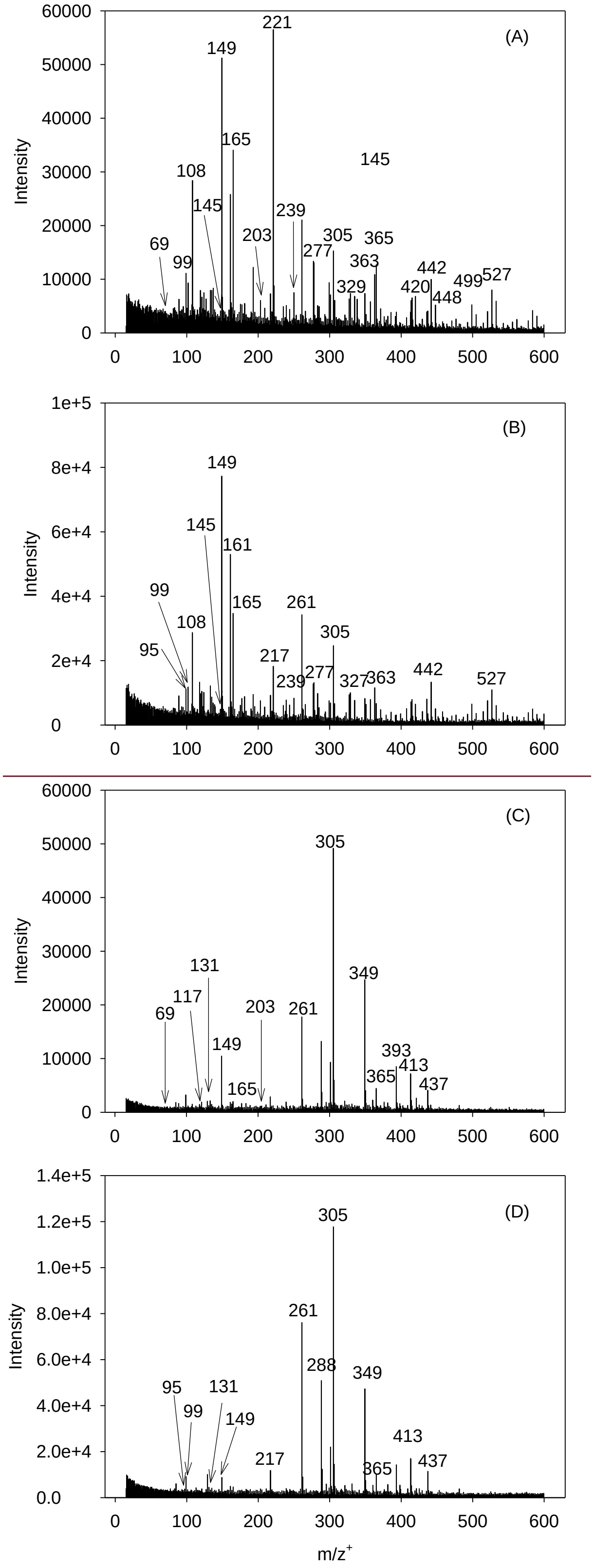


Figure 3: The decay of glyoxal in SA aerosols in the humid (A) and in the dry chamber (B), and in AS aerosols in the dry chamber (C) (τ = lifetime)

5


(A)
Intensity
60000
50000
40000
30000
20000
10000
0
221
149
165
108
145
239
203
305
365
69
277
99
363
442
329
420
499
527
448
145
0
100
200
300
400
500
600
(B)
Intensity
1e+5
8e+4
6e+4
4e+4
2e+4
0
149
145
161
99
165
261
108
305
95
217
277
239
327
363
442
527
0
100
200
300
400
500
600
(C)
Intensity
60000
50000
40000
30000
20000
10000
0
305
131
349
117
69
203
261
149
393
365
413
165
437
0
100
200
300
400
500
600
(D)
Intensity
1.4e+5
1.2e+5
1.0e+5
8.0e+4
6.0e+4
4.0e+4
2.0e+4
0.0
305
261
288
349
95
131
99
149
413
217
365
437
0
100
200
300
400
500
600
m/z+

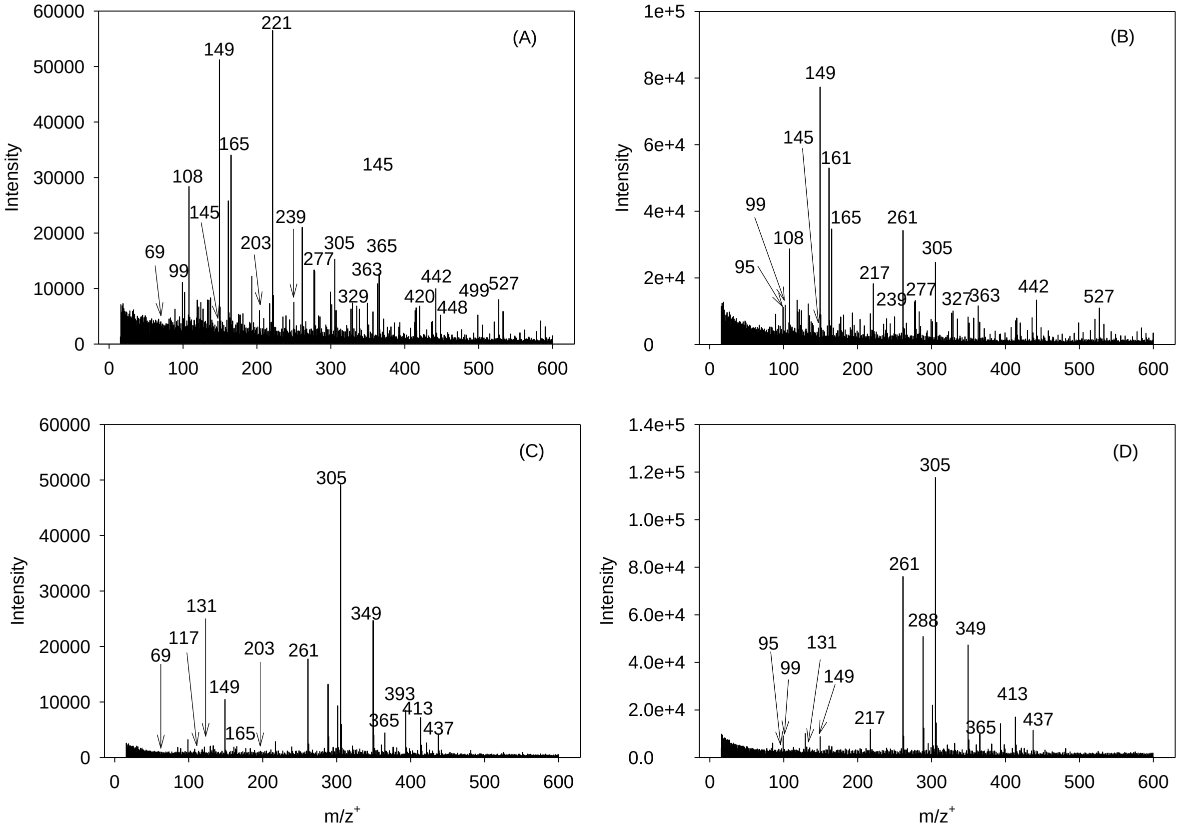


Figure 4: Positive-mode mass spectra for 3 hour-irradiated AS aerosols (A) and SA aerosols (B) in the humid chamber, and AS aerosols (C) and SA aerosols (D) in the dry chamber

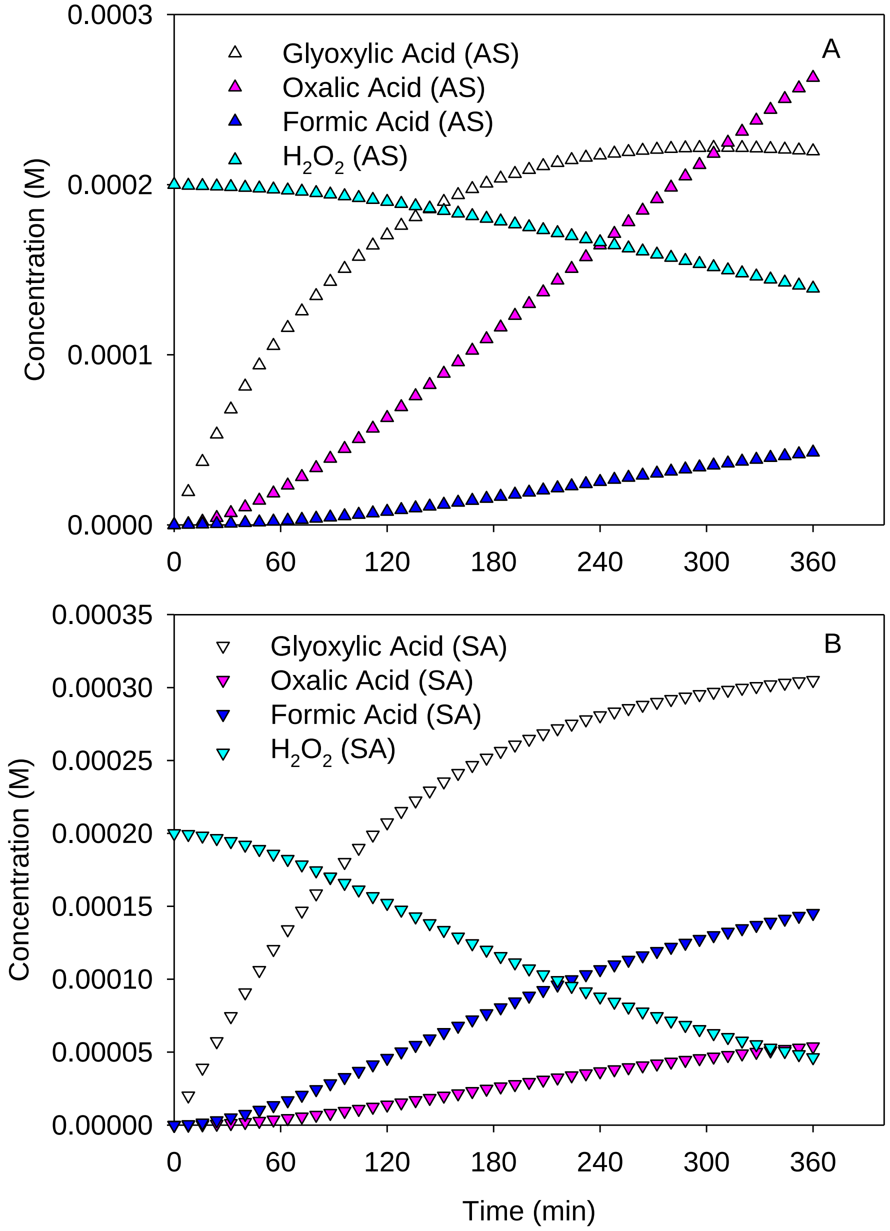


Figure 5: Simulated concentrations in ALW of AS aerosols (A) and SA aerosols (B) during 3 hour irradiation in the humid chamber

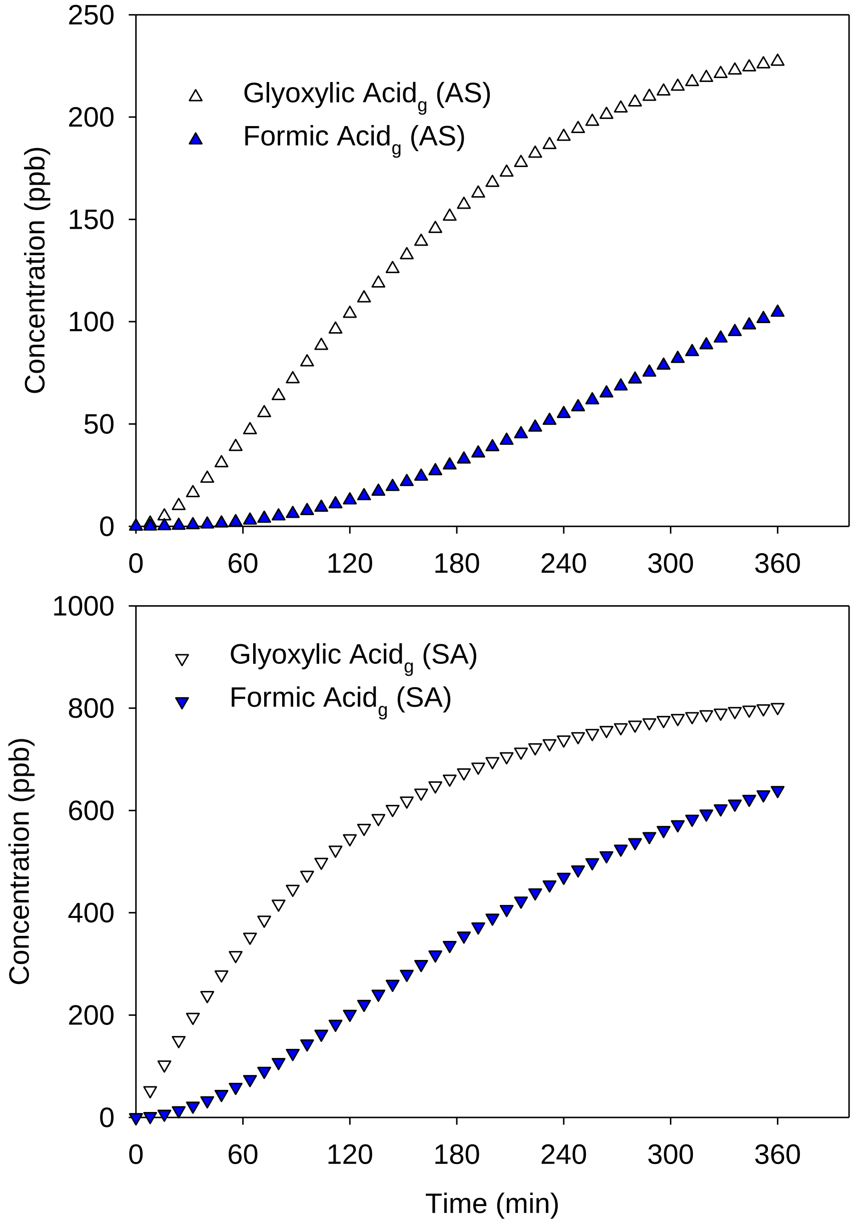


Figure 6: Gas-phase simulations of glyoxylic acid and formic acid evaporated from AS aerosols (A) and SA aerosols (B) during 3 hour irradiation in the humid chamber

Supplementary Material

Photochemical Organonitrate Formation in Wet Aerosol

Yong Bin Lim, Hwajin Kim, Jin Young Kim and Barbara J. Turpin

Table S1. Experimental Conditions

No	**Atomized Solution Date**	**UV or Dark**	**RH_i (%)**	**RH_f (%)**	**T_i (K)**	**T_f (K)**	**$[NO/NO_x]_i$ (ppb)**	**$[NO/NO_x]_f$ (ppb)**	**$[O_3]_i$ (ppb)**	**$[O_3]_f$ (ppb)**	**ALW_i (%)**	**ALW_f (%)**
											pH	**pH**
1	AS + H_2O_2 + Gly 3/5/2015	UV	3.0	3.0	293	303	24.0/28.0	5.5/25.5	0	24.9	1.2	1.2
											6.1	6.0
2	AS + H_2O_2 + Gly 3/31/2015	UV	3.0	3.0	294	309	8.2/9.4	4.4/15.6	6.9	7.7	1.2	1.2
											6.1	5.9
3	AS + H_2O_2 + Gly 11/26/2015	UV	3.0	3.0	292	306	2.4/2.9	0/1.1	9.6	34.0	1.2	1.2
											6.1	5.9
4	AS + H_2O_2 + Gly 3/23/2015	UV	70.8	38.9	294	304	5.1/6.4	0.4/4.6	7.4	11.3	45.8	19.4
											4.5	4.8
5	AS + H_2O_2 + Gly 4/1/2015	UV	82.2	42.0	295	310	7.2/10.5	2.7/7.4	6.9	15.4	59.2	2.2
											4.4	4.6
6	AS + Gly 5/27/2015	UV*	69.4	34.8	298	310	54.7/55.5	23.3/38.7	13.0	18.0	44.3	1.7
											4.5	4.7
7	AS + H_2O_2 3/30/2015	UV	83.7	39.1	295	310	8.5/11.7	3.2/7.1	7.6	12.1	63.3	N/A
											4.4	N/A
8	AS + H_2O_2 + Gly 4/27/2015	Dark	3.0	3.0	297	297	17.2/19.1	17.2/19.1	6.4	5.9	1.2	1.2
											6.1	6.1
9	AS + H_2O_2 + Gly 4/28/2015	Dark	77.7	56.2	298	298	38.9/39.9	27.8/33.2	6.2	7.8	53.7	32.0
											4.4	4.6
10	AS + H_2O_2 + Gly 5/7/2015	Dark	71.7	64.9	298	298	15.8/16.9	15.6/17.1	5.6	6.3	46.7	39.8
											4.5	4.5
11	SA + H_2O_2 + Gly 3/9/2015	UV	7.1	3.0	293	304	80.9/83.5	41.6/77.7	0	7.7	32.4	26.5
											-1.0	-1.1
12	SA + H_2O_2 + Gly 3/25/2015	UV	82.0	44.8	294	307	21.6/23.9	15.2/19.7	6.2	8.5	74.2	53.1
											-0.6	-0.9
13	SA + H_2O_2 + Gly 5/6/2015	Dark	5	5	298	298	15.8/16.9	15.6/17.1	5.6	6.3	26.9	26.9
											-0.7	-0.7
14	SA + H_2O_2 + Gly 4/29/2015	Dark	77.6	77.1	298	298	15.8/18.0	15.7/17.5	6.1	6.3	70.9	70.6
											-1.1	-1.1

Note, AS = ammonium sulfate, SA = sulfuric acid, Gly = glyoxal, i = initial, f = final, ALW = fraction of aerosol liquid water in a wet aerosol, UV* = 1-hour irradiation, and N/A = no aqueous phase

Table S2. Elemental compositions of organic-inorganic compounds analyzed by UPLC-HR-Q-TOF-MS in the positive mode

Aerosols (Conditions)	m/z^+	Elemental Composition	Compound	Error (ppm)
AS (Solution)	69.0509	C3H5N2	Imidazole*	89.4
	116.9984	C2H6O4Na1	Glyoxal	-149.0
	133.0271	C2H2N6Na1	Imidazole	28.4
	248.0215	C4H3N9O3Na1	Imine	-14.5
	363.0174	C4H12N4O14Na1	Imine	-18.8
AS (Dry)	89.0307 (z = 2)	C10H10O3	Organic Compound	-2.8
	133.0920 (z = 2)	C16H26O3	Organic Compound	-11.6
	161.0986	C11H13O1	Organic Compound	15.6
	203.0880	C9H15O5	Organic Compound	-16.7
	283.1749	C11H24N4O3	Organic Compound	3.0
	365.1519	C12H26N2O9Na1	Imine	-3.2
	381.2726	C19H38N2O4Na1	Imine	0.6
AS (Humid)	107.9721 (z = 2)	C4H1O9Na1	Unidentified Peak	-30.2
	133.0865	C6H13O3	Organic Compound	4.4
	161.1082	C8H14N2Na1	Imidazole	9.6
	203.1023	C7H12N6Na1	Imidazole	3.6
	261.1322	C7H14N10Na1	Imidazole	5.1
	283.1749	C7H20N10O1	Imine	12.4
	363.0483	C15H4N10O1Na1	Imine	5.8
	381.2626	C20H38O5Na1	Organic Compound	3.8
	399.2664	C12H32N10Na1	Imidazole	-9.9
	441.9170	C13N1O17	Imine	2.1
	526.9000	C12N4O19	Imine	-9.3
SA (Solution)	93.0210	C2H5O4	Organic Compound	29.7
	117.0562	C5H9O3	Organic Compound	13.5
	149.0307	C6H6O3	Organic Compound	65.7
	172.9890	C4H6O6Na1	Organic Compound	-96.3
	252.9581	C7H2O9Na1	Organic Compound	-4.0
	277.1795	C15H26O3Na1	Organic Compound	7.5
	303.2102	C16H31O5	Organic Compound	-21.1
SA (Dry)	135.0011	C5H4O3	Organic Compound	-30.9
	261.1178	C15H17O4	Organic Compound	21.7
	305.1588	C14H25O7	Organic Compound	-2.2
	331.1749	C16H27O7	Organic Compound	-0.7
	349.1742	C14H30O8	Organic Compound	-26.0
	393.2035	C16H34O9	Organic Compound	-15.3
SA (Humid)	89.0297 (z = 2)	C10H10O3	Organic Compound	-14.0
	107.9653 (z = 2)	C4H1O9Na1	Organic Peroxide	-93.2
	133.0918 (z = 2)	C16H26O3	Organic Compound	-13.1
	161.0954	C11H13O1	Organic Compound	-4.3
	203.1078	C9H15O5	Organic Compound	-16.7
	239.1504	C10H23O6	Organic Compound	6.2
	261.1323	C10H22O6Na1	Organic Compound	5.5
	283.1720	C12H27O7	Organic Compound	-11.1
	305.1557	C12H26O7Na1	Organic Compound	-4.5
	327.1983	C14H31O8	Organic Compound	-9.3
	435.8400	C3H2N1O18S3	Organonitrogen-sulfate	-6.5

*Kampf et al., 2012

Table S3. Added reactions to the full kinetic model (Lim and Turpin, 2015 Supplementary Material)

	Reactions	**Rate constants (M^{1-n} s^{-1})**	**Ref**
1	$GLY_g \leftrightarrow GLY$	K_{eq} = 2e7 k_r = 1e5	(1, 2)
2	$GLYAC_g \leftrightarrow GLYAC$	K_{eq} = 9.12e3 k_r = 1e5	(2, 3)
3	$OXLAC_g \leftrightarrow OXLAC$	K_{eq} = 3.26e6 k_r = 1e5	(2, 3)
4	$HCO_2H_g \leftrightarrow HCO_2H$	K_{eq} = 3.55e3 k_r = 4.6e5	(2, 3)
5	$HCHO_g \leftrightarrow HCHO$	K_{eq} = 3.3e3 k_r = 4.6e5	(2, 3)
6	$GCOLAC_g \leftrightarrow GCOLAC$	K_{eq} = 1.18e4 k_r = 1e5	(2, 3)
7	$H_2O_{2g} \leftrightarrow H_2O_2$	K_{eq} = 1e5 k_r = 1e6	(2, 3)
	Gas-Phase Reactions	**Rate constants ($[molecules/cm^3]^{1-n}$ s^{-1})**	**Ref**
8	$GLY_g + OH_g \rightarrow$	9.7e-12	(4)
9	$HCO_2H_g + OH_g \rightarrow$	4.5e-13	(4)
10	$HCHO_g + OH_g \rightarrow$	8.5e-12	(4)
11	$GLYAC_g + OH_g \rightarrow$	6.2e-11	(5)
12	$OXLAC_g + OH_g \rightarrow$	2e-13	(5)
13	$GCOLAC_g + OH_g \rightarrow$	2.96e-13	(5)
14	$H_2O_2 \rightarrow 2OH$	3.77e-6	(3)

GLY = glyoxal; GLYAC = glyoxylic acid, OXLAC = oxalic acid; HCO_2H = formic acid; GCOLAC = glycolic acid; HCHO = formaldehyde; H_2O_2 = hydrogen peroxide

Reference

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2. Warneck P (1999) The relative importance of various pathways for the oxidation of sulfur dioxide and nitrogen dioxide in sunlit continental fair weather clouds. *PCCP* 1(24):5471-5483.
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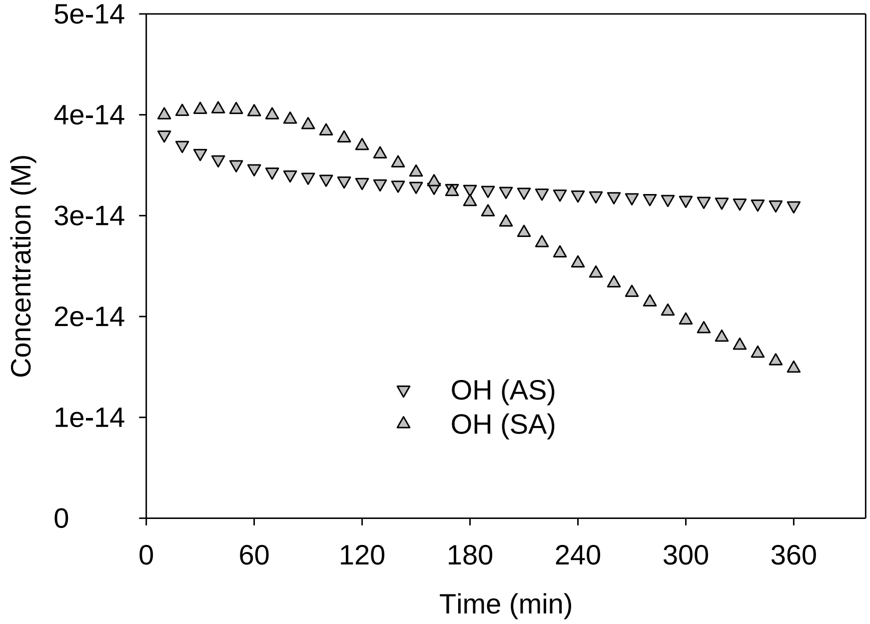

Fig. S1. The simulated concentrations of OH in ammonium sulfate aerosols (AS) and sulfuric acid aerosols (SA)

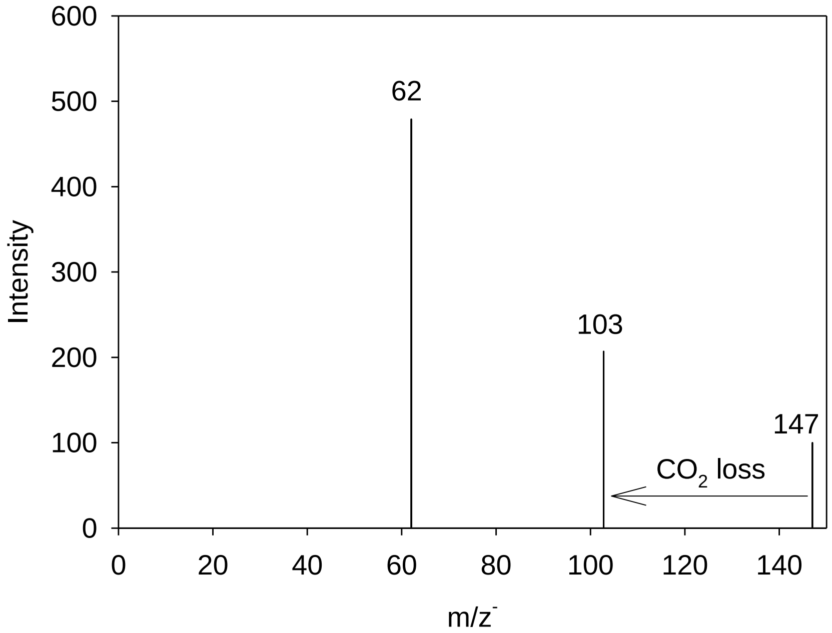

Figure S2. LC-MS/MS analysis for m/z$^-$ 147 from smog chamber AS aerosols

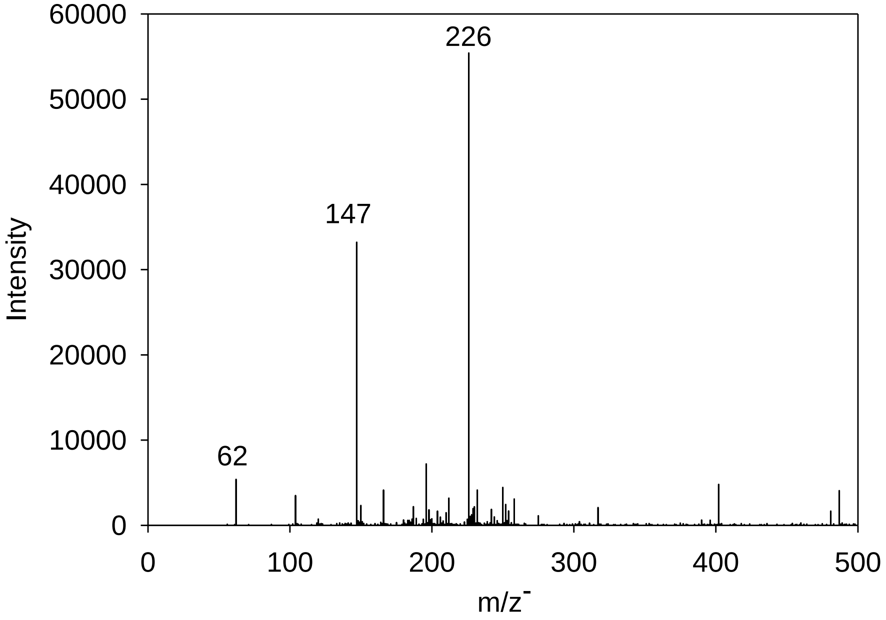

Figure S3. The mass spectrum for the mixture solution of glyoxal (7.6 mM) and nitric acid (15 mM) in the negative mode

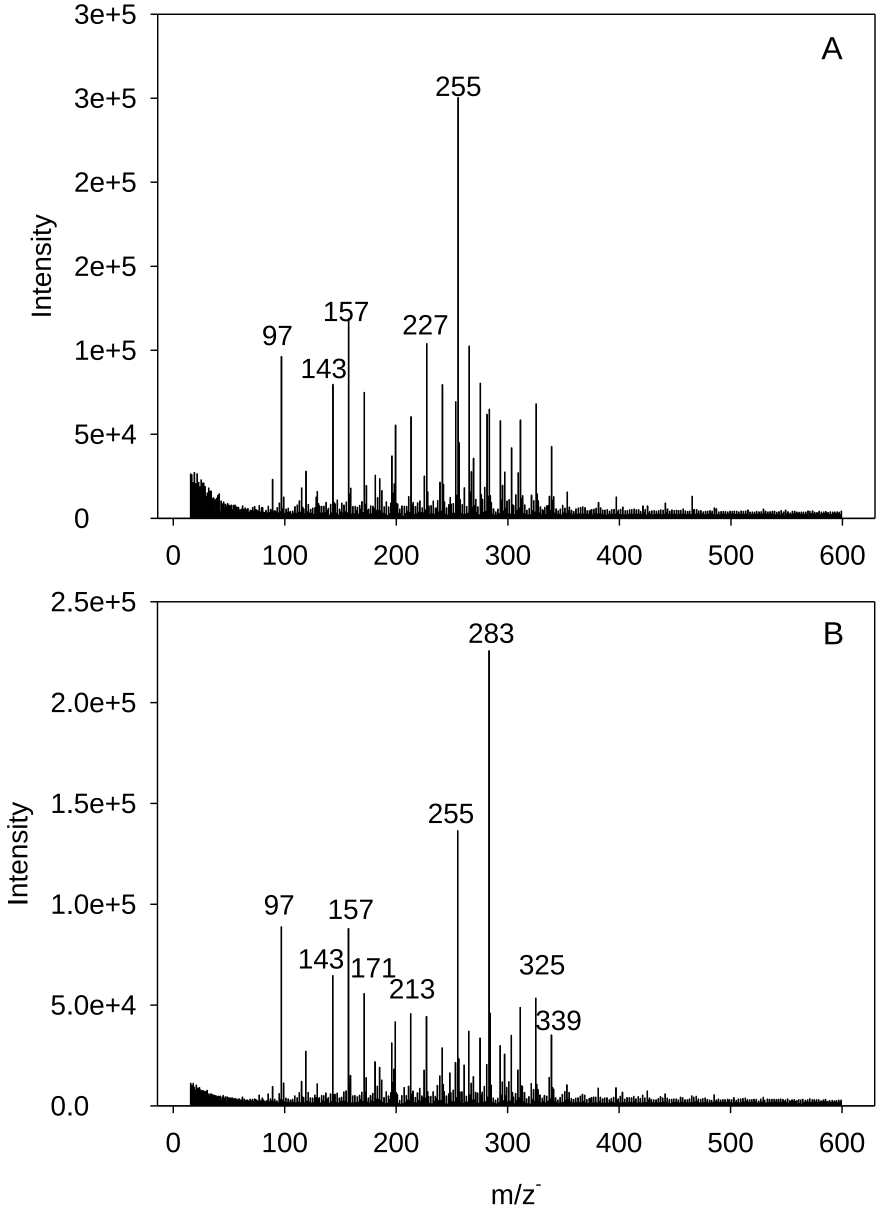

Figure S4. Negative-mode mass spectra for 3 hour dark reactions of glyoxal-H_2O_2-$(NH_4)_2SO_4$ aerosols (A) and glyoxal-H_2O_2-H_2SO_4 aerosols (B) under humid conditions (> 70 % RH)

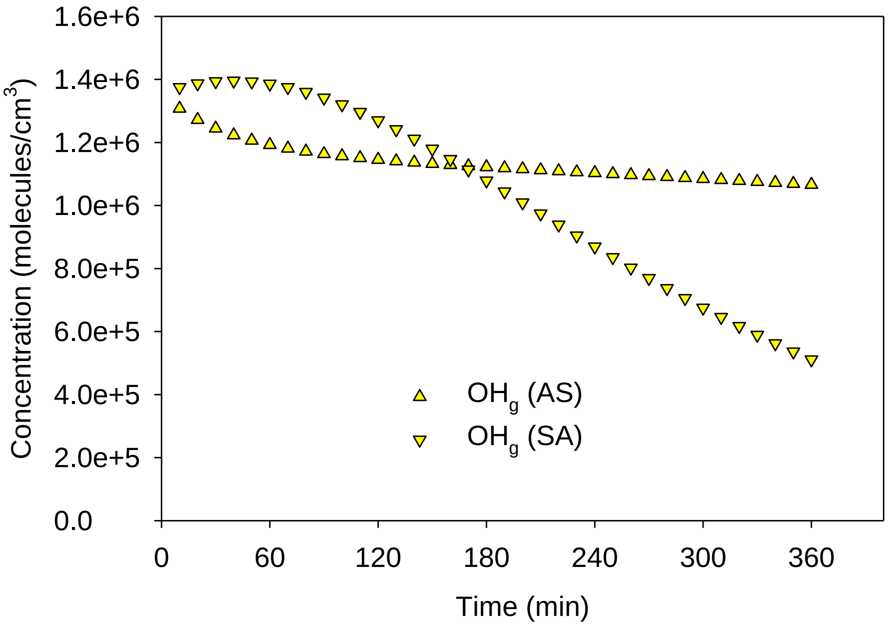

Fig. S5. The simulated gas-phase OH concentrations during photochemical reactions of AS aerosols (AS) and SA aerosols (SA)

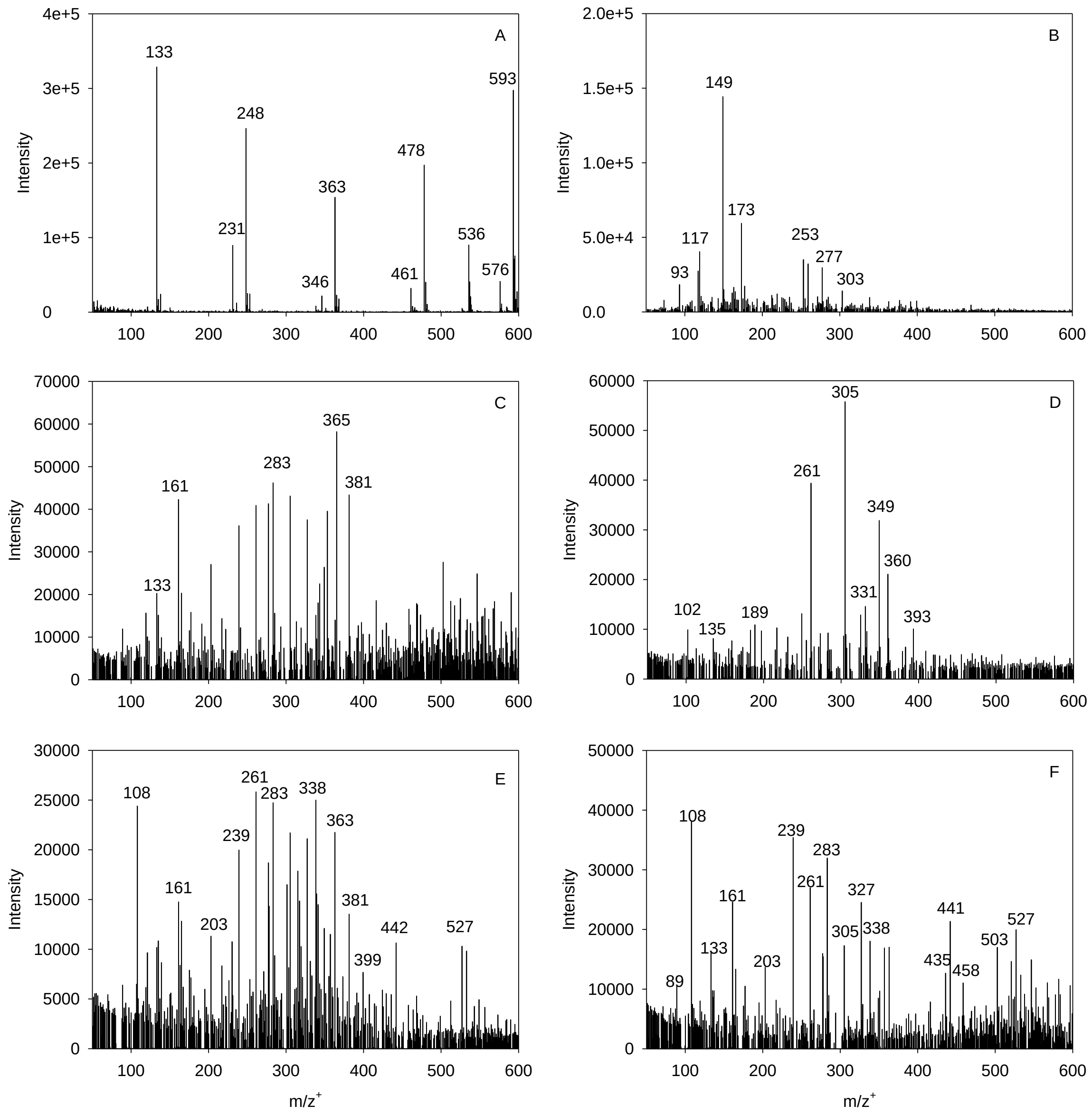

Fig. S6. Positive-mode mass spectra of dark reactions of glyoxal-H_2O_2-$(NH_4)_2SO_4$ (A, C and E) and glyoxal-H_2O_2-H_2SO_4 (B, D and F). A and B are solutions. C and D are dry aerosols and E and F are humid aerosols at time = 0 min

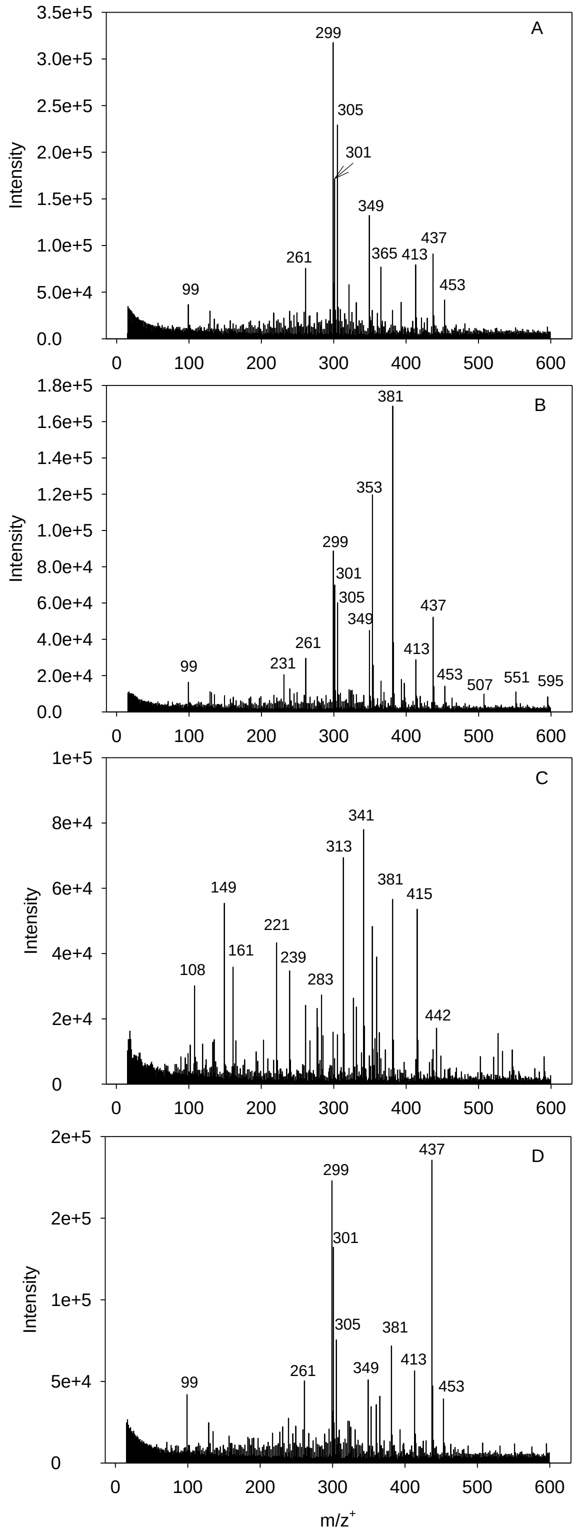

Fig. S7. Negative-mode mass spectra for 3 dark-reacted AS aerosols (A) and SA aerosols (B) in the humid chamber, and AS aerosols (C) and SA aerosols (D) in the dry chamber