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Glyoxal uptake on ammonium sulphate seed aerosol

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Glyoxal uptake on ammonium sulphate seed aerosol: reaction products and reversibility of uptake under dark and irradiated conditions

M. M. Galloway¹, P. S. Chhabra², A. W. H. Chan², J. D. Surratt³, R. C. Flagan^{2,4}, J. H. Seinfeld^{2,4}, and F. N. Keutsch¹

¹Dept. of Chemistry, University of Wisconsin-Madison, Madison, WI, USA

²Dept. of Chemical Engineering, California Institute of Technology, Pasadena, CA, USA

³Dept. of Chemistry, California Institute of Technology, Pasadena, CA, USA

⁴Dept. of Environmental Science and Engineering California Institute of Technology, Pasadena, CA, USA

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Correspondence to: F. N. Keutsch (keutsch@wisc.edu)

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Abstract

Chamber studies of glyoxal uptake onto neutral ammonium sulphate aerosol were performed under dark and irradiated conditions to gain further insight into processes controlling glyoxal uptake onto ambient aerosol. Organic fragments from glyoxal dimers and trimers were observed within the aerosol under dark and irradiated conditions; glyoxal oligomer formation and overall organic growth were found to be reversible under dark conditions. Analysis of high-resolution time-of-flight aerosol mass spectra provides evidence for irreversible formation of carbon-nitrogen (C-N) compounds in the aerosol. These compounds are likely to be imidazoles formed by reaction of glyoxal with the ammonium sulphate seed. To the authors' knowledge, this is the first time C-N compounds resulting from condensed phase reactions with ammonium sulphate seed have been detected in aerosol. Organosulphates were not detected under dark conditions. However, active oxidative photochemistry, similar to that found in cloud processing, was found to occur within aerosol during irradiated experiments. Organosulphates, carboxylic acids, and organic esters were identified within the aerosol. Our study suggests that both C-N compound formation and photochemical processes should be considered in models of secondary organic aerosol formation via glyoxal.

1 Introduction

Organic aerosol has been detected in substantial concentrations in urban and rural atmospheres (Zhang et al., 2007). The large contribution of organic aerosol to particulate matter has been attributed to secondary organic aerosol (SOA), though current models considerably underestimate SOA formation (de Gouw et al., 2005; Heald et al., 2005; Volkamer et al., 2006). In order to understand the possible health and climate effects of particulate matter, it is critical that the physical and chemical models of SOA formation be improved. Glyoxal (GL) is produced by a wide variety of biogenic and anthropogenic volatile organic compounds (VOCs), many of which are SOA precursors, and is consid-

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ered a tracer for SOA formation. One current model estimates global GL production of 45 Tg/yr, with roughly half due to isoprene photooxidation (Fu et al., 2008), and another one estimates 56 Tg/yr of global GL production with 70% being produced from biogenic hydrocarbon oxidation (Myriokefalitakis et al., 2008). In addition to acting as a tracer for SOA formation, GL has been suggested as a direct contributor to SOA (Sorooshian et al., 2006; Volkamer et al., 2007; Carlton et al., 2007; Ervens et al., 2008; Fu et al., 2008). A study comparing observed and modelled GL has suggested that GL could contribute at least 15% of the SOA in Mexico City (Volkamer et al., 2007), while a study using the GEOS-Chem model found the modelled GL contribution to SOA to be 2.6 Tg C/year out of a total of 29 Tg C/year (Fu et al., 2008).

Despite existing research aimed at elucidating SOA formation by GL, quantification of SOA yields as a function of conditions such as gas-phase GL mixing ratio, seed aerosol composition and pH, relative humidity, and irradiation are required in order to allow for the application of laboratory findings to ambient conditions. On a more fundamental level, it is desirable to achieve a detailed understanding of the processes contributing to SOA formation from GL as a function of the above conditions. GL is also promising as an instructive model system for compounds that can yield SOA via purely physical absorption processes and via complex condensed phase processes, such as oligomerization, organosulphate formation, condensation, and photochemical reactions.

The standard models that have been employed to explain organic gas-particle partitioning have generally assumed physical absorption processes (Pankow, 1994a,b; Odum et al., 1996). On this basis, GL, the smallest dicarbonyl, should have virtually no SOA yield because of its high vapour pressure (18 Torr at 20°C). However, GL partitions strongly to aqueous condensed-phase systems, which is reflected in a surprisingly high Henry's law constant, $K_{H,aq}^* = 3.6 \times 10^5 \text{ M/atm}$ for seawater (Zhou and Mopper, 1990). The Henry's law constant of GL is higher than that of atmospherically relevant monocarboxylic acids, including glyoxylic acid, the acid that results from oxidation of one of the aldehyde groups in GL. The high Henry's law constant has been explained

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by the hydration of the aldehyde groups, producing an effectively lower vapour pressure species in aqueous solution. In addition to the physical absorption processes, particle-phase chemical reactions have been identified as a possible driving force for uptake. Carbonyl-containing species are known to participate in aldol, acetal, and esterification reactions, which form low volatility compounds that add to SOA mass. Field and laboratory studies have also yielded evidence for the formation of oligomers within SOA (Gross et al., 2006; Reinhardt et al., 2007; Denkenberger et al., 2007) and it is well known that GL will polymerize in the presence of water (Whipple, 1970; Loeffler et al., 2006).

These properties of GL, together with its production via oxidation of many VOCs, have inspired chamber investigations into GL partitioning onto a variety of seed particles (Jang et al., 2002; Liggio et al., 2005a,b; Kroll et al., 2005; Corrigan et al., 2008). Liggio et al. (2005b) have demonstrated reactive uptake of GL onto several different types of seed aerosol using an Aerodyne aerosol mass spectrometer (AMS). The same study suggested that GL uptake onto ammonium sulphate (AS) aerosol is irreversible and enhanced with acidified seed. However, Kroll et al. (2005) observed negligible acid effect and reversible uptake that is possibly controlled by ionic strength, and concluded that GL uptake obeys a modified Henry's Law at equilibrium. Even so, there has been no definitive explanation of the large difference between the Henry's law constant determined from that study for AS seed aerosol, $K_{H,AS}^* = 2.7 \times 10^7$ M/atm (Kroll et al., 2005), and $K_{H,aq}^*$. Both Liggio et al. (2005b) and Kroll et al. (2005) observed hydration and oligomerization and, in addition, Liggio et al. (2005b) proposed irreversible formation of the organosulphate of GL (GL sulphate) to explain certain peaks in the AMS mass spectra. Volkamer et al. (2008) demonstrated that acetylene is an SOA precursor and estimated that almost all particle phase organic growth was due to its oxidation product, GL. SOA yields were shown to correlate with the liquid water content of the AS seed, which implies that the Henry's law constant is decreasing with increasing ionic strength over this AS concentration range. However, as the authors state, a Henry's law approach is not necessarily appropriate for photochemically driven uptake. For AS seed

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aerosol, organic growth under irradiated conditions was found to be 40% larger than in the work by Kroll et al. (2005), which was conducted under dark conditions. The study by Volkamer et al. (2008) did not observe any GL uptake on AS seed aerosol under dark conditions.

In light of these investigations, it is clear that particle-phase chemistry plays a crucial role in the gas/particle partitioning of GL, though the processes controlling uptake are still not clear. In this study, we examine the uptake processes onto wet AS seed aerosol using a variety of instrumentation in dark conditions and in the presence of light. Figure 1 shows the major processes that could be contributing to GL uptake. The processes that have been identified by previous studies are:

1. GL-hydrate formation is fast and reversible (Schweitzer et al., 1998). Hydration equilibria up to $\text{GL}\cdot 2\text{H}_2\text{O}$, the dominant form of GL in dilute aqueous solutions, are included in $K_{\text{H, aq}}^*$ (Zhou and Mopper, 1990). The GL concentrations in the study presented here are such that the dominant condensed phase forms of GL in aqueous solution are GL monomer and dimer. Some studies have demonstrated correlation of organic growth with water content of aerosol (Volkamer et al., 2008), whereas others have shown growth at extremely low water content and noted that $\text{GL}\cdot n\text{H}_2\text{O}$ concentrations appear to be independent of gas-phase GL concentrations (Corrigan et al., 2008).
2. Glyoxal oligomers (GL_n) have been detected by time-of-flight and quadrupole AMS studies of aerosol growth from GL uptake in chamber experiments (Kroll et al., 2005; Liggio et al., 2005b); no definitive evidence for GL_n in field samples has been found, likely due to analytical challenges. (GL_n) formation is reversible and slow (many minutes to hour timescales) in aqueous solutions (Whipple, 1970; Fratzke and Reilly, 1986), and there are indications from a previous study that it is reversible in AS aerosol (Kroll et al., 2005).
3. GL sulphates are of much interest as they have been detected via filter sampling methods in field samples (Surratt et al., 2007, 2008; Gómez-González et al.,

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2008) and in chamber studies of isoprene oxidation under intermediate- to high- NO_x conditions (Surratt et al., 2008). However, their contribution to $K_{\text{H,AS}}^*$ is unclear as are the formation conditions for GL sulphates in general.

In this study we aim to address the relative contribution of individual processes to overall GL uptake as well as which of these processes are effectively reversible, meaning reversible over aerosol lifetimes. These questions are important for evaluating applicability of laboratory studies to ambient conditions and net SOA yields from GL. If most GL uptake is effectively reversible, the organic aerosol will revolatilize at lower GL gas-phase concentrations upon transport away from GL sources or at night. Net SOA yields from a specific process will be higher if that process is irreversible.

2 Experimental procedures

Experiments were performed in Caltech's indoor, dual 28 m^3 Teflon environmental chambers (Cocker et al., 2001; Keywood et al., 2004). Each chamber has a dedicated Differential Mobility Analyzer (DMA, TSI model 3081) coupled with a condensation nucleus counter (TSI model 3760) for measuring aerosol size distribution, and number and volume concentration. Temperature, relative humidity (RH), O_3 , NO, and NO_x were continuously monitored. AS seed particles were generated by atomization of a 0.015 M aqueous AS solution using a constant rate atomizer. GL was prepared by heating a mixture of solid GL trimer dihydrate (Sigma, minimum 97%) and phosphorus pentoxide (P_2O_5) to $\sim 160^\circ\text{C}$ under vacuum. The monomer was collected in an LN_2 trap as a yellow solid and stored overnight at -20°C . Before each experiment, the frozen monomer was allowed to vaporize into a 500 mL glass bulb and introduced into the chamber using a gentle air stream. The chamber was kept at $\sim 60\%$ RH. The concentration of an inert tracer, cyclohexane, was monitored using a gas-chromatograph with flame ionization detector (GC-FID, Agilent 6890N).

Dark experiments typically began by introducing gas-phase GL into a dark chamber and allowing the concentration to equilibrate over ~ 10 h. Approximately 160 ppb_v (part-

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per-billion by volume) of cyclohexane was also added as a tracer for dilution. Once the gas-phase GL concentration reached a steady state, AS seed was introduced and the resulting organic growth was monitored by both the DMA and a high resolution time-of-flight AMS (HR-ToF-AMS, hereby referred to as AMS). After organic growth levelled off, the chamber air mass was diluted with clean hydrocarbon-free air to investigate the reversibility of uptake. The amount of dilution was calculated by monitoring the cyclohexane concentration with the GC-FID. In some experiments, AS seed was added first, and then GL, though the results are the same.

Experiments with irradiation began similarly to dark experiments but when the addition of GL or AS seed was complete, the chamber lights were turned on. No external OH or NO_x source was added, and no dilution was performed in irradiated experiments.

A blank experiment was conducted in which wet AS seed was atomized into a humid chamber without GL present. A negligible organic signal was measured in the absence of radiation, most likely due to background organics from the chamber walls. Under irradiation, miniscule organic growth was reported.

2.1 Teflon filter collection and offline chemical analysis

Teflon filters (PALL Life Sciences, 47 mm diameter, 1.0 μm pore size, teflo membrane) were collected from each experiment for offline chemical analysis. Filter sampling was initiated when the aerosol volume reached its maximum (constant) value, as determined by the DMA. Depending on the total volume concentration of aerosol in the chamber, the duration of filter sampling was 3.6–4.1 h, which resulted in ~5.1–5.8 m³ of total chamber air sampled. Collected filters were extracted in high-purity methanol, dried, and then reconstituted with 250 μL of a 1:1 (v/v) solvent mixture of 0.1% acetic acid in water and 0.1% acetic acid in methanol (see Surratt et al., 2008 for details). All filter extracts were analyzed by a Waters ACQUITY ultra performance liquid chromatography (UPLC) system, coupled to a Waters LCT Premier XT time-of-flight mass spectrometer (TOFMS) equipped with an electrospray ionization (ESI) source. The ESI source was operated in both negative (–) and positive (+) ion mode; GL SOA com-

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ponents were only detected in the negative ion mode. The TOFMS instrument was operated with a mass resolution of 12 000, allowing for accurate mass measurements of all detected SOA components formed from GL reactive uptake. All other operating conditions for this technique have been fully described elsewhere (Surratt et al., 2008).

Blank Teflon filters were extracted and treated in the same manner as the samples; none of the SOA products detected on the filter samples collected from the GL chamber experiments were observed in these blanks, indicating that these SOA components were not introduced during sample storage and/or preparation. Furthermore, to ensure that the SOA components observed were not an artefact formed from the collection of gaseous GL onto filter media, a blank filter was collected under dark conditions from the chamber containing a well mixed concentration of GL ($\sim 2 \text{ ppm}_v$) and analyzed with UPLC/ESI-HR-TOFMS. This blank was sampled for the same duration as a sample filter. No SOA components characterized in the present study or significant contaminants were observed, consistent with the lack of observed aerosol growth in the absence of light and AS seed aerosol. All filters used for UPLC/ESI-HR-TOFMS analysis were examined within 1–2 days of the filter extraction/sample preparation. Following their initial analysis, sample extract solutions were stored at -2°C . Selected samples were reanalyzed a month after initial extraction and showed no signs of degradation.

2.2 Aerodyne aerosol mass spectrometer

Real-time particle mass spectra were collected continuously by the AMS, which is described in detail elsewhere (Canagaratna et al., 2007, and references therein). The AMS switched once every minute between a high resolution “W-mode” and a lower resolution, higher sensitivity “V-mode”. The “V-mode” data were analyzed using a fragmentation table to separate out sulphate, ammonium, and organic spectra and to time-trace specific mass-to-charge ratios. “W-mode” data were analyzed using a separate high-resolution spectra toolbox known as PIKA to determine the chemical formulas contributing to distinct mass-to-charge ratios. Since GL easily fragments to produce CH_2O^+ , the fragmentation table was corrected so that the organic signal at

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m/z 30 equalled its total signal minus the contribution from air. The nitrate contribution was changed to approximately 1.3 times the nitrate signal at m/z 46 as this was the 30/46 ratio during ammonium nitrate calibrations.

2.3 Madison laser-induced phosphorescence instrument

5 Gas-phase GL was detected via Laser-Induced Phosphorescence (LIP) using the Madison LIP Instrument described in Huisman et al. (2008). This instrument utilizes a White-type multipass cell in a 2-pass configuration with gated photon counting and is highly sensitive, permitting specific, direct, in situ measurement of GL with a one-minute limit of detection (3σ) of 6 ppt_v (part-per-trillion by volume) in a 32-pass configuration.
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3 Results

3.1 Glyoxal uptake in the absence of light

For a typical experiment, gas-phase GL was present in the chamber and equilibrated with the chamber walls prior to the introduction of AS seed particles. Organic growth
15 began immediately upon particle addition, and reached a maximum after approximately 10 h; over this time period, sulphate and ammonium decreased due to particle wall losses. A representative unit-mass AMS spectrum is shown in Fig. 2. The fragments of interest to this study are summarized in Tables 1 and 2. The most significant fragments are m/z 44, 58, 68, 135, 145, and 175. This is in general accord with that observed
20 by Liggio et al. (2005a), though certain masses such as m/z 192 and 193 have lower signals in this study. The precursor to each fragment marked in Fig. 2 is listed in Table 1 and the fragment identity is unequivocally confirmed by the high-resolution spectra obtained in “W-mode”, verifying many of the assignments made by Liggio et al. (2005a). Masses larger than or equal to m/z 77 represent ion fragments of oligomers; as an

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example, the high-resolution peak for m/z 135 is shown in Fig. 3a. In the high resolution spectra, the only fragment ion found to contain both sulphur and carbon is m/z 79 (CH_3SO_2^+); however, the signal intensity is similar to that in the blank experiment. Filter sample analysis did not detect GL sulphates under dark conditions, as can be seen in the comparison between an experiment with glyoxal added to the system (Fig. 4a) and a blank experiment (Fig. 4b).

After particle growth has stopped, the chamber was diluted with clean air to investigate the reversibility of GL uptake. Upon dilution, the concentrations of tracer, gas-phase GL, and particle-phase organic mass, sulphate, and ammonium decreased. The gas-phase GL concentration decreased by 25–40% of the initial concentration and the organic signal decreased relative to the tracer signal. To remove the effect of the decrease in particle number density due to wall loss and to dilution, the organic and several marker signals are normalized to sulphate. The normalized organic signal and GL markers at m/z 58 and m/z 105 still decrease after dilution. Figure 5 shows this for two separate dilution experiments.

Several fragments were observed by the AMS to have different temporal characteristics (and thus uptake kinetics) than the total organic or GL_n signal. Relatively strong signals occurred at m/z 41, 68, 69, and 70. Weaker signals, approximately 5–10 times lower in magnitude, were also detected at other masses, the largest fragment occurring at m/z 96. The signal at m/z 68 increased immediately upon seed injection and grew steadily, even after no further change in total organic growth was observable within the uncertainty of that measurement. Furthermore, during dilution, the signal continued to increase when normalized to the sulphate signal. We hypothesise that these fragments originate from compounds containing carbon and nitrogen, as discussed below.

3.2 Glyoxal uptake in the presence of light

The AMS spectrum in irradiated experiments initially resembled that of dark uptake experiments, with many of the same marker fragments prominent, but changed quickly. As under non-irradiated conditions, gaseous GL partitioned immediately to the AS seed

under UV light. However, it did so at a slower rate, and the GL marker signal decayed faster than wall loss once growth reached a maximum; this maximum is reached earlier than in the experiments under dark conditions and the fractional contribution of m/z 44 and m/z 68 increased (Fig. 6). The fragment with m/z 44 can be confidently assigned as CO_2^+ , and in AMS spectra is considered an indicator of the oxidation state of organic aerosol, and its increase in irradiated experiments points to an increasingly oxidized aerosol. In agreement with this, numerous highly oxidized organic species were detected via the UPLC/ESI-HR-TOFMS analysis.

4 Discussion

4.1 Glyoxal sulphate formation

The fragment ions m/z 145 and 175, which were previously assigned the formulas $\text{CH}_5\text{O}_6\text{S}^+$ and $\text{C}_2\text{H}_7\text{O}_7\text{S}^+$, respectively by Liggio et al. (2005a), were unequivocally determined to be $\text{C}_5\text{H}_5\text{O}_5^+$ and $\text{C}_6\text{H}_7\text{O}_6^+$, respectively (Fig. 3a and b) with the AMS in “W-mode”. The detection of these fragments demonstrates the existence of trimers or larger GL_n in the aerosol. Liggio et al. (2005a) suggested that these fragments correspond to fragmentation products of GL sulphates formed from a proposed aqueous reaction of sulphate or bisulphate with GL. If this proposed mechanism were correct, it would be the only evidence for the formation of GL sulphates in chamber aerosol resulting from GL uptake. The current study is in the unique position to unambiguously determine the chemical formulas of both fragment ions due to the employment of the high-resolution “W-mode”, which is not possible with a quadrupole AMS. No sulphate esters were detected by the UPLC/ESI-HR-TOFMS analysis of filter samples (Fig. 4). This evidence suggests that GL sulphate does not form in dark GL uptake experiments with neutral pH AS seed.

Our results do not rule out that sulphates were formed in the study by Liggio et al. (2005b), and our irradiated experiments clearly demonstrate that GL sulphate can form.

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Figure 4 shows that GL sulphate is measured in filter samples obtained during irradiated experiments. The AMS did not detect GL sulphate, most likely due to a high degree of fragmentation of this compound. GL sulphate has previously been detected in filter samples from isoprene photooxidation experiments conducted in the Caltech chamber (Surratt et al., 2008), but only under intermediate- and high-NO_x conditions, which favour GL production, and only with acidic seed. Ambient organic aerosol collected from K-putszta, Hungary (Gómez-González et al., 2008) and from the south-eastern US (Surratt et al., 2008) has also been found to contain GL sulphate. This is the first report of GL sulphate being measured in chamber filter samples of GL uptake. Although these findings could suggest a photochemical mechanism of GL sulphate formation, we do not have evidence for this and most laboratory studies that have investigated organosulphate formation have implicated acid catalysis in their formation. Indeed, judged by the increasing *m/z* 44 marker, particle-phase GL is clearly oxidized in the presence of UV light, although no OH source was added. Bulk experiments performed by Carlton et al. (2007) show that aqueous GL in the presence of H₂O₂ and UV light yields oxalic acid and formic acid. Oxidation was clearly observed in our experiments and the most plausible oxidation products of GL are glyoxylic, oxalic, and formic acids, although it is unclear which products should be expected from oxidation of the GL_{*n*}. Analysis of filter samples identified glyoxylic, glycolic and formic acids, which could increase the acidity of the aerosol and enable GL sulphate formation.

4.2 Carbon-nitrogen containing compound formation

Although no significant AMS fragments containing both sulphur and carbon are found, several fragments in the high-resolution spectra are found to contain nitrogen together with carbon, hydrogen and occasionally oxygen (Table 2). Mass fragments in the AMS spectra with strong signals at *m/z* 41 and 68 are assigned as C₂H₃N⁺ and C₃H₄N₂⁺ (see Fig. 7a), respectively. These fragments are more consistent with formation of a substituted imidazole compound than with (linearly) oligomeric carbon-nitrogen (C-N) containing species. Furthermore, upon inspection of the high-resolution peak at *m/z* 96,

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it can be seen that most of the signal is a result of a molecular ion with the formula ($C_4H_4N_2O^+$, Fig. 7b), which can be attributed to 1H-imidazole-2-carboxaldehyde. From these exact mass fragments measured with the AMS, we predict the formation of imidazoles in aqueous aerosol containing GL and ammonia. The production of a very stable aromatic compound such as an imidazole may, in fact, be the thermodynamic driving force behind this reaction and could explain why carbon-nitrogen containing fragments are observed in the AMS. This is in contrast to the case of organic nitrates, which fragment easily via loss of the nitrogen moiety. Little experimental data are available on the physical properties of 1H-imidazole-2-carboxaldehyde, though it is predicted to have a vapour pressure of 1.43×10^{-3} Torr (SciFinder Scholar, 2008). The low vapour pressure makes it a viable candidate for an SOA constituent.

Since no NO_x was added or present in the chamber before GL addition, the only source of labile nitrogen is ammonium from AS. Therefore, the C-N ions likely arise from fragmentation of products of a reaction between GL and ammonium. Although the ammonium ion is not a nucleophile and is not expected to react with GL, there will be a non-negligible concentration of ammonia in equilibrium with ammonium at neutral pH. The reaction of GL, ammonia and formaldehyde is an established organic reaction for synthesis of imidazole (Debus, 1858). As GL is the only aldehyde present in the aerosol, the general Debus mechanism would predict the formation of 1H-imidazole-2-carboxaldehyde as shown in Fig. 8. Since the abundant ammonium is a weak acid, it is possible that it can facilitate the condensation reactions. According to the standard NIST spectrum, 1H-imidazole-2-carboxaldehyde should fragment under electron impact ionization to produce strong signals at m/z 41, 68, and 96 (NIST Webbook, 2008), which is in agreement with the AMS spectra from this study. As judged by the AMS, the C-N compounds contribute $\sim 0.5\%$ of total organic mass, but the sensitivity of the AMS for these compounds or the GL_n has not been calibrated, and it is unlikely such a calibration can be achieved for the oligomers.

Dilution has very little effect on the relative growth of m/z 68, implying that GL-ammonia reactions are irreversible with respect to the lifetime of chamber aerosol.

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Imidazole compounds have not been previously detected in AS seed aerosol chamber studies, and the mass spectrum published by Liggio et al. (2005a) does not show a peak at m/z 68. However, that spectrum was for GL uptake on acidified aerosol at low pH, which likely prevents formation of the proposed compound. Low pH values will reduce the concentrations of ammonia by many orders of magnitude, effectively preventing formation of these compounds. Whereas previous studies addressed the effect of added gas-phase ammonia (Na et al., 2006, 2007) and organic amines (Angelino et al., 2001; Silva et al., 2008) on SOA formation, to the authors' knowledge, no direct chemical evidence for formation of C-N containing compounds via reaction of any carbonyl with AS seed aerosol has been documented.

4.3 Overall organic growth and glyoxal oligomer formation

Analysis of the AMS spectra collected indicates strong evidence for GL_n within the aerosol (see Fig. 2). It is important to note that fragments with one or two carbons do not necessarily arise only from GL monomers in the particle phase. They can also be fragmentation products of larger oligomers; thus C1 and C2 fragments are a result of fragmentation of at least a monomer, C3 and C4 fragments are the result of fragmentation from at least a dimer, and so on. The GL and GL_n mass fragments stop growing in parallel with overall organic growth and show analogous behaviour to total organic growth upon dilution. Organic growth in our study reached a plateau, providing evidence for a steady-state point, which could either be due to a depletion of a reactant in an intrinsically irreversible process or because equilibrium, with a corresponding modified Henry's law constant, is achieved. The dilution experiments provide key evidence that this plateau is not caused by the depletion of a reactant: when the chamber air mass is diluted, organic aerosol content decreases relative to sulphate, implying a loss of GL from the aerosol phase.

For the dark GL uptake experiments, only C-N compounds, GL and GL_n were identified, while no GL sulphate was found. The fact that C-N compounds are clearly formed irreversibly and only contribute a small part of the organic AMS signal and that overall

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organic growth as well as GL and GL_n growth are clearly reversible, suggests strongly that overall growth is dominated by GL and GL_n . The studies by Liggio et al. (2005a,b) were conducted on timescales (~ 4 h) in which equilibrium was not yet achieved in our studies. We have therefore compared our organic growth during the first 4 h with that of Liggio et al. (2005a,b) for experiments at similar relative humidities of 49% (Liggio et al., 2005a,b) and 55% (this study) and gas-phase GL concentrations of 5.1 ppb_v (Liggio et al., 2005a,b) and ~ 80 ppb_v (this study). The organic/sulphate ratio after 4 h in the work by Liggio et al. (2005a) is ~ 16 , which is more than an order of magnitude larger than in this study (~ 0.35), and we expect that the difference would have been even larger if we had employed the lower GL mixing ratios of the work by Liggio et al. (2005a,b). Furthermore, the curvature of the first 4 h in the study presented here shows a decreasing uptake rate in agreement with the fact that equilibrium is achieved after about 10 h, whereas the curvature in the work by Liggio et al. (2005a) does not show such a trend. The average aerodynamic diameter of the seed aerosol in the study by Liggio et al. (2005a) is initially smaller and thus the uptake rate per volume of seed aerosol is expected to be faster than in this study, but it is unlikely that this alone can explain the discrepancy. In a more recent study, Volkamer et al. (2008) concluded that photochemical GL uptake on AS seed aerosol was likely to be reversible although uptake was 40% larger and kinetics significantly faster than in this study and the study of Kroll et al. (2005). Interestingly, the study by Volkamer et al. (2008) found no GL uptake under dark conditions on AS seed aerosol. We cannot currently determine a particular reason why the two non-irradiated studies show two different types of uptake (irreversible and reversible) at different rates, information that is critical if understanding of these processes is to be applied to ambient studies.

Reversible partitioning of GL between the particle and gas phase at equilibrium can be described by Henry's law. For dilute solutions Henry's law will have the form

$$K_H^* = \frac{[GL]}{\rho_{GL}} \quad (1)$$

with K_H^* being the effective Henry's law constant, $[GL]$ the sum of the concentrations

of particle-phase GL and GL hydrates, and p_{GL} the (gas-phase) GL partial pressure. From the magnitude of organic growth in this and other studies and the AMS spectra, one concludes that GL_n can contribute to uptake and one can formulate a modified Henry's law constant:

$$K_{H,mod}^* = \frac{[GL]_{TOTAL}}{p_{GL}} \quad (2)$$

where $[GL]_{TOTAL}$ is the total GL concentration expressed in GL monomer equivalents. From Eqs. (1) and (2) it follows that effective modified Henry's law constants correspond to the slope of a plot of $[GL]_{TOTAL}$ versus p_{GL} . $K_{H,mod}^*$ is equivalent to $K_{H,AS}^*$ for the discussion presented here, but is used to express that it is a Henry's law constant for high particle-phase GL concentrations. Such plots are shown in Fig. 9, for a combined dataset of the neutral AS seed aerosol data from this study and those by Kroll et al. (2005) and for the acidified AS seed aerosol data by Kroll et al. (2005). The latter set is not included in a combined dataset, as it is expected to have active particle-phase chemistry other than GL oligomer formation. The data presented in these plots can also be found in Table 3. $[GL]_{TOTAL}$ is related to experimental observables via Eq. (3) and p_{GL} is measured directly,

$$[GL]_{TOTAL} = \frac{\Delta V \times \rho}{MW \times V_{eq}} \quad (3)$$

with ΔV being the observed volume change (via DMA) once equilibrium is achieved, ρ the density of GL in the particle-phase, $MW=58.04$ g/mol the molecular weight of GL, and V_{eq} the equilibrium total aerosol volume. No information is available on the repartitioning of water on GL uptake. Therefore, Eq. (3) assumes that the entire volume change is due to GL uptake and that there is no repartitioning of water. There are several different ways to estimate the density of glyoxal oligomers; from the density of an aqueous solution or from the predicted density of the individual oligomers. The density of GL_n estimated from the commercially available 40% w/w GL solution is calculated

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to be $\rho=2.14\text{ g/cm}^3$, assuming the density of water to be $\rho_{\text{H}_2\text{O}}=1.0\text{ g/cm}^3$. However, this is not a rigorous calculation due to the uncertainty in the partial molar volumes. The density of GL used in this work is $\rho=1.94\text{ g/cm}^3$, which is the average of the literature predictions for the density of isolated GL monomer, dimer and trimer dihydrates (SciFinder Scholar, 2008). The thermodynamic definition of Henry's law applies to a system at equilibrium and the aerosols in this study are liquid, single-phase systems, thus the total equilibrium aerosol volume is used. The average Henry's law constant is determined using Eq. (2), which can be related to experimental observables via Eq. (3) to obtain

$$\frac{\Delta V \times \rho}{MW \times V_{eq}} = K_{H,\text{mod}}^* \times \rho_{\text{GL}} \quad (4)$$

A linear fit of the combined data for $K_{H,\text{mod}}^*$ gives $K_{H,\text{mod}}^*=4.4 \times 10^7\text{ M/atm}$ (Fig. 9a). Fits of the data from Kroll et al. (2005) and this study separately give values of $3.6 \times 10^7\text{ M/atm}$ and $4.4 \times 10^7\text{ M/atm}$, respectively. Kroll et al. (2005) assumed a unit density of 1 g/cm^3 and calculated a value of $K_{H,\text{mod}}^*=2.7 \times 10^7\text{ M/atm}$. Using unit density and the combined dataset, we calculate $K_{H,\text{mod}}^*=2.4 \times 10^7\text{ M/atm}$. This value is slightly smaller due to the use of the final aerosol volume as the equilibrium volume in the work presented here. The Henry's law constant determined in this manner for the dataset of Volkamer et al. (2008) and the acidified AS seed aerosol of Kroll et al. (2005) are $4.2 \times 10^7\text{ M/atm}$ and $4.5 \times 10^7\text{ M/atm}$, respectively. However, the quality of the fit for the former is very poor ($R^2=0.1$) in contrast to all other fits ($R^2>0.7$). This poor fit is due to the point with the lowest RH (and thus liquid water content). Henry's law is dependent on water within the system, as evidenced by the fact that $K_{H,\text{aq}}^*$ is much smaller than $K_{H,\text{AS}}^*$. In the work by Kroll et al. (2005), the Henry's law constant was determined by plotting the organic aerosol mass ($\Delta V \times \rho$) as a function of the product of GL partial pressure and initial aerosol volume. The plot thus corresponds to rearranging Eq. (4) to give

$$\Delta V \times \rho = K_{H,\text{mod}}^* \times \rho_{\text{GL}} \times MW \times V_{eq} \quad (5)$$

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For a linear fit of Eq. (5), $K_{H,\text{mod}}^* = 4.7 \times 10^7 \text{ M/atm}$ for the combined data set, $4.3 \times 10^7 \text{ M/atm}$ for the acidified dataset by Kroll et al. (2005), and $8.9 \times 10^7 \text{ M/atm}$ for the dataset by Volkamer et al. (2008) (Fig. 9b). Each of these fits have excellent R^2 value. Volkamer et al. (2008) correctly noted that applying Henry's law to their data is not necessarily valid, as it corresponds to photochemical uptake, which, as this work shows, likely involves irreversible particle phase processes. The agreement of $K_{H,\text{mod}}^*$ determined from Fig. 9a and b for the combined dataset is excellent, giving us confidence in this value and the experimental data.

However, as mentioned above and as Fig. 9a shows, $[\text{GL}]_{\text{TOTAL}}$ is sufficiently high that substantial oligomerization is expected. Based on values of $[\text{GL}]_{\text{TOTAL}}$ in Table 3 and Fig. 9a, the laboratory determined GL dimer equilibrium constant for aqueous systems is $K_{\text{dim, aq}} = 0.56 \text{ M}^{-1}$ (Fratzke and Reilly, 1986), and neglecting higher oligomerization, the GL dimer concentrations, $[\text{GL}_2]$, for the combined neutral AS dataset under dark conditions are calculated to be between 1–4 M. The assumption of a substantial degree of oligomerization is supported by the AMS data, and no data are available for $K_{\text{dim, AS}}$, the dimer equilibrium constant for AS aerosol. It is surprising that a high quality linear fit is achievable, as the above Henry's law treatment (Eqs. 4 and 5) that assumes a linear dependence of $[\text{GL}]_{\text{TOTAL}}$ on p_{GL} should be incorrect as $K_{H,\text{mod}}^*$ should be a function of p_{GL} . This can be readily shown with a simplified system in which only monomers and dimers are considered. The modified Henry's law constant, $K_{H,\text{mod}}^*$, (Eq. 2) for high particle-phase GL concentrations can then be expressed as:

$$K_{H,\text{mod}}^* = \frac{[\text{GL}]_{\text{TOTAL}}}{p_{\text{GL}}} = \frac{[\text{GL}] + 2[\text{GL}_2]}{p_{\text{GL}}} \quad (6)$$

which can be rearranged to:

$$[\text{GL}]_{\text{TOTAL}} = K_H^* p_{\text{GL}} + 2K_{\text{dim}} K_H^{*2} p_{\text{GL}}^2 \quad (7)$$

with K_H^* the effective Henry's law constant for oligomer free solutions (i.e. assuming low $[\text{GL}]_{\text{TOTAL}}$) and

$$K_{\text{dim}} = \frac{[\text{GL}_2]}{[\text{GL}]^2} \quad (8)$$

This simplified model serves only to highlight that there should be a nonlinear dependence of $[\text{GL}]_{\text{TOTAL}}$ on p_{GL} and a linear dependence of $K_{\text{H,mod}}^*$ on p_{GL} . Particle-phase GL increases linearly with p_{GL} at low p_{GL} , whereas there is a quadratic dependence at high p_{GL} . In effect, Fig. 9a should show a positive curvature. However, no such trend is observed for the combined dataset. A quadratic fit of Eq. (7) fixed at the origin is of slightly better quality than the linear fit but this is not proof for a nonlinear dependence of $[\text{GL}]_{\text{TOTAL}}$ on p_{GL} , as such an improvement is expected upon introduction of an additional fit parameter for a limited dataset. The Henry's law constant derived from the fit is $K_{\text{H}}^* = 3 \times 10^7 \text{ M/atm}$ and $K_{\text{dimer}} = 0.04 \text{ M}^{-1}$, substantially lower than for aqueous systems, which is unrealistic in view of the AMS data. A quadratic fit of Eq. (7) which is not constrained to have zero intercept gives an unphysical negative Henry's law constant. We currently cannot reconcile the observation of a high degree of oligomerization with an apparently linear dependence of $[\text{GL}]_{\text{TOTAL}}$ on p_{GL} .

4.4 Glyoxal uptake under irradiated conditions

We present the first analysis of products of organic photochemistry during irradiated GL uptake with AS seed aerosol. Within the framework of Fig. 1, the photochemical reactions that are occurring should add additional product channels in the condensed phase, so a higher uptake would be expected under irradiated conditions. The recent study by Volkamer et al. (2008) found that, judged by application of a modified Henry's law constant to the photochemical system, GL uptake under irradiated conditions was about 40% higher than that measured by Kroll et al. (2005) and that the photochemical uptake rate was very high. No OH source was added in our study and thus conditions are not identical to those employed by Volkamer et al. (2008). However, there is a marked difference in the fate of GL in the particle phase even without the OH source: GL sulphate and organic acids are formed. As discussed earlier, GL sulphate formation

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could be photochemical, but is more likely a result of the formation of organic acids, which provide conditions that allow acid catalysis for sulphate ester formation. The change in pH does not appear to be large enough to prevent imidazole formation.

The relative signal strength of m/z 44, an indicator of oxidized organic aerosol in the AMS spectra, shows that the particle phase is becoming significantly more oxidized over the duration of the irradiated experiments. This is supported by the organic acids found in filter sample analysis: formic, glyoxylic and glycolic acids, the latter a disproportionation product of GL, all of which have smaller Henry's law constants than GL. The formic acid and glycolic acid are observed as an ester, a higher molecular weight condensation product. If oxidation to volatile products, such as carbon dioxide, is not significantly faster than condensation, e.g. the formic-glycolic acid ester, or oxidation products, e.g. oxalic acid, that form SOA, the net SOA yield under irradiated conditions should be higher than under dark conditions, as additional product channels are available. These additional product channels also make Henry's law analysis of uptake inapplicable. In contrast to the study of Volkamer et al. (2008), which generally found such increased uptake, overall organic growth was reduced under irradiated conditions in this study as compared to those under dark conditions. Enhanced loss of particle-phase GL in the presence of light was observed, but while it is possible that rapid oxidation to higher volatility compounds, such as formic, glyoxylic, and glycolic acids, and subsequent partitioning of these to the gas phase is competing with GL oligomer formation and reaction of the oxidation products to higher molecular weight compounds, it is likely that decreasing humidity and increasing temperature upon irradiation cause significant amounts of GL to repartition to the gas phase. GL photolysis in the gas phase is also possible; however, since the walls act as a substantial reservoir of GL that is at steady state with the gas phase, this is less likely. In fact, during the irradiated GL uptake experiment shown in Fig. 6, the gas-phase GL concentrations remained constant at ~ 150 ppb_v throughout the experiment. A quantitative comparison of SOA yields between dark and irradiated conditions is not possible for this work.

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4.5 Implications to ambient aerosol

GL and other α -dicarbonyls, such as methylglyoxal, are common oxidation products of both biogenic and anthropogenic VOCs. The concentration of these α -dicarbonyls is typically highest during the day and thus SOA formation under irradiated conditions is likely to be more important than under dark conditions. However, for a detailed understanding of the processes depicted in Fig. 1 and their contribution to SOA formation under ambient conditions, it is desirable to address these processes separately, therefore an analysis of GL uptake under dark and under irradiated conditions is helpful. This study shows that GL uptake involves both reversible processes, such as growth via GL monomer and oligomers, and irreversible processes, such as C-N compound formation and photochemical oxidation reactions. The reversible processes are likely less relevant to ambient SOA formation as they will repartition GL to the gas phase upon decreasing GL gas-phase concentrations, such as night time or transport away from GL sources. However, they provide a pathway for uptake of GL into the particle phase, allowing the irreversible processes to proceed. The majority of organic growth in the chamber studies under dark conditions occurs via GL uptake with subsequent oligomer formation, but ambient GL concentrations are substantially lower (2–3 orders of magnitude), so it is less likely the organic character of the aerosol will involve multiple GL molecules such as oligomers and 1H-imidazole-2-carboxaldehyde. It is likely that additional reversible processes, such as reactions with other aldehydes, and irreversible processes, such as formation of different substituted imidazoles via reaction with other aldehydes, exist in ambient aerosol. The formation of these imidazoles through the Debus mechanism requires α -dicarbonyls, so other types of aldehydes or dicarbonyls will not readily yield aromatic systems via reaction with ammonia. Because α -dicarbonyls and aldehydes are ubiquitous, the discovery of this new reaction pathway allows for the potential production of many different compounds. GL is likely the most important α -dicarbonyl for formation of imidazoles. The Henry's law constant for GL is larger than that for methylglyoxal ($K_{H,aq,MGL}^* = 3.2 \times 10^4 \text{ M/atm}$) the most abun-

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dant α -dicarbonyl, and thus it partitions more strongly to aqueous aerosol. However, Matsunaga et al. (2004) detected higher levels of methylglyoxal than GL in ambient particulate matter, indicating that the high gas phase mixing ratios of methylglyoxal may make it an important contributor to SOA formation. As the underlying reasons for the large difference between $K_{H, \text{aq}}^*$ and $K_{H, \text{mod}}^*$ are not known, it is difficult to estimate the Henry's law constant for methylglyoxal for AS seed aerosol. Kroll et al. (2005) did not observe any organic growth for methylglyoxal, but the growth from imidazole, which proceeds via an α -dicarbonyl monomer, might have been below the detection threshold. This study suggests that methods should be developed to allow analysis of field aerosol samples with respect to this class of compound, and potentially also for compounds derived from methylglyoxal, which is typically present in higher concentrations in areas in which biogenic VOC chemistry dominates (Spaulding et al., 2003). Finally, the study shows that photochemical reactions produce oxidation products of GL. However, the monomers found in this study, such as formic acid, glycolic acid and glyoxylic acids have lower Henry's law constants than GL and thus will not necessarily increase SOA yields. An exception would be the production of oxalic acid and higher molecular weight compounds, such as esters, which would increase SOA yields.

5 Conclusions

This study provides new insights into processes that can contribute to SOA formation from GL and the degree of reversibility of these processes. Reversibility is judged with respect to the experimental timescales, which were as long as 26 h after initiation of organic growth. We demonstrate that:

1. GL sulphate (i.e. organosulphate of GL) does not form under dark conditions with neutral AS seed aerosol,

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2. carbon-nitrogen containing compounds form irreversibly with neutral AS seed aerosol,
3. overall GL uptake and GL oligomer formation in the particle phase are reversible for neutral AS seed aerosol under dark conditions,
- 5 4. there is clear evidence for active photochemistry for GL uptake under irradiated conditions, including formation of GL sulphate, glyoxylic acid, glycolic acid, and formic acid. Further studies characterizing additional condensed-phase oxidation products are required to evaluate this question.

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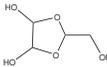
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Table 1. GL fragments observed via AMS and suggested structures from which the fragments are formed.

<i>m/z</i>	Fragment Formula	Suggested Fragment Structure
29	CHO ⁺	
58	C ₂ H ₂ O ₂ ⁺	
77	C ₂ H ₅ O ₃ ⁺	
88	C ₃ H ₄ O ₃ ⁺	
105	C ₃ H ₅ O ₄ ⁺	
117	C ₄ H ₅ O ₄ ⁺	
135	C ₄ H ₇ O ₅ ⁺	
145	C ₅ H ₅ O ₅ ⁺	
175	C ₆ H ₇ O ₆ ⁺	

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Table 2. Fragments containing both carbon and nitrogen observed via AMS and suggested chemical formulas.

	<i>m/z</i>	Fragment formula
Strong ions	41	C ₂ H ₃ N ⁺
	68	C ₃ H ₄ N ₂ ⁺
	69	C ₃ H ₃ NO ⁺
	70	C ₃ H ₄ NO ⁺
Weak ions	46	CH ₄ NO ⁺
	52	C ₃ H ₂ N ⁺
	53	C ₃ H ₃ NO ⁺
	57	C ₂ H ₃ NO ⁺
	68	C ₃ H ₂ NO ⁺
	96	C ₄ H ₄ N ₂ O ⁺

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Table 3. Experimental conditions and results from this study and Kroll et al. (2005).

Experiment	Seed ^a	[Glyoxal] ppb _v	RH	Seed volume ^b , <i>V</i> μm ³ /cm ³	ΔV μm ³ /cm ³	[GL] _{TOTAL} ^c μg/cm ³
Kroll 1	AS	55	47.5%	65.3	5.80	11.3
Kroll 2	AS	153	54.5%	86.8	18.80	36.5
Kroll 3	AS	126	53.5%	86.5	14.50	28.2
Kroll 4	AS	110	44.5%	68.5	7.60	14.8
Kroll 5	AS	158	54.5%	91.7	21.30	41.4
Kroll 6	AS/SA	25	31.0%	77.4	0.70	1.4
Kroll 7	AS/SA	174	48.5%	115.4	11.80	22.9
Kroll 8	AS/SA	93	50.0%	97.3	10.70	20.8
Kroll 9	AS/SA	60	52.5%	97.6	10.30	20.0
This study 1	AS	168	65%	84.0	18.8	36.6
This study 2	AS	87	56%	67.0	10.7	20.9
This study 3	AS	215	56%	87.0	40.4	78.6

^a AS=ammonium sulphate, SA=sulphuric acid.

^b As measured by the DMA and corrected for wall loss.

^c Calculated assuming $\rho=1.94$ g/cm³.

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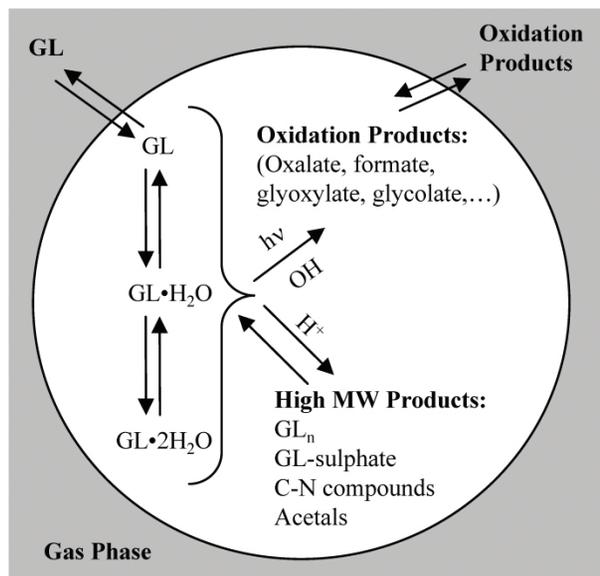


Fig. 1. Processes contributing to GL uptake on AS seed aerosol. GL=GL monomer; GL·H₂O=monohydrate; GL·2H₂O=dihydrate; high molecular weight (MW) products include GL_n, organosulphates of GL, and carbon-nitrogen containing compounds; oxidation products include oxalate, formate, glyoxylate, and glycolate and their oxidation products.

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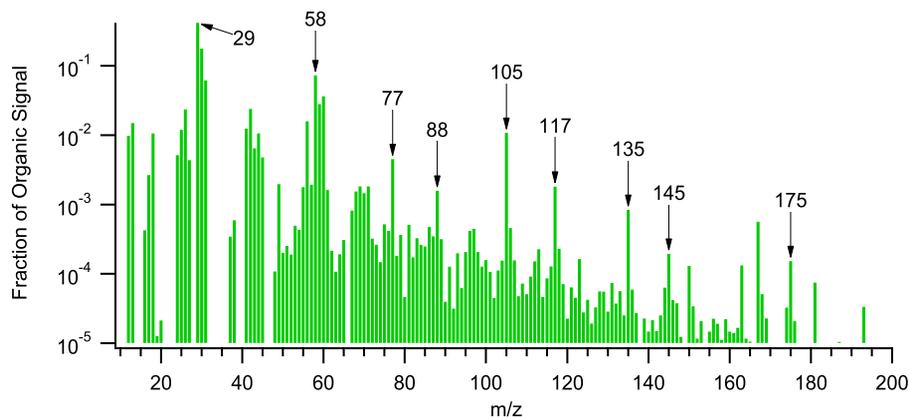


Fig. 2. Representative unit-mass AMS spectrum. Distinct GL and GL oligomer marker peaks are shown. The compound from which each fragment was formed is listed in Table 1.

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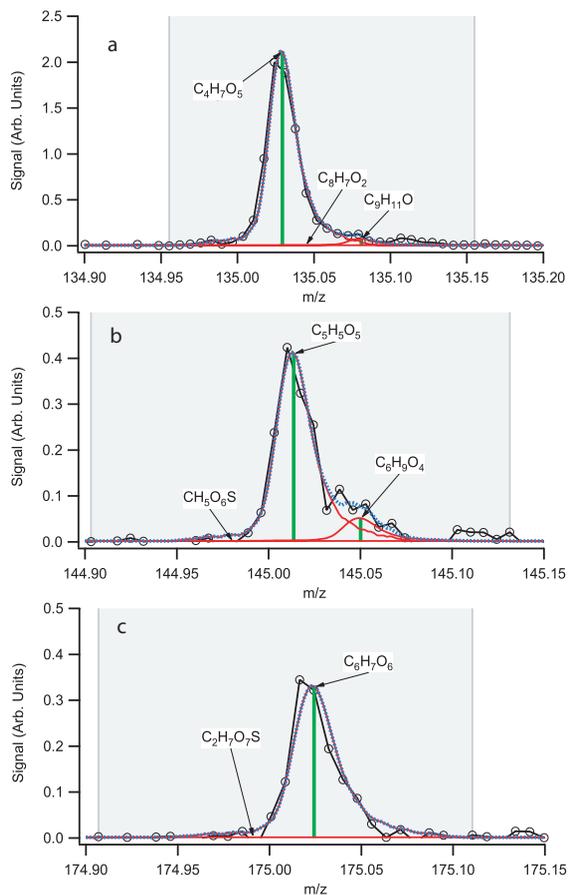


Fig. 3. High-resolution (“W-mode”) AMS peaks allow unequivocal assignment of a C₄H₇O₅⁺ formula to the m/z 135, C₅H₅O₅⁺ formula to the m/z 145, and C₆H₇O₆⁺ formula to the m/z 175 fragment ions.

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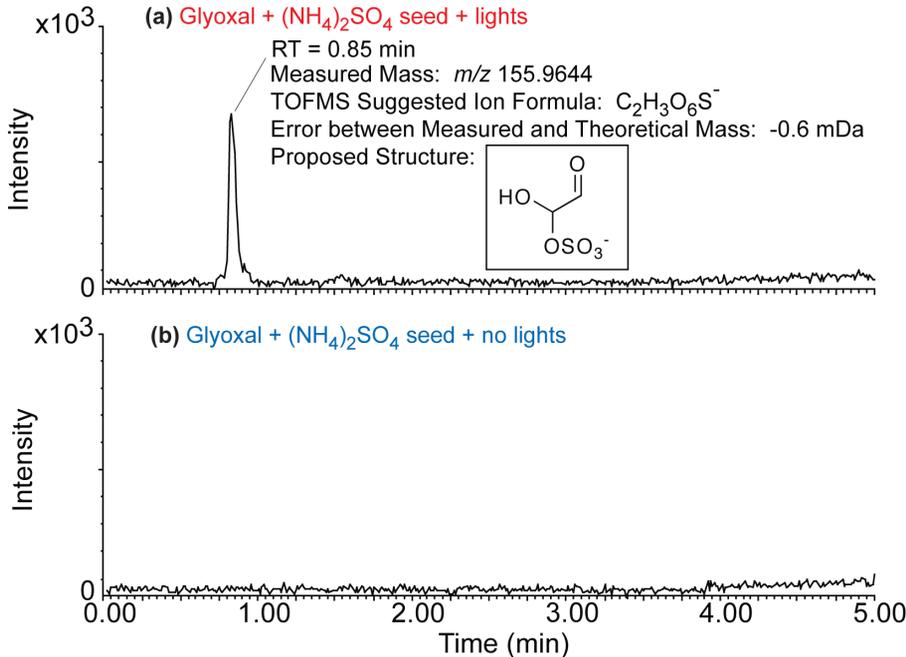


Fig. 4. UPLC/ESI-TOFMS extracted ion chromatograms (EICs) of m/z 155 for two selected GL experiments. The comparison of these two EICs reveals that GL sulphate only forms under irradiated conditions when using non-acidified AS seed aerosol.

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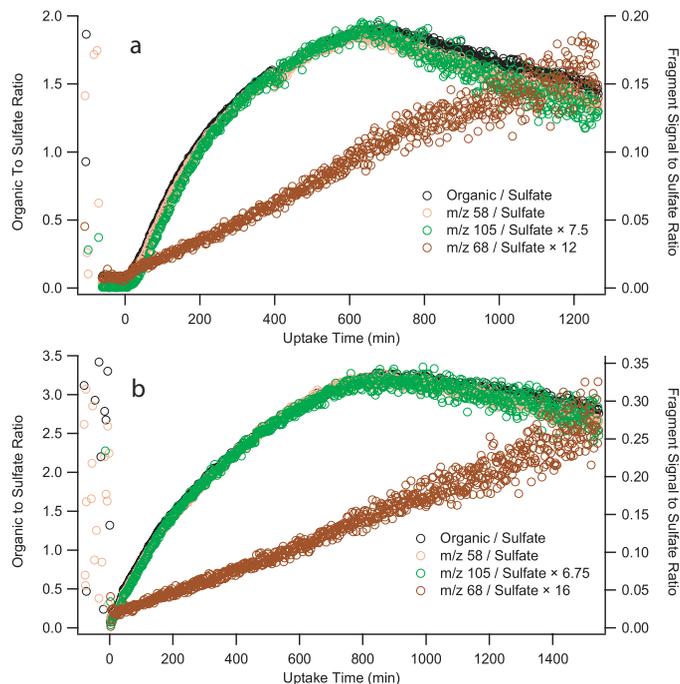


Fig. 5. The two panels show the time traces of total organic, m/z 58, 105, and 68 fragment ions normalized by the sulphate ion signal for two dilution experiments. Upon dilution, the normalized organic and GL marker signals decrease by 30%, and 17%, respectively, which is less than the 40% and 25% reduction in gas-phase GL concentrations. However, the system has clearly not equilibrated and thus further loss of particle-phase GL is expected. In contrast to the reversible behaviour of total organic and GL and GL oligomer growth, the growth of the m/z 58 marker has markedly different characteristics, indicating irreversible uptake.

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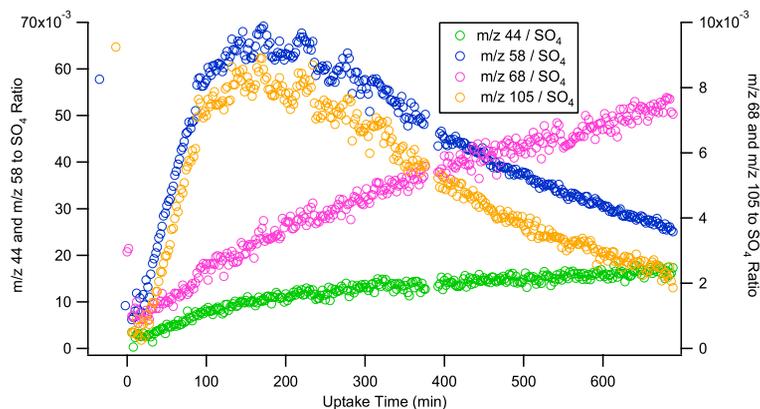


Fig. 6. The sulphate normalized GL and GL oligomer marker signals m/z 58 and 105 increase rapidly on introduction of seed aerosol under irradiated conditions, but decrease rapidly without any dilution taking place, which is in marked difference to the dark experiments. The m/z 44, and in particular, 68 marker signals increase steadily during these experiments, indicating oxidation of the organic fraction of the aerosol and continued imidazole formation.

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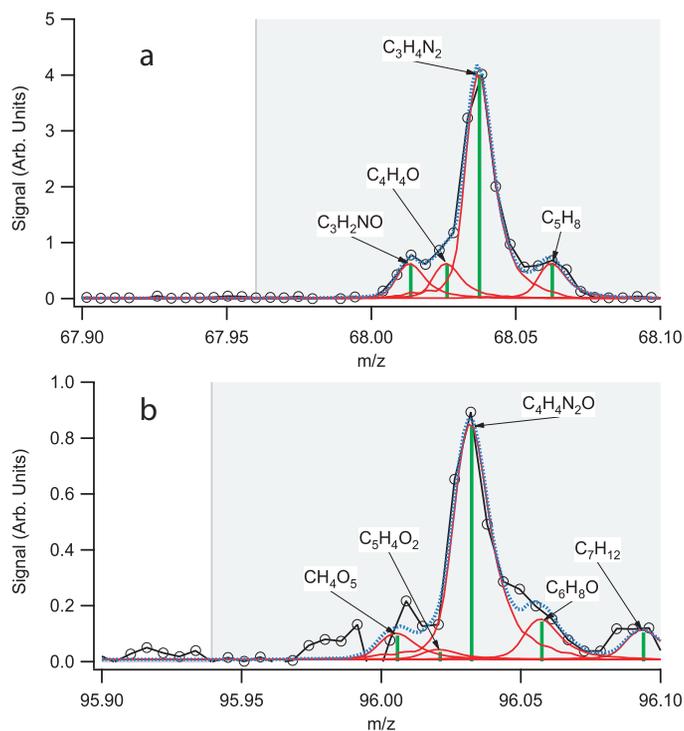


Fig. 7. High-resolution (W-mode) AMS peaks allow unequivocal assignment of a $C_3H_4N_2^+$ formula to the m/z 68, $C_4H_4N_2O^+$ formula to the m/z 96 fragment ions.

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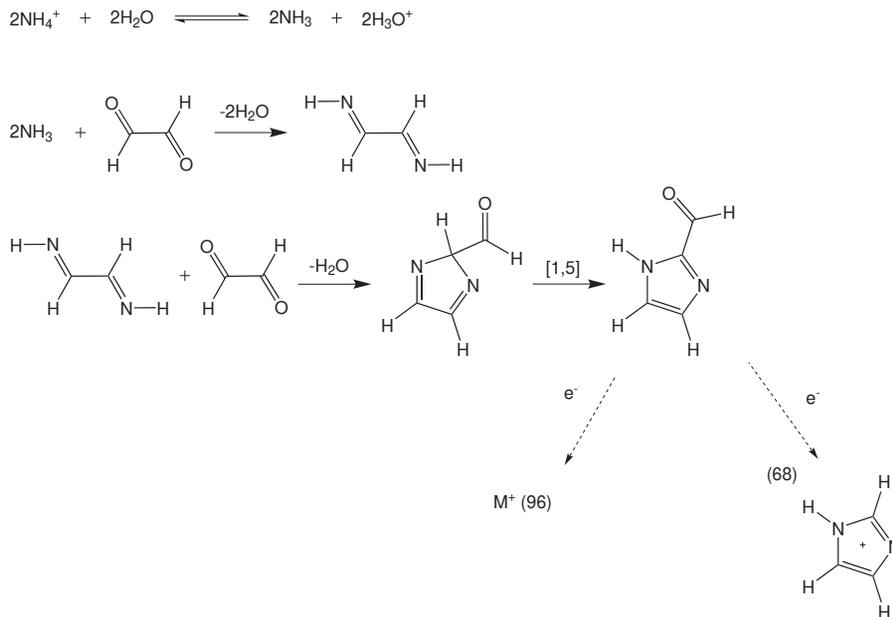


Fig. 8. Proposed formation mechanism of 1H-imidazole-2-carboxaldehyde and observed m/z 68 and 96 fragment ion.

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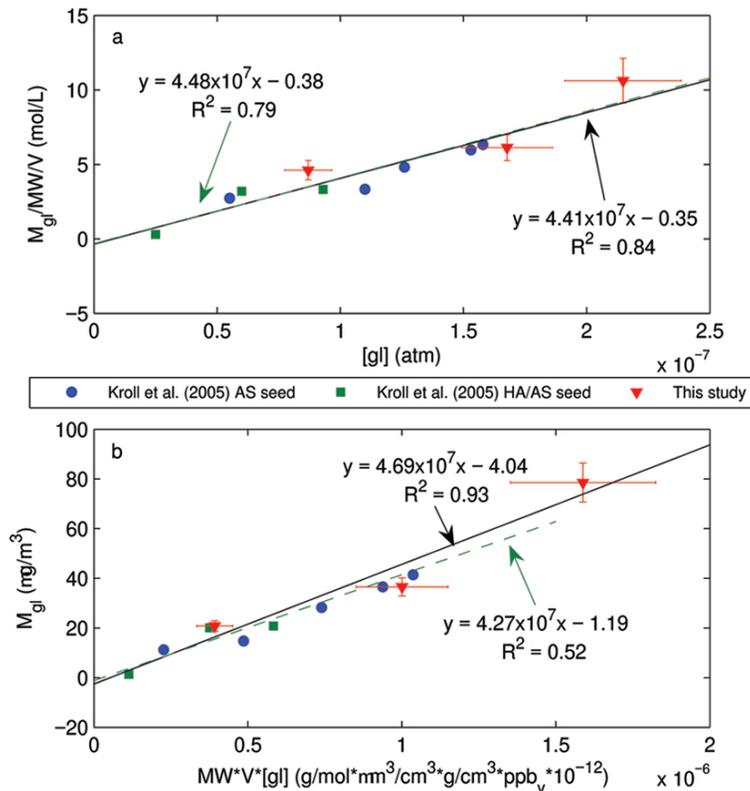


Fig. 9. The top panel shows a plot of particle-phase GL concentration as a function of GL partial pressure for a combined dataset of the neutral AS seed aerosol data from this study and those by Kroll et al. (2005) (red and blue markers, respectively), the acidified AS seed aerosol data by Kroll et al. (2005) (green markers). The slope of the fits corresponds directly to the Henrys law constant. The bottom panel shows the organic aerosol mass as a function of the product of the final aerosol volume, GL partial pressure, and the GL molecular weight, for which the slope also corresponds to the Henrys law constant.

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