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A quantification method for methylglyoxal oligomers and its application on 1,3,5-trimethylbenzene SOA

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Abstract

Methylglyoxal is often described to form oligomeric compounds in the aqueous particle phase which might have a significant contribution to the formation of aqueous secondary organic aerosol (aqSOA). Thus-far, no suitable method for the quantification of methylglyoxal oligomers is available despite the great effort spent for structure elucidation. In the present study a simplified method was developed to quantify methylglyoxal oligomers as a sum parameter. The method is based on the thermal decomposition of oligomers into methylglyoxal monomers. Formed methylglyoxal monomers were detected using PFBHA (o-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride) derivatisation and gas chromatography/mass spectrometry (GC/MS) analysis. The method development was focused on the heating time (varied between 15 and 48 hours), pH during the heating process (pH = 1 - 7), and heating temperature (50°C, 100°C) and optimised values for these conditional parameters are presented.

The developed method was applied to quantify methylglyoxal oligomers formed during the OH-radical oxidation of 1,3,5-TMB in the Leipziger aerosol chamber (LEAK). Oligomer formation was investigated as a function of seed particle acidity and relative humidity. A fraction of methylglyoxal oligomers of up to 8% of the produced organic particle mass was found, highlighting the importance of those oligomers formed solely by methylglyoxal for SOA formation. Overall, the present study provides a new and suitable method for quantification of methylglyoxal oligomers in the aqueous particle phase.

1. Introduction

Aromatic compounds represent a large fraction of the total emitted hydrocarbon mass contributing such as up to 52% to the hydrocarbon mass in China (Liu et al., 2008). One of these aromatic compounds is 1,3,5-trimethylbenzene (1,3,5-TMB), which was measured in the gas phase in concentrations ranging from 0.7 to 40.6 µg m^{-3} (Gee and Sollars, 1998; Khoder, 2007). 1,3,5-TMB can be oxidised in the gas phase leading to low-volatile oxidation products which partition into the particle phase and form secondary organic aerosol (SOA). Oxidation products of 1,3,5-TMB were investigated in a number of literature studies (e. g. Huang et al., 2015; Baltensperger et al., 2005; Kalberer et al., 2004; Kalberer et al., 2006; Paulsen et al., 2005; Healy et al., 2008; Cocker et al., 2001; Smith et al., 1999; Metzger et al., 2008; Wyche et al., 2009; Yu et al., 1997) and methylglyoxal was found as an oxidation product (Metzger et al., 2008; Healy et al., 2008; Cocker et al., 2001; Smith et al., 1999; Wyche et al., 2009; Baltensperger et al., 2005; Rickard et al., 2010; Kalberer et al., 2004; Yu et al., 1997; Kleindienst et al., 1999; Muller et al., 2012; Nishino et al., 2010; Hamilton et al., 2003; Tuazon et al., 1986; Bandow and Washida, 1985) with a fraction of the particle mass of up to 2% (Healy et al., 2008; Cocker et al., 2001). Methylglyoxal has often been described to form oligomeric compounds in the aqueous particle phase (see, e. g. Herrmann et al., 2015 for an overview; De Haan et al., 2009; Kalberer et al., 2004; Loeffler et al., 2006; Zhao et al., 2006; Sareen et al., 2010; Altieri et al., 2008). These oligomers are supposed to play an important role in the formation of aqueous secondary organic aerosols (aqSOA; e. g. Kalberer et al., 2004).

In general, oligomeric compounds can be formed in the aqueous particle phase through aldol condensation (e. g. Tilgner and Herrmann, 2010; Sareen et al., 2010; Sedehi et al., 2013; Krizner et al., 2009; Barsanti and Pankow, 2005; De Haan et al., 2009; Yasmeen et al., 2010), acetal/hemiacetal formation (Kalberer et al., 2004 and Yasmeen et al., 2010), esterification (Altieri et al., 2008; Sato et al., 2012; Tan et al., 2010; De Haan et al., 2011; Sedehi et al., 2013), imine formation (Altieri et al., 2008; Sato et al., 2012; Tan et al., 2010; De Haan et al., 2011; Sedehi et al., 2013), polymerisation, and radical – radical reactions (Schaefer et al., 2015; Tan et al., 2012; Lim et al., 2013).

During the last decade, huge efforts were undertaken to detect and identify oligomeric compounds. As it can be seen from Table 1, a number of mass spectrometric methods were used including (matrix assisted) laser desorption/ionisation mass spectrometry (MALDI-MS, LDI-MS), Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS), and electrospray ionisation mass spectrometry (ESI/MS, ESI/MS/MS). In addition, spectroscopic methods like UV/Vis (ultraviolet-visible spectroscopy), FTIR (Fourier transform infrared spectroscopy), and NMR (nuclear magnetic resonance spectroscopy) analysis were used for identification.

Despite the effort for structure elucidation of oligomeric compounds a suitable quantification method is not available. Mostly, an overall contribution of oligomers to the particle mass was determined using e.g. a volatility tandem differential mobility analyser (VTDMA). Kalberer et al., 2004 determined an oligomer contribution of 50% to the particle mass formed by the photooxidation of 1,3,5-TMB. In a further experiment, oligomer mass fractions of 80% and 90% were determined with a VTDMA-based approach for 1,3,5-TMB and α-pinene (Kalberer et al., 2006). Alfarra et al., 2006 investigated the photooxidation of 1,3,5-TMB and found an increase of the oligomer fraction of 3.1 and 3.7% hour^{-1}. A particulate oligomer fraction of 50% was reported for 1,3,5-TMB and α-pinene by Baltensperger et al., 2005. Dommen et al., 2006 detected a contribution of oligomers increasing from 27% to 44% in the first 5 hours to organic particle mass formed in the photooxidation of isoprene. Nguyen et al., 2011 investigated oligomers from isoprene photooxidation with ESI-MS and nano-DESI-MS (nanospray desorption electrospray ionisation) connected to a high resolution linear ion trap (LTQ-) orbitrap. They calculated an oligomer fraction of 80 – 90%.

De Haan et al., 2009 estimated the oligomer fraction formed by methylglyoxal in the aqueous phase concluding that 37% of methylglyoxal are dimers and oligomers with NMR. In another approach it was estimated that after 4 days in aqueous particles containing amino acids, 15% of the carbonyl compounds are oligomers (Noziere et al., 2007). Contrary, with ammonium sulfate particles 30% of the carbonyl compounds are converted into oligomers (Noziere et al., 2007). These estimations are based on the rate constants for oligomer formation which were determined in the study by Noziere et al., 2007. Besides these estimations, quantification of oligomeric compounds was also conducted using surrogate compounds (Surratt et al., 2006, Zappoli et al., 1999, and Gao et al., 2004) or synthesised authentic standards (Birdsall et al., 2013).

In summary, a variety of methods exists which quantify the fraction of oligomeric compounds derived from methylglyoxal, but the results are contradicting due to the lack of a suitable method of quantification and second, due to different reaction conditions used in the studies. Thus, the present study presents a foundation approach for a reliable quantification of methylglyoxal oligomers in laboratory-generated SOA.

2. Experimental

2.1 Chemicals and standards

1,3,5-TMB (≥ 99.8%), hydrochloric acid (37%), tetramethylethylene (99%), and sodium hydroxide (50 – 52%) were obtained from Sigma-Aldrich (Hamburg, Germany). *O*-(2,3,4,5,6-pentafluorobenzyl)-hydroxylamine hydrochloride (≥99%), methylglyoxal (40% in water), and ammonium hydrogensulfate (98%) were purchased from Fluka (Hamburg, Germany). Sulfuric acid (98%) was obtained from Merck KGaA (Darmstadt, Germany). Dichloromethane (Chromasolv 99.8%) was obtained from Riedel-de Haen (Seelze, Germany) and ammonium sulfate (99.5%) was purchased from Carl Roth (Karlsruhe, Germany). Ultrapure water was used to prepare the seed particle solutions, the authentic standards, and to extract the filter samples (Milli-Q gradient A 10, 18.2 MΩ cm, 3 ppb TOC, Millipore, USA).

2.2 Chamber experiments

The OH-radical oxidation of 1,3,5-TMB was investigated in the aerosol chamber LEAK (Leipziger Aerosolkammer). A detailed description of the aerosol chamber can be found elsewhere (Mutzel et al., 2016). The conditions of the experimental runs are summarised in Table 2. The experiments were conducted in the presence of ammonium hydrogensulfate particles or ammoniumsulfate particles mixed with sulfuric acid to achieve different seed acidities. As OH-radical source the ozonolysis of tetramethylethylene (TME) was used (Berndt and Böge, 2006). O_3 was produced by UV irradiation of O_2 with an O_2 flow rate of 5 L minute^{-1}. O_3 was injected at the beginning of the experiments and ≈ 26 ppbv of TME was introduced into the aerosol chamber in steps of 15 minutes. 1,3,5-TMB (≈ 92 ppb) was injected into the aerosol chamber using a microliter-syringe. The oxidation of 1,3,5-TMB was studied at relative humidities (RH) between ≈ 0% and 75% adjusted by flushing the aerosol chamber with humid or dry air. The consumption of the precursor compound (ΔHC) was monitored over the reaction time of 90 minutes with a proton-transfer-reaction time-of-flight mass spectrometer (PTR-TOF MS). The volume size distribution of the seed particles was measured with a scanning mobility particle sizer (SMPS). An average density of 1 g cm^{-3} was used to calculate the increase of the organic particle mass (ΔM). To collect the particle phase after the experiments 1.2 m^3 of the chamber volume was sampled on a PTFE filter (borosilicate glass fiber filter coated with fluorocarbon, 47 mm in diameter, PALLFLEX T60A20, PALL, NY, USA) connected to a denuder (URG-2000-30B5, URG Corporation, Chapel Hill, NC, USA) (Kahnt et al., 2011) to avoid artefacts caused by adsorption of gas-phase organic compounds onto the filter.

2.3 Sample preparation

For method development, PTFE filter samples from aerosol chamber experiments were used. The following method parameters were investigated: heating time, pH during the heating process, and heating temperature (Table 3).

2.3.1 Filter extraction

Two halves of the PTFE filters were cut into small pieces. Each filter half was extracted separately with 1 mL H_2O for 30 minutes using an orbital shaker (700 rpm, revolutions per minutes). They were shaken again separately with 1 mL H_2O for 30 minutes and flushed at the end of the procedure with 1 mL H_2O resulting in two 3 mL extracts. The extract of one half of the filter was used for oligomer measurements (extract 1) and with the second one methylglyoxal monomers were quantified which were not a building block of oligomers (extract 2). A detailed description of the derivatisation procedure can be found in Rodigast et al., 2015.

2.3.2 Derivatisation procedure

Extract 1 – Methylglyoxal oligomers

For quantification of methylglyoxal oligomers the extract was acidified and heated to decompose the oligomeric bonds. The pH was adjusted with hydrochloric acid (37%) or sodium hydroxide (1 mol L^{-1}) to pH = 1, 3, 5, and 7 while heating temperatures of 50°C and 100°C were investigated. For the derivatisation of the formed monomeric methylglyoxal, 300 µL of *o*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA, 5 mg mL^{-1}) was added to the sample solution after 2 minutes of the heating process. Different heating times were tested varying between 15 hours and 48 hours. After the derivatisation was completed the extracts were allowed to cool down to room temperature.

Extract 2 – Methylglyoxal monomer

The second half of the filters was used to quantify monomeric methylglyoxal. The filters were prepared according to the method described by Rodigast et al., 2015.

2.3.3 Extraction for GC/MS analysis

After derivatisation of both filter extracts (extract 1 and 2), derivatised methylglyoxal was extracted at pH = 1 for 30 minutes with 250 µL of dichloromethane using an orbital shaker (1500 rpm; Rodigast et al., 2015). 1 µL of the organic phase was used for GC/MS analysis and the measurement was repeated for three times to ensure reliable GC/MS signals.

For quantification, a 5-point calibration was performed at the beginning of each chromatographic run using a standard solution of methylglyoxal in a concentration range of 0.13 to 8 µmol L^{-1}.

2.4 Instrumentation

The samples were analysed using a GC System (6890 Series Agilent Technologies, Frankfurt, Germany) coupled with an electron ionisation quadrupole mass spectrometer in splitless mode with an inlet temperature of 250°C (Agilent 5973 Network mass selective detector, Frankfurt, Germany). The derivatives were separated with a HP-5MS UI column (Agilent J & W GC columns, 30 m × 0.25 mm × 0.25 µm) using the following temperature program: 50°C isothermal for 2 minutes and elevated to 230°C (10 °C $minute^{-1}$). The temperature of 230°C was held constant for 1 minute and ended with 320°C for 10 minutes.

3. Results

Hastings et al., 2005 investigated the influence of the temperature of the GC inlet on the detection of oligomeric compounds. These authors concluded that oligomers decompose into monomer building blocks at higher inlet temperatures ($\geq$ 120°C) which caused problems for oligomer quantification. In the present study a quantification method is proposed to decompose oligomers into methylglyoxal monomers due to heating, acidification and PFBHA derivatisation prior GC/MS injection.

(E) and (Z) isomers of methylglyoxal were formed during PFBHA derivatisation resulting in two peaks in the GC/MS chromatogram. For quantification, the sum of these peaks was used to avoid an over- or underestimation of methylglyoxal due to variations of the isomer peak ratio during the heating process.

3.1 Method development

Influence of heating time

The influence of the heating time was examined with PTFE filters which were sampled after the OH-radical oxidation of 1,3,5-TMB at RH = 75% in the presence of NH_4HSO_4 seed particles (experiment #3). To investigate the effect of the heating time on the cleavage of the oligomeric compounds, the aqueous filter extracts (extract 1) were acidified to pH = 1 and heated to 100°C for 15 – 48 hours. The results were compared to the unheated aqueous filter extract (extract 2) to determine the increase of methylglyoxal concentration due to decomposition of the oligomer. Additionally, a 6.25 µmol L^{-1} standard solution of methylglyoxal was acidified and heated for different times to exclude an effect of the heating process on the derivatisation. The results are illustrated in Fig. 1a.

The highest methylglyoxal concentration can be found after a heating time of 24 hours. After 24 hours, methylglyoxal concentration was about six times higher ($c = 1.82 \pm 0.14$ µmol L^{-1}) in comparison to the unheated filter extract ($c = 0.29 \pm 0.01$ µmol L^{-1}). To exclude that the higher methylglyoxal concentrations were only a result of a better PFBHA derivatisation during heating, a methylglyoxal standard solution was also heated for 24 hours (Fig. 1b). A methylglyoxal concentration of $c = 5.32 \pm 0.05$ µmol L^{-1} was found which corresponds to a recovery of ≈ 85%. Thus, an effect of the heating process on the derivatisation can be excluded indicating that the higher methylglyoxal concentration was caused by decomposition of oligomers into monomers.

One filter extract was heated for 15 hours and allowed to stand at room temperature for 9 hours (sample a) to reach a total derivatisation time of 24 hours (as it was optimised for PFBHA derivatisation by Rodigast et al., 2015). To exclude reoligomerisation processes of methylglyoxal in sample a, one filter extract was heated for 15 hours and measured directly after the heating process (sample b). As it can be seen in Fig. 1a both filter samples (sample a and b) showed lower methylglyoxal concentrations than after heating for 24 hours. Lower methylglyoxal concentration of sample b might be caused by an incomplete derivatisation due to the immediate measurement of the filter extract after 15 hours heating time. In comparison, the lower concentration in sample a might be caused by reoligomerisation of methylglyoxal.

To probe this hypothesis a 6.25 µmol L^{-1} methylglyoxal standard was heated for 15 hours and measured immediately (like sample a) or, alternatively, was allowed to stand at room temperature for 9 hours (like sample b). In Fig. 1b a lower methylglyoxal concentration can be observed for the immediately measured sample (3.11 ± 0.20 µmol L^{-1}) compared to the sample after 9 hours at room temperature (5.84 ± 0.27 µmol L^{-1}). Thus, it can be concluded that a derivatisation time of 24 hours is needed for a complete derivatisation despite the heating process. This supports the hypothesis that methylglyoxal monomers were not completely derivatised, if the filter sample was heated for 15 hours and directly measured (sample b). Based on the incomplete derivatisation after 15 hours heating time, methylglyoxal monomers are able to react again under oligomer formation during the 9 hours at room temperature. The rate constants are reported to be $k = 5 \times 10^{-6}$ M^{-1} minutes^{-1} for ammonium ion catalysed and $k \leq 1 \times 10^{-3}$ M^{-1} minutes^{-1} for H_3O^+ catalysed aldol reaction (Sareen et al., 2010). Naturally, both of these ions might be present in the aqueous filter extract.

Longer heating times than 24 hours (30 and 48 hours) led to lower methylglyoxal concentrations in the filter samples as well. A possible explanation might be the decomposition of the derivatised compound during the long heating process. As no decrease of the concentration was observed in the methylglyoxal standard solution (Fig. 1b) the loss of the derivatisation group is unlikely as a reason for the lower concentrations. Based on the outlined results, a heating time of 24 hours was chosen.

The pH during the heating process was investigated even if pH = 1 was found as an optimal pH for the PFBHA derivatisation (Rodigast et al., 2015)

Influence of pH

The effect of the pH was examined with PFTFE filters, which were sampled after the OH-radical oxidation of 1,3,5-TMB at RH = 50% in the presence of NH_4HSO_4 particles (experiment #2). The pH was varied between pH = 1 and pH = 7.

As it can be seen in Fig. 2a the highest methylglyoxal concentration can be found at pH = 1. The methylglyoxal concentration was about two times higher at pH = 1 (c = 1.01 ± 0.11 µmol L^{-1}) compared to the filter extract, which was neither heated nor acidified (c = 0.45 ± 0.01 µmol L^{-1}). An increasing pH leads to a lower methylglyoxal concentration which can be observed for filter samples (Fig. 2a) as well as for methylglyoxal standard solution (Fig. 2b). As this was observed for both types of samples it appears that the pH influences the derivatisation and/or the oligomer decomposition. As no influence of the pH on the PFBHA derivatisation reaction is reported by Rodigast et al., 2015, it can be concluded that the effect of the pH is connected to thermal decomposition of the oligomeric compounds. In summary, based on these results pH = 1 was used.

Influence of heating temperature

To examine the effect of the heating temperature, filter samples of experiment #2 were used. The heating temperature was varied between 50°C and 100°C and the filter extracts were heated for 24 hours at pH = 1. A temperature above 100°C cannot be used to avoid evaporation of water and/or target compounds. Fig. 3a shows the influence of the temperature on the decomposition of the methylglyoxal oligomers into monomers. Higher concentration of methylglyoxal can be detected with higher temperature. The results illustrated in Fig. 3a indicate that a higher temperature than 50°C is needed to decompose the oligomeric compounds. In comparison to the filter, which was neither acidified nor heated, the concentration was increased by a factor of two if the extract was heated to 100°C. Fig. 3b shows no significant influence of the temperature on the methylglyoxal standard solution. Thus, an influence of the heating temperature on the derivatisation procedure can be excluded.

Based on these results, the PTFE filter extracts from the aerosol chamber experiments were acidified to pH = 1 and heated for 24 hours to 100°C to decompose oligomeric compounds into methylglyoxal. Noticeably, among the investigated filter samples no other carbonyl compounds showed an increase after thermal decomposition indicating that oligomers present in the particle phase of 1,3,5-TMB oxidation are solely methylglyoxal oligomers and/or oligomers of other carbonyl compounds need different conditions for decomposition.

The developed method was afterwards applied to laboratory-generated SOA formed by the oxidation of 1,3,5-TMB.

3.2 SOA yield and growth curves of 1,3,5-TMB oxidation

SOA formation of 1,3,5-TMB was investigated in a number of literature studies mostly in the presence of NO_x and under variation of the hydrocarbon to NO_x ratio ($[HC]/[NO_x]$ ratio). Healy et al., 2008 determined SOA yields (Y_{SOA}) of 1,3,5-TMB photooxidation in a range of 4.5 – 8.3%. Further studies determined Y_{SOA} between 0.29% and 15.6% (Table 4) under variation of the $[HC]/[NO_x]$ ratio and concluded that SOA formation is enhanced at low NO_x mixing ratios (Sato et al., 2012; Kleindienst et al., 1999; Baltensperger et al., 2005; Wyche et al., 2009; Odum et al., 1997; Paulsen et al., 2005; Cocker et al., 2001). Only Cao and Jang, 2007 investigated SOA yields in the absence of NO_x and reported values between 7.1 and 13.8%. The SOA yields (Y_{SOA}) were also determined in the present study for all conducted experiments based on the ratio of ΔM to ΔHC (Table 2). Y_{SOA} varied between 4 and 7% dependent on reaction conditions and is in good agreement to literature values.

For a further investigation of SOA-formation processes of 1,3,5-TMB, Fig. 4a illustrates the dependency between the consumption of 1,3,5-TMB (ΔHC) and the produced organic particle mass (ΔM). Particle growth started directly after the experiment was initialised indicating that the oxidation leads immediately to the formation of condensable products as first-generation oxidation products. These products condensate on the pre-existing seed particles resulting in the immediate particle growth observed in Fig. 4a. Differences of the growth curves in dependence on the seed particles (NH_4HSO_4 and $(NH_4)_2SO_4/H_2SO_4$) were not observed concluding that the seed particle acidity (Table 5) has no influence on the SOA formation of 1,3,5-TMB. This is in good agreement with the studies by Cocker et al., 2001 and Wyche et al., 2009 which observed no differences of SOA formation in the presence or absence of seed particles during the photooxidation of 1,3,5-TMB with NO_x. Cao and Jang, 2007 found also only a small influence of seed particle acidity on SOA formation.

Fig. 4a showed great differences in the growth curves under variation of RH. ΔM is the highest at RH = 0% (ΔM = 18.1 – 19.7 µg m^{-3}) whereas ΔM is the lowest under humid conditions (RH = 50% and 75%, ΔM = 11.3 – 11.7 µg m^{-3} and 13.9 – 14.2 µg m^{-3}). Due to the variation of RH in the aerosol chamber the liquid water content (LWC) of the particles is changing (Table 5). The LWC was calculated using model II from the extended aerosol thermodynamic model (E-AIM; Clegg et al., 1998). With increasing RH the LWC of the seed particle increases as well. The LWC of the seed particles influences i) the partitioning of the compounds from the gas phase into the particle phase and ii) the formation and/or further reaction in the particle phase (Zuend et al., 2010; Cocker et al., 2001; Seinfeld et al., 2001; Fick et al., 2003). These two effects might influence the SOA formation under different relative humidities.

An effect can also be seen in Fig. 4b. The SOA formation is enhanced at RH = 0% leading to the highest SOA yields of $Y_{SOA} \approx 7\%$ for both seed particles. Higher RH resulted in lower Y_{SOA} between 4 and 5%. These findings are in good agreement with the study by Cao and Jang, 2007, which observed lower Y_{SOA} values at elevated RH.

The influence of RH on SOA formation is controversially discussed in the literature (Hennigan et al., 2008; Fick et al., 2003; Edney et al., 2000; Saxena and Hildemann, 1996; Baker et al., 2001; Hasson et al., 2001, Cocker et al., 2001). Edney et al., 2000 and Seinfeld et al., 2001 reported an enhanced SOA formation of hydrophilic compounds under humid conditions and a lowered SOA formation of hydrophobic compounds. This is also supported by Saxena and Hildemann, 1996 which found an enhanced partitioning of organic compounds with several hydroxyl groups at higher LWCs of the particles. This might lead to the conclusion that the OH-radical oxidation of 1,3,5-TMB results in the formation of hydrophobic compounds which showed an enhanced partitioning under dry conditions. Additionally, the formation of oligomeric compounds can be enhanced at lower RH values resulting in higher Y_{SOA} due to the increasing conversion of the monomeric building blocks and their enhanced partitioning into the particle phase.

3.3 Particulate methylglyoxal

Methylglyoxal is reported in the literature as an important oxidation product of 1,3,5-TMB (Metzger et al., 2008; Healy et al., 2008; Cocker et al., 2001; Smith et al., 1999; Wyche et al., 2009; Baltensperger et al., 2005; Rickard et al., 2010; Kalberer et al., 2004; Yu et al., 1997; Kleindienst et al., 1999; Muller et al., 2012; Nishino et al., 2010; Hamilton et al., 2003; Tuazon et al., 1986; Bandow and Washida, 1985) with yields in the particle phase between 0.7 and 2%.

The fraction of methylglyoxal in the particle phase in dependency on the reaction conditions is shown in Fig. 5a, with resulting fractions between ≈ 0.6% and ≈ 2.2%. With increasing RH the fraction decreases for both seed particles. Methylglyoxal has the highest fraction under dry conditions (1.73 ± 0.20% and 2.17 ± 0.20% for NH_4HSO_4 and $(NH_4)_2SO_4/H_2SO_4$) and with $(NH_4)_2SO_4/H_2SO_4$ seed particles.

Healy et al., 2008 measured a contribution of methylglyoxal to SOA mass of 2.06 ± 0.08% from the photooxidation of 1,3,5-TMB in the presence of NO_x at RH = 50%. In the present study a methylglyoxal fraction of 1.24 ± 0.04% for NH_4HSO_4 seed particles and 0.80 ± 0.08% for $(NH_4)_2SO_4/H_2SO_4$ seed particles was determined at RH = 50%. Thus, the contribution is slightly lower than measured by Healy et al., 2008. In comparison, Cocker et al., 2001 measured a particulate fraction of 0.72%.

The dependency of particulate methylglyoxal on RH could be a result of the influence of RH on the partitioning from the gas- into the particle phase or on further reactions in the particle phase forming oligomers. This has been investigated in a number of studies (e. g. De Haan et al., 2009; Kalberer et al., 2004; Loeffler et al., 2006; Zhao et al., 2006; Sareen et al., 2010; Altieri et al., 2008).

3.4 Methylglyoxal oligomers

A method was developed to determine the contribution of methylglyoxal oligomers to the produced organic particle mass ΔM. The method is based on the thermal decomposition of the methylglyoxal oligomers. Thus, the concentration of monomeric methylglyoxal was determined prior and after thermal decomposition. The concentrations were converted into the fraction of methylglyoxal oligomers of ΔM using the molar mass of methylglyoxal (Mw = 72.06 g mol^{-1}; Table 6). An oligomer fraction of ≈ 2 up to 8% was observed.

Fig. 5b shows the dependency of the detected methylglyoxal oligomers on the relative humidity with NH_4HSO_4 and $(NH_4)_2SO_4/H_2SO_4$ seed particles. In the presence of NH_4HSO_4 seed particles the highest oligomer fraction (8.2 ± 0.7%) can be observed with RH = 0% whereas in the presence of $(NH_4)_2SO_4/H_2SO_4$ seed particles the oligomer fraction is the lowest (2.1 ± 0.4%) under dry conditions. A possible explanation for the opposite trend could be a different oligomer formation mechanism dependent on the different seed particles. The type of accretion reaction might change with pH (Yasmeen et al., 2010). In Table 5 the pH of the seed particles were calculated with E-AIM. NH_4HSO_4 particles have pH = 0.1 and 1.2 at RH = 50% and 75%. In comparison $(NH_4)_2SO_4/H_2SO_4$ seed particle are less acidic (pH = 4.0 at RH = 50% and pH = 4.2 at RH = 75%).

It was postulated by Yasmeen et al., 2010 that a lower pH (pH < 3.5) favor acetal/hemiacetal formation whereas at high pH (pH = 4 - 5) aldol condensation are more relevant. This has been supported by Sedehi et al., 2013 and Sareen et al., 2010.

Thus, in the presence of strong acidic NH_4HSO_4 seed particles acetal/hemiacetal formation might be the favored oligomer formation mechanism. Oligomerisation via acetal/hemiacetal formation occurs under water loss (Yasmeen et al., 2010). Higher RH in the aerosol chamber LEAK leads to higher LWCs in the seed particles (Table 5). With higher LWC in the particles the chemical equilibrium shifts towards the precursor compound resulting in a lower methylglyoxal oligomer fraction (Kalberer et al., 2004; Liggio et al., 2005). The pH of NH_4HSO_4 particles decreases with decreasing RH (Table 5). Acetal/hemiacetal formation is an acid-catalysed reaction and thus oligomer formation might be enhanced under dry conditions due to a lower pH (Liggio et al., 2005).

In the presence of $(NH_4)_2SO_4/H_2SO_4$ seed particles the oligomer fraction increases with increasing RH (Fig. 5b). As it was mentioned, aldol condensation can be assumed as the favored accretion reaction (Yasmeen et al., 2010). Aldol condensation includes as a first step aldol addition followed by a loss of water. The loss of water is irreversible, thus the aldol condensation will not be inhibited with higher LWC of the seed particles.

Other accretion reactions can contribute to the formation of methylglyoxal oligomers with $(NH_4)_2SO_4/H_2SO_4$ seed particles as well. Altieri et al., 2008 detected products formed through acid-catalysed esterification at pH ≈ 4. This equilibrium reaction involves the loss of water as it was reported for acetal/hemiacetal formation (Lim et al., 2010). Thus, it can be expected that with higher LWCs the contribution of esterification reactions to oligomer formation decreases.

Imidazole formation was also postulated as possible oligomer-formation mechanism for methylglyoxal (Sedehi et al., 2013; De Haan et al., 2011). It was found that imidazole formation is of minor importance compared to aldol condensation (Sedehi et al., 2013). However, imidazole formation involves also a loss of water, thus is does not provide a feasible explanation for the higher oligomer fraction at higher RH with $(NH_4)_2SO_4$/H_2SO_4 seed particles.

Radical – radical reactions are also postulated as a possible reaction pathway to form oligomers (Schaefer et al., 2015; Lim et al., 2013; Rincon et al., 2009; Lim et al., 2010; Sun et al., 2010). Radical-radical reactions of methylglyoxal might occur following the H - atom abstraction of methylglyoxal with OH radicals and a subsequent recombination of the resulting alkyl radicals (as discussed for glyoxal in Schaefer et al., 2015). The contribution of radical – radical reactions to oligomer formation is not well understood as obviously, the reaction of alkyl radicals with oxygen tends to suppress this pathway. Nevertheless, it can be expected, that with higher LWC of the seed particles and thus with a higher reaction volume, the absolute amount of methylglyoxal in the particle phase might increases, but not its particle-phase concentrations. For aerosol particle systems, ionic strength effects (Herrmann et al., 2015) are able to influence the uptake of methylglyoxal into the particle phase as well. Waxman et al. (2015) observed a salting-out effect for methylglyoxal for all investigated seed particles at higher ionic strengths.

Low pH combined with high solute concentrations as calculated for the present aerosol particles, can trigger isomerisation (or switching) reactions as discussed by Herrmann et al., 2015. Overall, a clear discussion on how radical-radical reaction might be affected by increasing LWC (through increasing RH) and by pH is difficult at the current level of knowledge.

In summary, the present study provides a reliable quantification method of methylglyoxal oligomers formed by 1,3,5-TMB oxidation. The fraction of oligomeric substances formed solely by methylglyoxal oligomerisation varied dependent on RH and seed particle acidity between 2 – 8%, which is lower than the determined values by Kalberer et al., 2004 and Baltensperger et al., 2005 (varying between 50 and 80%). In the present study only methylglyoxal oligomers were quantified, thus there might be oligomers originating from other monomers than methylglyoxal, which were not determined in the present study leading to lower oligomer fractions of ΔM compared to the literature studies. The obtained data are not fully conclusive and literature studies are often contradicting. Thus, more experiments are necessary to get a clearer picture about the influence of RH and particle phase acidity on oligomer formation and to explain the non-linear relation between the oligomer fraction and RH.

4. Summary

In the present study a method was developed to quantify oligomers formed from methylglyoxal. The method is based on the thermal decomposition of methylglyoxal oligomers into monomers. The formed methylglyoxal monomers were detected with PFBHA derivatisation and GC/MS analysis. The influence of heating time, pH and heating temperature on the decomposition of methylglyoxal oligomers was systematically investigated. The best result was achieved with a heating time of 24 hours at 100°C and pH = 1. The method was applied to methylglyoxal oligomers formed during the oxidation of 1,3,5-TMB resulting in an oligomer fraction of up to

≈ 8%. A contradicting dependency of the oligomer fraction under varying RH with NH_4HSO_4 and $(NH_4)_2SO_4/H_2SO_4$ seed particles was found, which might be caused by different oligomer formation mechanisms.

Overall, the present method provides an important step revealing the amount of oligomers present in the particle phase, their tentative formation mechanism and their importance for aqSOA formation.

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Table 1: Overview of methods for structure elucidation of oligomeric compounds (after Hallquist et al., 2009).

Method	Reference
(Matrix assisted) laser desorption/ionisation mass spectrometry (MALDI-MS, LDI-MS)	Dommen et al., 2006; Kalberer et al., 2004; Kalberer et al., 2006; Reinhardt et al., 2007; Holmes and Petrucci, 2006; Surratt et al., 2006; Denkenberger et al., 2007
Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR-MS)	Kundu et al., 2012; Altieri et al., 2008; Tolocka et al., 2004; Hall and Johnston, 2012; Denkenberger et al., 2007; Tan et al., 2012
On-line atmospheric pressure chemical ionisation tandem mass spectrometry (APCI tandem MS)	Muller et al., 2008
Aerosol mass spectrometry (AMS)	Sareen et al., 2010; Schwier et al., 2010; Bahreini et al., 2005; Heaton et al., 2007
Electrospray ionisation mass spectrometry (ESI/MS, ESI/MS/MS)	Altieri et al., 2008; Hall and Johnston, 2012; Surratt et al., 2006; Yasmeen et al., 2010; Hastings et al., 2005; Bones et al., 2010; Surratt et al., 2007; Hamilton et al., 2006; Sadezky et al., 2006; Sato et al., 2012; Noziere et al., 2010; Tolocka et al., 2004; Iinuma et al., 2004; Nguyen et al., 2011; Bahreini et al., 2005
Aerosol time of flight mass spectrometry (ALTOFMS)	Huang et al., 2015
Gas chromatography mass spectrometry (GC/MS)	Hastings et al., 2005; Surratt et al., 2006; Szmigielski et al., 2007; Angove et al., 2006
Ion trap mass spectrometry (IT-MS)	Surratt et al., 2006; Gao et al., 2004
Photoelectron resonance capture ionisation-aerosol mass spectrometry (PERCI-MS)	Zahardis et al., 2005
Ultraviolet-visible spectroscopy (UV/Vis)	Nemet et al., 2004; Noziere and Esteve, 2005; Bones et al., 2010; Song et al., 2013; Casale et al., 2007; Alfarra et al., 2006; Drozd and McNeill, 2014; Noziere and Cordova, 2008
Fourier transform infrared spectroscopy (FTIR)	Loeffler et al., 2006; Bones et al., 2010; Jang et al., 2003; Jang and Kamens, 2001; Holmes and Petrucci, 2006
nuclear magnetic resonance spectroscopy (NMR)	Nemet et al., 2004; Bones et al., 2010; Angove et al., 2006; Garland et al., 2006; Kua et al., 2013; De Haan et al., 2011

Table 2: Experiments in the aerosol chamber LEAK for the OH radical oxidation of 1,3,5-TMB. All experiments were conducted at 293 K and with 91.9 ppb 1,3,5-TMB.

Experiment number	seed	RH [%]	O_{3ini} [ppb]	ΔHC [ppb]	ΔM [µg m^{-3}]	SOA yield Y_{SOA} [%]
#1	78 mmol L^{-1} NH_4HSO_4	≈ 0	≈ 137	57.2	19.7	7.00
#2	78 mmol L^{-1} NH_4HSO_4	50	≈ 133	55.2	11.3	4.12
#3	78 mmol L^{-1} NH_4HSO_4	75	≈ 134	56.2	14.2	5.14
#4	60 mmol L^{-1} $(NH_4)_2SO_4$/ 0.4 mmol L^{-1} H_2SO_4	≈ 0	≈ 132	56.2	18.1	6.55
#5	60 mmol L^{-1} $(NH_4)_2SO_4$/ 0.4 mmol L^{-1} H_2SO_4	50	≈ 135	56.5	11.7	4.21
#6	60 mmol L^{-1} $(NH_4)_2SO_4$/ 0.4 mmol L^{-1} H_2SO_4	75	≈ 144	57.2	13.9	4.94

1,3,5-TMB: 1,3,5-Trimethylbenzene; RH: Relative humidity

Table 3: Investigated method parameters and used PTFE filters from 1,3,5-TMB oxidation for method development.

Parameter	Range	Filter of experiment
Heating time	15, **24**, 30, 48 hours	#3
pH	**1**, 3, 5, 7	#2
Heating temperature	50, **100** °C	#2

Selected parameters given in **bold**.

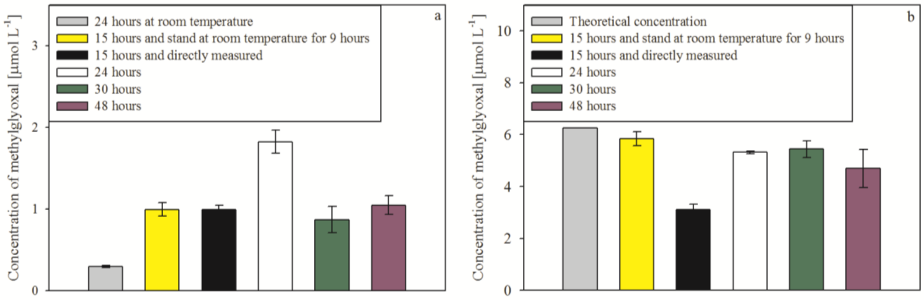

Figure 1: Influence of the heating time on the detected methylglyoxal concentrations in filter samples (a) and the methylglyoxal standard solution (b).

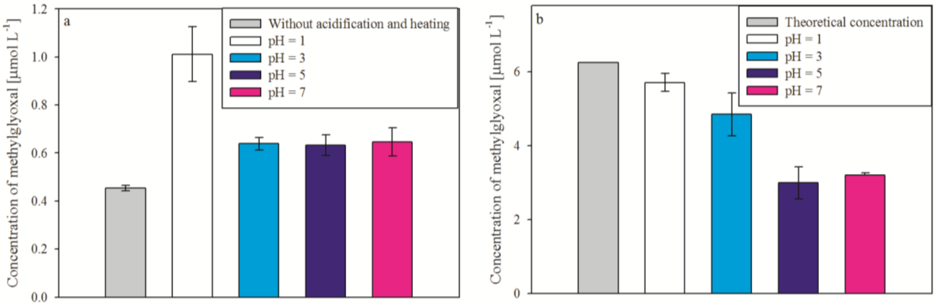

Figure 2: Influence of pH on the detected methylglyoxal concentration in filter samples (a) and the methylglyoxal standard solution (b).

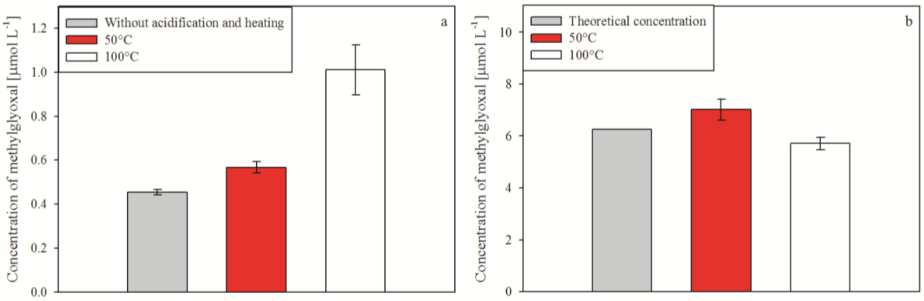

Figure 3: Influence of the heating temperature on the detected methylglyoxal concentration in filter samples (a) and the standard solution (b).

Table 4: SOA yields (Y_{SOA}) of 1,3,5-TMB reported in the literature.

SOA yield Y_{SOA} [%]	**Reference**
2.81 - 7.91	Cocker et al., 2001
4.5 – 8.34	Healy et al., 2008
2.5 ± 0.1 – 15.6 ± 1.0	Sato et al., 2012
3.1	Odum et al., 1997
0.41 ± 0.1	Kleindienst et al., 1999
0.29 – 6.36	Wyche et al., 2009
4.7 ± 0.7	Paulsen et al., 2005
7.1 ± 0.3 – 13.8 ± 0.6	Cao and Jang, 2007

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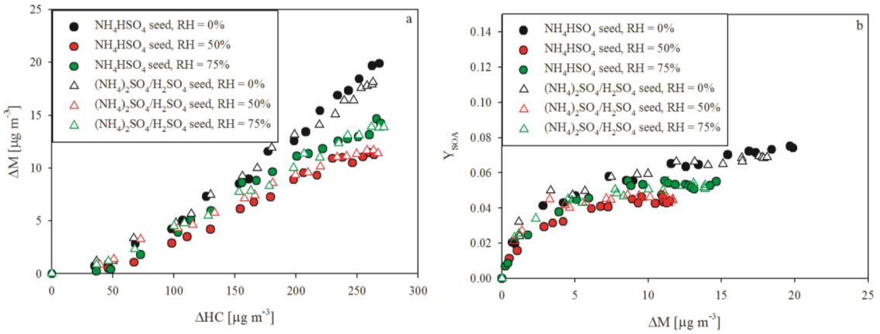

Figure 4: SOA growth curve (a) and yield curve (b) of the OH radical oxidation of 1,3,5-TMB in the presence of NH_4HSO_4 or $(NH_4)_2SO_4/H_2SO_4$ seed under variation of RH.

Table 5: LWC and pH of the seed particles calculated with E-AIM.

seed	RH [%]	pH_{seed}[a]	LWC [g m^{-3}][a]
78 mmol L^{-1} NH_4HSO_4	≈ 0	-[b]	-[b]
78 mmol L^{-1} NH_4HSO_4	50	0.1	6.66 × 10^{-6}
78 mmol L^{-1} NH_4HSO_4	75	1.2	12.29 × 10^{-6}
60 mmol L^{-1} $(NH_4)_2SO_4$/0.4 mmol L^{-1} H_2SO_4	≈ 0	-[b]	-[b]
60 mmol L^{-1} $(NH_4)_2SO_4$/0.4 mmol L^{-1} H_2SO_4	50	4.0	4.25 × 10^{-6}
60 mmol L^{-1} $(NH_4)_2SO_4$/0.4 mmol L^{-1} H_2SO_4	75	4.2	11.56 × 10^{-6}

LWC: Liquid water content; [a] pH and LWC of the seed particles were calculated for different RH using model II from the extended aerosol thermodynamic model (E-AIM; Clegg et al., 1998); [b] calculation of the pH and LWC was not possible due to the low relative humidity of RH ≈ 0%. A RH = 10% is set as lower limit in E-AIM.

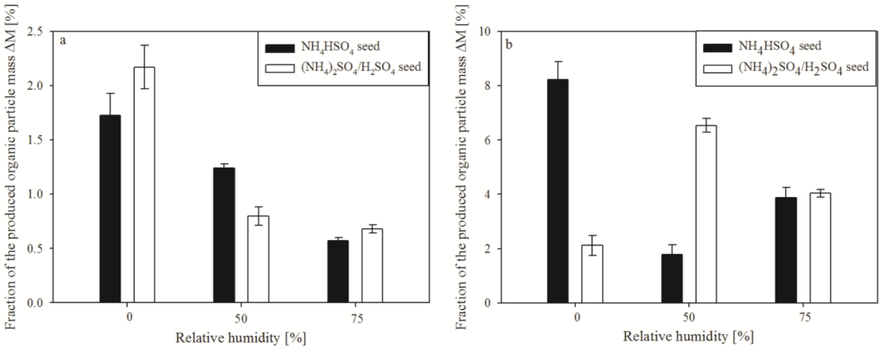

Figure 5: Contribution of methylglyoxal (a) and their oligomers (b) to the produced organic particle mass (ΔM) with NH_4HSO_4 and $(NH_4)_2SO_4/H_2SO_4$ seed particles under variation of the relative humidity.

Table 6: Fraction of methylglyoxal oligomers of ΔM calculated with a molar mass of methylglyoxal (72.06 g mol^{-1}).

Experiment number	Oligomer fraction of ΔM [%]
1	8.2 ± 0.7
2	1.8 ± 0.4
3	3.9 ± 0.4
4	2.1 ± 0.4
5	6.5 ± 0.3
6	4.0 ± 0.1