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Characterization of non-photochemically formed oligomers from methylglyoxal: a pathway to produce secondary organic aerosol through cloud processing during night-time

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Abstract

Aqueous-phase oligomer formation from methylglyoxal, a major atmospheric photooxidation product, has been investigated in a simulated cloud matrix under dark conditions. The aim of this study was to explore an additional path producing secondary organic aerosol (SOA) through cloud processes without photochemistry during nighttime. Indeed, atmospheric models still underestimate SOA formation, as field measurements have revealed more SOA than predicted. Soluble oligomers (n=1–8) formed in the course of acid-catalyzed aldol condensation and acid-catalyzed hydration followed by acetal formation have been detected and characterized by positive and negative ion electrospray ionization mass spectrometry. Aldol condensation proved to be a favorable mechanism under simulated cloud conditions, while hydration/acetal formation was found to strongly depend on the pH of the system. The aldol oligomer series starts with a β-hydroxy ketone via aldol condensation, where oligomers are formed by multiple additions of $C_3H_4O_2$ units (72 Da) to the parent β-hydroxy ketone. Ion trap mass spectrometry experiments were performed to structurally characterize the major oligomer species. A mechanistic pathway for the growth of oligomers under cloud conditions and in the absence of UV-light and OH radicals, which could substantially enhance in-cloud SOA yields, is proposed here for the first time.

1 Introduction

Secondary organic aerosol (SOA) is a substantial component of total organic particulate matter but little is known about the composition of SOA through cloud processing. It has been proposed that, like sulfate, SOA can form through cloud processing, where the high hydroxyl radical concentration in the interstitial spaces of clouds can lead to oxidation of reactive organic molecules to form highly water soluble compounds such as aldehydes (Blando and Turpin, 2000; Ervens et al., 2004; Lim et al., 2005). In-cloud SOA production from alkenes and aldehydes, including isoprene, has been modelled by Lim et al. (2005), where gas-phase isoprene oxidation produces water soluble compounds including glycolaldehyde, glyoxal and methylglyoxal. The partition of the latter products into cloud droplets depends on their reactive uptake coefficients, and, after uptake in the aqueous phase, they can undergo diverse chemical reactions leading to heavier and less volatile molecules. When the cloud droplets evaporate, the low volatility organics remain in part in the particle phase yielding SOA.

Methylglyoxal is found widely in urban, rural, and remote environments (Kawamura et al., 1996, 2005). It is produced in high yield from the oxidation of biogenic volatile organic compounds (VOCs) (e.g., isoprene) (Smith et al., 1999; Atkinson and Arey, 2003; Ham et al., 2006) and anthropogenic VOCs (e.g., mono- and polycyclic aromatics: "BTEX" = benzene, toluene, ethylbenzene, xylenes (Atkinson, 2000; Atkinson and Arey, 2003). Fu et al. (2008) have constructed a global budget of atmospheric glyoxal and methylglyoxal with the goal of quantifying their potential for global SOA formation via irreversible uptake by aqueous aerosols and clouds. An annual global production of 140 Tg of methylglyoxal has been estimated, where biogenic isoprene is the major precursor contributing with 79%, and acetone (mostly biogenic) is the second most important one.

Irreversible heterogeneous uptake of dicarbonyls in clouds or aerosols (probably due to various oligomerization processes) has been suggested as a significant source of SOA (Volkamer et al., 2007). Three aqueous-phase chemical processes have been proposed which could lead to irreversible uptake of methylglyoxal by aqueous aerosols and cloud droplets:

- The first process involves oxidation to form non-volatile organic acids such as glyoxylic, pyruvic, and oxalic acid (Ervens et al., 2004; Crahan et al., 2004; Warneck, 2005; Sorooshian et al., 2006; Sorooshian et al., 2007).
- The second process involves oligomerization of dicarbonyls essentially via hydration and acetal reactions (Schweitzer et al., 1998; Kalberer et al., 2004; Liggio et al., 2005a, b; Hastings et al., 2005; Zhao et al., 2006; Loeffler et al., 2006).

- The third process involves aqueous-phase oxidation of dicarbonyls to organic acids which then oligomerize via esterification (Altieri et al., 2006, 2008).

These three processes have the potential to account for the high oligomer and organic acid concentrations detected in ambient aerosols (Carlton et al., 2007; Denkenberger et al., 2007).

Methylglyoxal is an important intermediate in in-cloud reactions of many reactive organic compounds. The atmospheric lifetime of methylglyoxal is estimated at ~1.6 hr, against photolysis and oxidation by the OH radical, but methylglyoxal can also be taken up by aqueous aerosols and cloud droplets on account of its high water solubility. To ascertain the fate of methylglyoxal in view of its short life-time in the atmosphere, dark chamber experiments have been carried out under simulated cloud conditions. The present work focuses on the mechanistic and structural elucidation of the oligomers formed in the aqueous phase under cloud conditions at night-time.

2 Experimental

2.1 Sample preparation

Methylglyoxal (MGly) solutions were prepared using commercial 40 wt% methylglyoxal in water (Fisher Scientific) and ultrapure water (Millipore ultrapure water system, maximum resistivity 18 MΩ cm). Experiments were carried out in a 175 mL thermostatted (14–15°C) and light-protected cell (electrochemistry reaction cell). With the goal of simulating the cloud conditions in a bulk system, different concentrations (10^{-4} to 10^{-5} mol L^{-1}) of inorganic salts ($(NH_4)_2SO_4$, Na_2SO_4) and H_2SO_4 (10^{-6} mol L^{-1}) were added with a syringe to a continuously stirred solution of MGly (10^{-3} mol L^{-1}). A limited range of acidic conditions, pH=3–5 and ionic strengths was produced and analyzed.

2.2 Electrospray-mass spectrometry (ESI-MS)

Samples were taken every 20–30 min from the reaction cell, diluted with methanol (1:1 (v/v) ratio) and the pH of the final solution was monitored with a micro pH meter. Then, these solutions were introduced into the electrospray source of a linear ion trap mass spectrometer (LXQ, Thermo Scientific, San Jose, CA, USA) at a flow rate of $5\,\mu\text{L}\,\text{min}^{-1}$. First-order spectra were acquired in the range *m/z* 50–1000 in both the positive and negative ion modes. The ion trap and electrospray source were operated under the following conditions: sheath gas flow (nitrogen), $0.75\,\text{L}\,\text{min}^{-1}$; auxiliary gas flow (nitrogen), $1.5\,\text{L}\,\text{min}^{-1}$; source voltage, +/−5 kV; capillary temperature, 250°C; and maximum ion injection time, 200 ms.

The ESI-MS technique uses a soft ionization process that does not fragment compounds and provides molecular weight information with unit mass resolution. The LXQ ion trap mass spectrometer was also used to obtain structural information for a selected number of ions. To achieve fragmentation, a selected ion is collided with the buffer gas (helium) of the ion trap, and fragments are analyzed (MS/MS or MS^2, MS^3 if the process is repeated on fragments of MS^2). For MS^2 and MS^3 experiments, an isolation width of 2 *m/z* units and a normalized collision energy level of 35% were applied.

3 Results and discussion

3.1 Mass spectral results

After one hour in the simulated cloud medium, the first-order mass spectra of the MGly reaction mixture revealed a complex composition with *m/z* values between 200 and 800 (Figs. 1 and 2). The complexity of the spectra increased with reaction time. The spectra showed regular patterns of mass differences (12, 14 and 16 units) suggesting the presence of several oligomer systems with overlapping peaks (Kalberer et al., 2004; Limbeck et al., 2003; Tolocka et al., 2004). Moreover, by using electrospray ionization adducts with alkali metal ions (i.e., Na^+, K^+), the chloride ion (Cl^-) and methanol could be formed complicating structural interpretation. Nevertheless, higher-molecular weight (MW) compounds are produced from MGly at relatively low concentrations in a simulated cloud medium without photochemical action. This chemical process occurs quickly as the abundance of ions with higher *m/z* ratios considerably increases within an hour and strongly depends on the initial MGly concentration, acidity and ionic strength (NH_4^+, Na^+, SO_4^{-2}). In the present study, only relevant results pertaining to cloud conditions will be discussed. It was observed that the NH_4^+ ion has the ability to catalyze oligomerization reactions, hence, for further analysis only ammonium sulphate was chosen. By increasing the concentration of MGly, to simulate the evaporation of the cloud droplet, the production of higher-MW compounds is quasi instantaneous.

3.2 Potential oligomerization mechanisms

In order to better characterize the numerous ions observed in the ESI mass spectra, it is relevant to understand which type of reactions and products are possible when reacting methylglyoxal in slightly acidic medium at low temperature and low concentrations of inorganic salts (natural cloud conditions).

3.2.1 Hydration/acetal formation followed by acid-catalyzed oligomerization

Several studies dealing with the self-oligomerization of glyoxal provided evidence for hydration followed by acetal/hemiacetal formation (Kalberer et al., 2004; Liggio et al., 2005a; Hasting et al., 2005). This self-oligomerization could lead to different molecular structures but it has been shown that the dominant oligomer forms via this mechanism are five-membered ring systems with intervening single bonds. Indeed, these structures are stable as a result of the free rotation of the central C-C bond as compared to other rigid six-membered ring structures. This mechanism that was first established for glyoxal is likely to occur for methylglyoxal in acidic medium, as proposed by Zhao et al. (2006) and shown in Scheme 1.

3.2.2 Acid-catalyzed aldol condensation

A key structural feature of MGly is its methylketone function. Indeed, the keto-form is in equilibrium with the enol-form in aqueous media by tautomerization. In our study, the enol-form of MGly is stabilized by the acidic medium and the conjugation with the second carbonyl group. MGly can therefore undergo an aldol condensation as proposed in Scheme 2. In this case, oligomerization proceeds by the successive addition of a β-hydroxy ketone unit. It was observed in our study that this type of accretion reaction does occur at higher pH than the hydration/acetal formation (first mechanism) and therefore could be more favored in a cloud medium. If these aldol oligomers are formed in the cloud droplet, they will have sufficiently low volatility to transform into new SOA molecules when droplet evaporation occurs. Further dehydration of these compounds could take place via crotonization, leading to highly conjugated molecules (Scheme 3). The UV-visible absorbing properties of these conjugated systems could change the optical properties of aerosols and as such influence the earth's radiation budget as well as promote the formation of cloud condensation nuclei.

3.3 Structural elucidation of the oligomers

Since accretion reactions of MGly operate under cloud conditions via both mechanisms (i.e., aldol condensation and hydration/acetal formation), an effort was done to characterize the accretion products at the molecular level. To this aim, the analysis of the products was performed for reactions occurring at higher pH values (i.e., pH=4–5) considering that these conditions can give more insights into those occurring in clouds. It was noted that accretion reactions via aldol condensation are more prominent at higher pH values, while those via hydration/acetal formation followed by acid-catalyzed oligomerization could not be detected until the pH value was decreased below 3.5.

3.3.1 Interpretation of (+)ESI mass spectral data

When the samples obtained at higher pH values (4.5–5) were analyzed, two distinct Gaussian distributions of peaks were observed in the positive ion mode; the first one in the *m/z* range 100–500 and another in the *m/z* range 500–800 (Fig. 1). A regular pattern with mass differences of 72 mass units between major peaks was observed, consistent with an oligomeric system. Control experiments with only MGly standard solution were also performed but no oligomer formation was observed. Ions in the first Gaussian distribution were observed at *m/z* 159, 231, 271, 303, 329, 343, 375, 383, 401, 447 and 487, while ions in the second one were detected at *m/z* 519, 527, 559, 583, 599, 617, 635, 655, 671 and 727. The MS^n fragmentation behavior of major ions at *m/z* 271, 303, 375 and 447 indicates the presence of hemiacetal groups. Two successive neutral losses of 32 u, corresponding to methanol, were observed, consistent with two hemiacetal groups. The formation of the double hemiacetal can be explained by addition of methanol (i.e., the solvent used in ESI to dilute the sample) to the carbonyl functions. Following the loss of two molecules of methanol, there was a unique loss of 72 u. The major ions at *m/z* 583, 655 and 727 in the second Gaussian distribution showed four successive losses of methanol followed by a unique loss of 72 u. Hence, oligomer molecules with four hemiacetal groups were identified in addition to oligomers containing two hemiacetal groups (i.e., at *m/z* 591, 559, 519 and 487). This formation of four hemiacetal groups was not observed for lower-MW oligomers.

The second most abundant ion series in the first Gaussian distribution (i.e., at *m/z* 203, 275, 347, 419, and 491) and in the second one (i.e., at *m/z* 635, 617, 689) were identified as oligomers containing two hydroxyl groups because they resulted in two successive losses of 18 u, corresponding to H_2O. After the loss of two H_2O molecules, again a unique loss of 72 u was noted. Figure 4 illustrates MS^2 spectra of oligomer molecules containing four monomer units (n=4) and terminal hemiacetal or gem-diol functions, along with a set of MS^2 spectra corresponding to the basic oligomer series containing terminal keto groups with n between 4 and 8. The fragmentations observed in the three oligomer series are summarized in Fig. 5.

The first oligomer series (Fig. 5; white circles) comprises products formed by self-oligomerization of MGly via aldol condensation. The first ion of the white series corresponds to sodiated MGly $[\mathrm{MGly+Na}]^+$ (m/z 95) as MGly will have affinity for Na^+ which is present in electrospray ion source. The addition of 72 u is consistent with β-hydroxy-ketone ($C_3H_4O_2$, enol form) addition via the aldol condensation mechanism. The oligomer pattern could be followed until m/z 599, which is attributed to the aldol product ion $[8\,\mathrm{MGly+Na}]^+$. Beyond m/z 600, the spectra became too crowded, making assignment of ion structures difficult. Selected hypothetical structures based on mass spectral interpretation for oligomer series up to n=4 are presented in Table 1. In addition, no evidence was found for structures formed through the first oligomerization mechanism (five-membered-ring systems) at the higher pH values.

Upon decrease of the pH to a value ≤3.5 oligomerization via the acetal/hemiacetal mechanism (Fig. 2) became predominant. An oligomer system could be discerned with distinct ions at m/z 180, 236, 252, 270, 306, 324, 342, 396, 486, 594, 666, 738 and 810 (Fig. 7). Abundant ions are at m/z 236, 252, 270, 306, 324 and 342, corresponding to major species of the oligomer series. The ion at the lowest m/z value (180) corresponds to the protonated dimer, which can be explained by reaction between the double gem-diol form of MGly (MW 108) (72+18+18=108) and another molecule of hydrated MGly. In a similar way, a trimer with MW 252 (and higher oligomers) can be generated by reaction of the dimer (or higher oligomers) and the gem-diol form of an additional molecule of MGly. Selected hypothetical structures up to oligomer series n=4 based on mass spectral interpretation are presented in Table 2. An intriguing observation is that these oligomers are detected in the positive ion ESI mode as molecular radical cations and not as protonated molecules. A straightforward explanation for this phenomenon could not readily be formulated. In order to find support for the structure of the tetramer detected at m/z 342, MS^n (n=2, 3 and 4) spectra were recorded (Fig. 8). The fragmentation pathways support the proposed hypothetical structures.

3.3.2 Interpretation of (−)ESI mass spectral data

To further support the identification of the oligomer series proposed above, negative mode analysis was also performed for the two reaction mixtures in both pH ranges (i.e., pH=3–4 and 4–5). For oligomers produced by aldol condensation, deprotonated molecules of the first Gaussian distribution in addition to deprotonated crotonization products were observed (Fig. 6). The formation of the deprotonated molecules is explained by proton abstraction from mildly acidic protons that are available in aldol oligomers. Indeed, each oligomer formed by aldol condensation contains a terminal methylketone part which can tautomerize to an enol group from which a proton can be abstracted (Table 1). Major ions with a regular mass difference of 72 u are seen at *m/z* 143, 215, 287, 359, and 431, corresponding to those observed in the positive mode. Loss of H_2O (18 u) was also observed from some of the major ions, i.e., from *m/z* 287, 359 and 431, affording product ions at *m/z* 269, 341 and 413, respectively (crotonization). In contrast, deprotonated molecules for the five-membered-ring oligomers formed by acetal reactions were not observed, which could be explained by the electron releasing nature of adjacent methyl groups hindering the ionization of hydroxyl groups.

No evidence was found in the present study for organosulfate formation in aqueous solutions simulating a cloud medium. Organosulfates were detected previously in chamber studies where gaseous dicarbonyls from the photooxidation of isoprene in the presence of acidic ammonium sulphate seed aerosol were reactively taken up in the particle phase and sulfated (Liggio et al., 2005a; Surratt et al., 2007). Organosulfates would afford deprotonated molecules in (−)ESI-MS at a *m/z* value equal to (M+97) and characteristic product ions (i.e., the bisulfate anion at *m/z* 97 $[HSO_4]^-$ and the radical anion at *m/z* 80 $[SO_3]^{-\bullet}$). The lack of organosulfate formation in aqueous solutions simulating dark cloud reactions is in agreement with results obtained in a recent study by Galloway et al. (2009) on organosulfate formation from glyoxal, which demonstrated that in addition to reactive uptake irradiated conditions (or photochemistry) are required for the formation of organosulfates.

4 Conclusions: atmospheric implications

Based on ESI-MS results obtained in the positive and negative ionization modes, the structures of major oligomers formed by aldol condensation and hydrate/acetal formation could be assigned (Tables 1 and 2). The results show that in cloud conditions, the self-oligomerization of MGly occurs preferentially via aldol condensation instead of hydrate/acetal formation because it is favored at higher pH. Thus, in areas where acid seed aerosols are present in high concentrations, the latter mechanism is expected to be important. The pH is probably a limiting factor for the hydrate/acetal formation mechanism in clouds. This result is supported by calculations carried out by Barsanti and Pankow (2005) that indicated that aldol condensation is thermodynamically favorable for methylglyoxal at atmospheric concentrations. In the same way, Nozière and Esteve (2007) established the formation of aldol condensation products from heavier carbonyl compounds in strong acidic media (96–75 wt% H_2SO_4). More recently, Shapiro et al. (2009) reported the formation of light-absorbing (UV) materials, and attributed them to aldol products formed by glyoxal solutions (pH=4). The present study is, to our knowledge, the first one where, on the basis of interpretation of mass spectral data, structural support is presented for the formation of aldol condensation products and related gem-diol products from MGly in cloud conditions.

Although formation of aldol products is kinetically favorable, the process does not appear to occur in the presence of light when OH radicals are present (Altieri et al., 2008). In the latter study, the formation of oligo-esters formed from organic acid monomers seems to be predominant. It is therefore proposed here that aldol and acetal oligomer formation could be an important process during night-time and contribute to SOA production. Further research on the stability of aldol and acetal oligomers and the effect of different parameters (i.e., pH, ionic strength and ionic composition) on their formation is in progress.

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Table 1. Ion structures attributed to selected aldol condensation products on the basis of interpretation of ESI mass spectra.

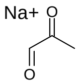
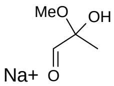
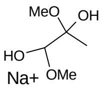
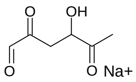
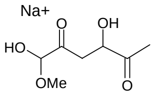
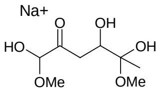
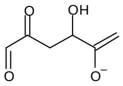
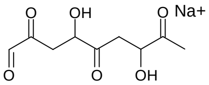
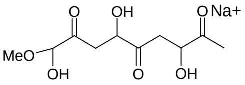
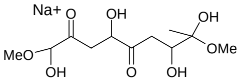
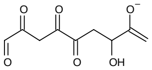
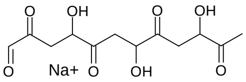
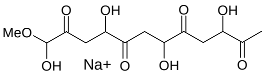
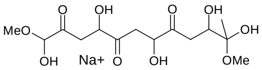
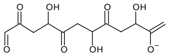
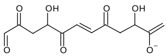
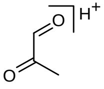
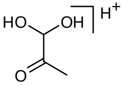
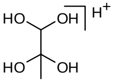
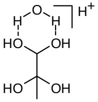
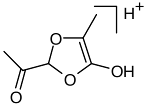
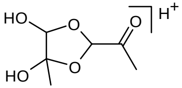
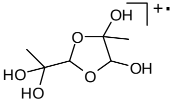
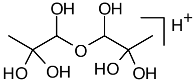
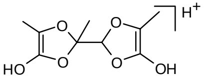
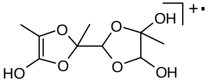
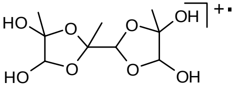
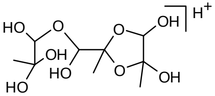
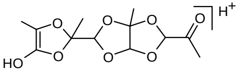
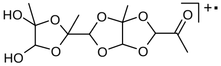
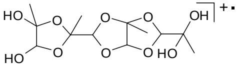
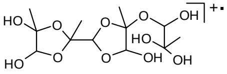
	Positive mode			Negative mode
monomer	 *m/z* 95	 *m/z* 127	 *m/z* 159	not observed
2-mer	 *m/z* 167	 *m/z* 199	 *m/z* 231	 *m/z* 143
3-mer	 *m/z* 239	 *m/z* 271	 *m/z* 303	 *m/z* 215
4-mer	 *m/z* 311	 *m/z* 343	 *m/z* 375	 *m/z* 287  *m/z* 269

Table 2. Ion structures attributed to hydration/acetal products on the basis of interpretation of ESI mass spectra.

	ESI-MS Positive mode			H$_2$O Complexes
monomer	 *m/z* 73	 *m/z* 91	 *m/z* 109	 *m/z* 129
2-mer	 *m/z* 145	 *m/z* 163	 *m/z* 180	 *m/z* 199
3-mer	 *m/z* 217	 *m/z* 234	 *m/z* 252	 *m/z* 271
4-mer	 *m/z* 289	 *m/z* 306	 *m/z* 324	 *m/z* 342

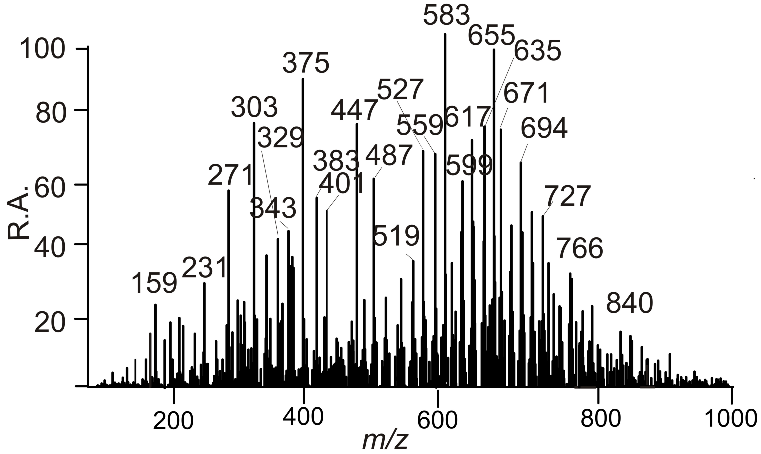


Fig. 1. ESI-MS spectra (positive mode) obtained from the reaction mixture of MGly (10^{-3} mol L^{-1}) with ammonium sulfate (10^{-4} mol L^{-1}) at pH=4.5 and T=15°C after one hour reaction.

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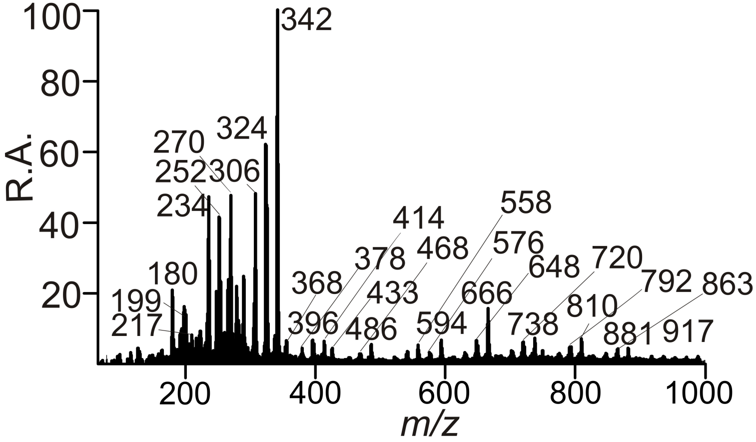

Fig. 2. ESI-MS spectra (positive mode) obtained from the reaction mixture of MGly (10^{-3} mol L^{-1}) with ammonium sulfate (10^{-4} mol L^{-1}) at pH=3.2 and T=15°C after one hour reaction.

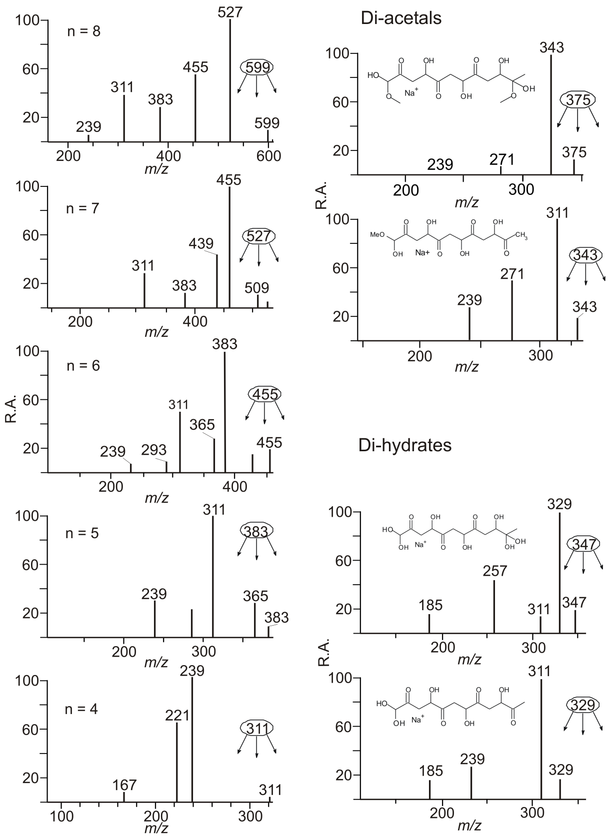

Fig. 3. Successive MS^2 fragmentation of ions formed in (+)ESI-MS of a series of oligomers (n=4–8), and corresponding acetals and hydrates obtained from the reaction mixture of MGly (10^{-3} mol L^{-1}) with ammonium sulfate (10^{-4} mol L^{-1}) at pH=4.5 and T=15°C after one hour reaction.

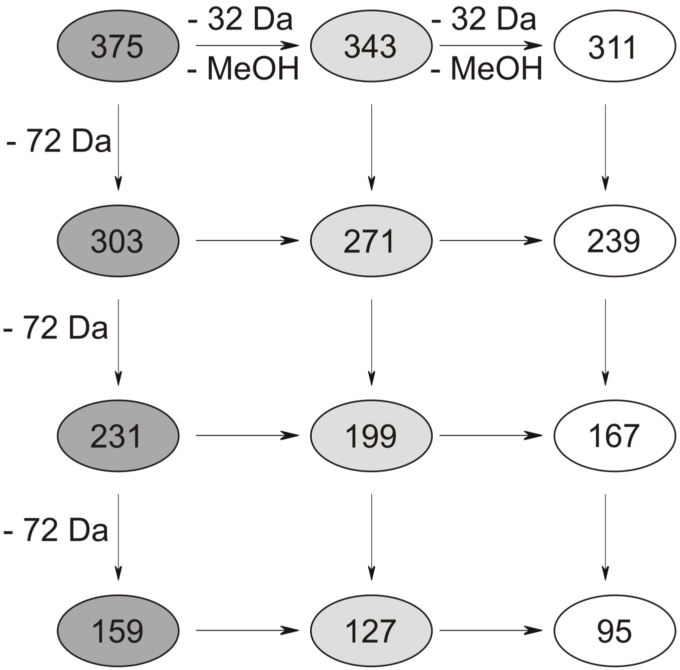

Fig. 4. Fragmentation sequence for the three oligomer series observed in ESI-MS (positive mode) from the reaction mixture of MGly (10^{-3} mol L^{-1}) with ammonium sulfate (10^{-4} mol L^{1}) at pH=4.5 and T=15°C after one hour reaction.

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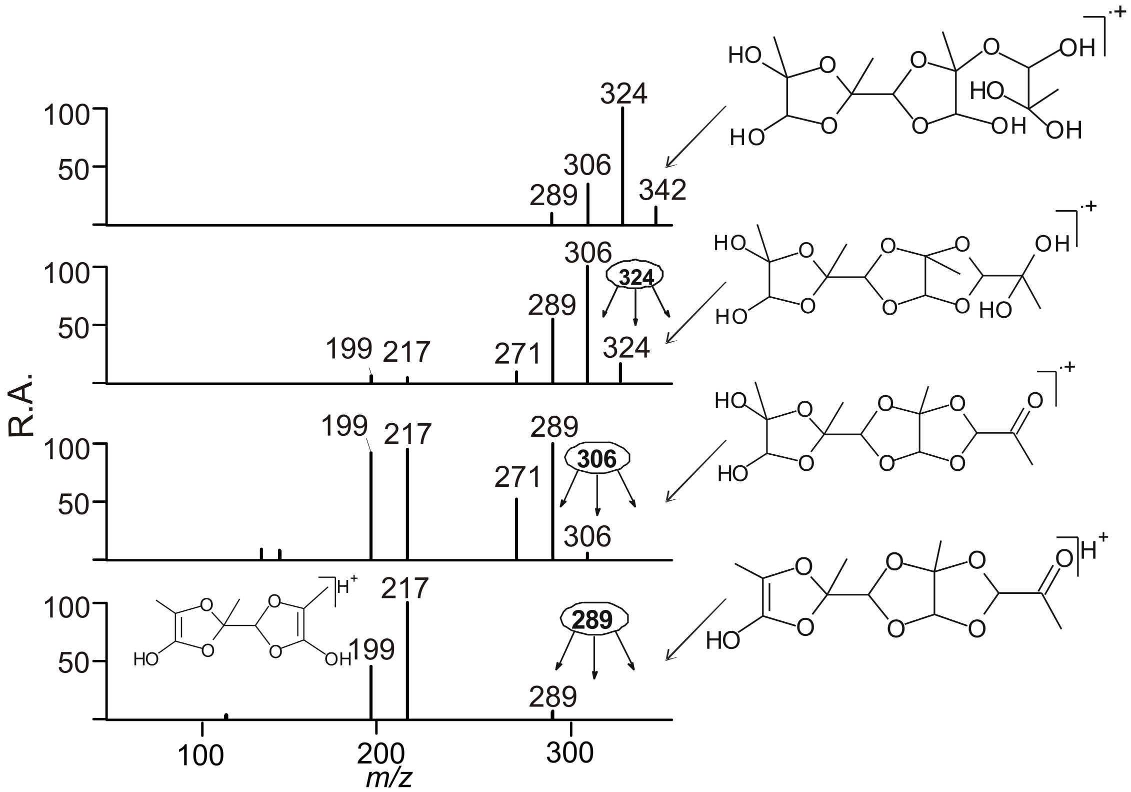

Fig. 5. Successive MS^2 and MS^3 fragmentation spectra of one of the major acetal ions (*m/z* 324) present in the (+)ESI MS spectrum obtained from the reaction mixture of MGly with ammonium sulfate at pH=3.2 and T=15°C after one hour reaction.

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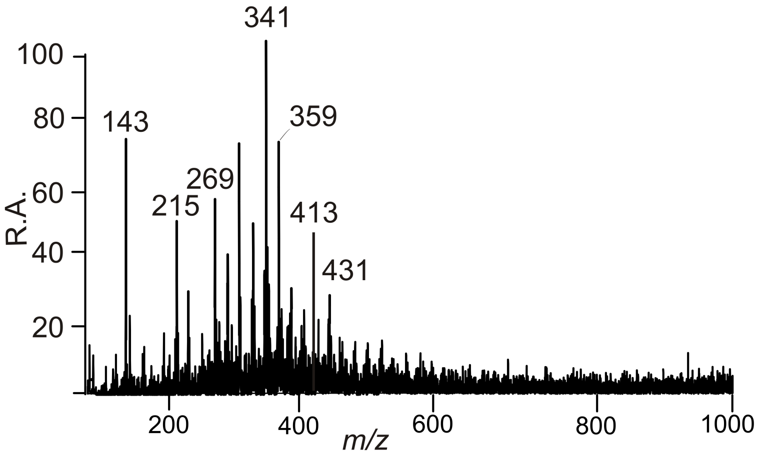

Fig. 6. ESI-MS spectra (negative mode) obtained from the reaction mixture of MGly (10^{-3} mol L^{-1}) with ammonium sulfate (10^{-4} mol L^{-1}) at pH=4.5 and T=15°C after one hour reaction.

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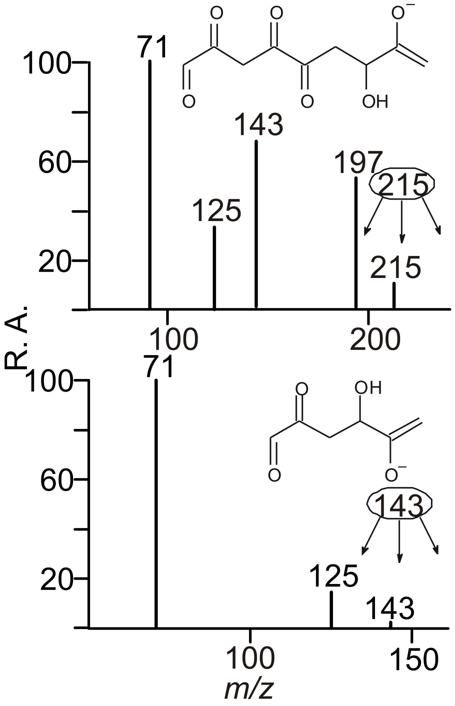
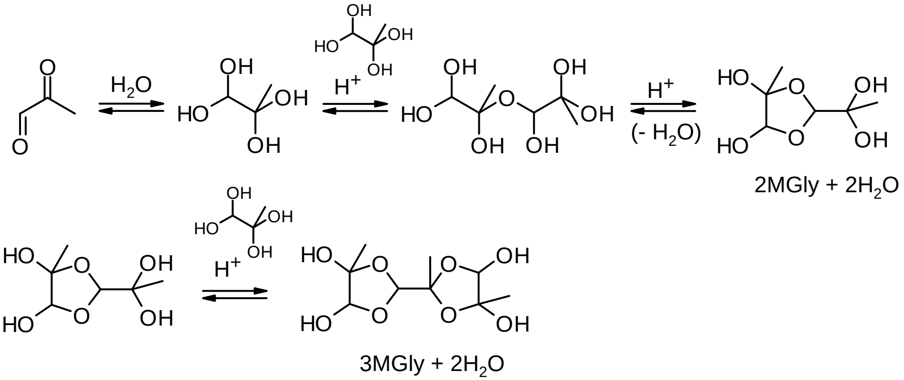
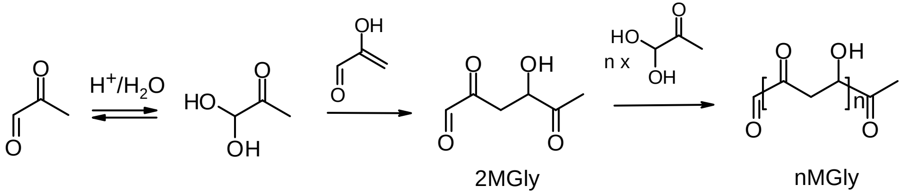


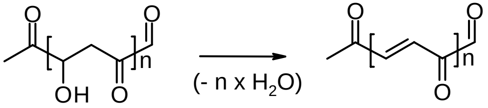
Fig. 7. Successive MS^2 and MS^3 fragmentation spectra (negative mode) of the deprotonated oligomers at *m/z* 215 and 143, obtained from the reaction mixture of MGly (10^{-3} mol L^{-1}) with ammonium sulfate (10^{-4} mol L^{-1}) at pH=4.5 and T=15°C after one hour reaction.



Scheme 1. Potential mechanism for hydration/acetal formation from aqueous MGly solutions.



Scheme 2. Potential mechanism for formation of aldol condensation products from aqueous MGly solutions.



Scheme 3. Potential mechanism for dehydration of aldol condensation products leading to SOA during cloud evaporation.