



# Mechanisms leading to oligomers and SOA through aqueous photooxidation: insights from OH radical oxidation of acetic acid and methylglyoxal

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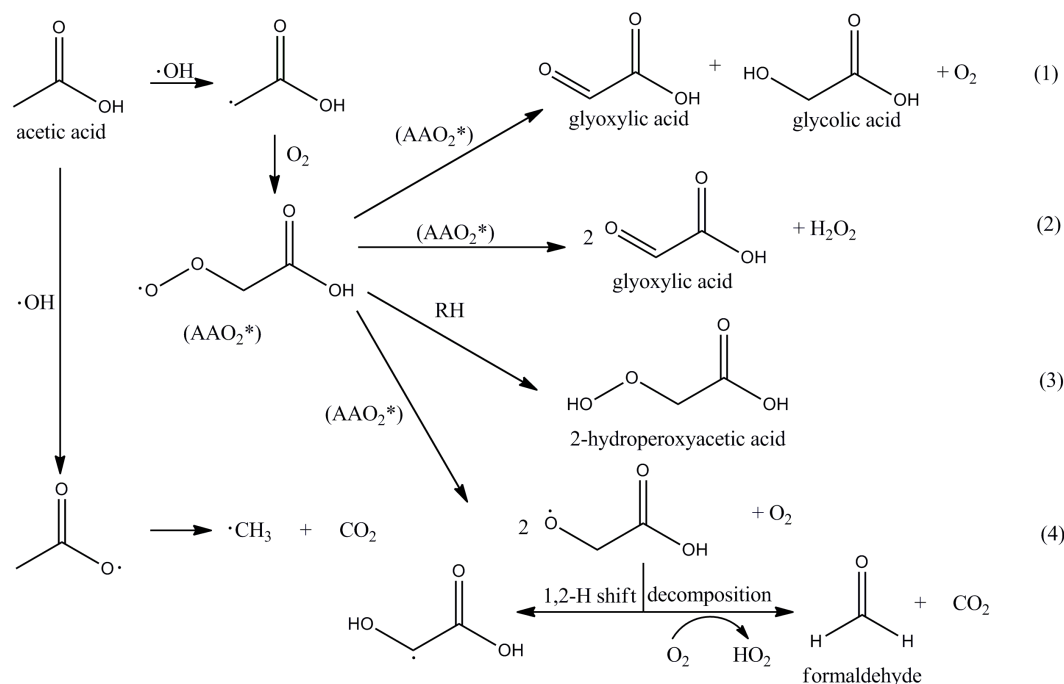
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**Abstract.** Previous experiments have demonstrated that the aqueous OH radical oxidation of methylglyoxal produces low volatility products including pyruvate, oxalate and oligomers. These products are found predominantly in the particle phase in the atmosphere, suggesting that methylglyoxal is a precursor of secondary organic aerosol (SOA). Acetic acid plays a central role in the aqueous oxidation of methylglyoxal and it is a ubiquitous product of gas phase photochemistry, making it a potential “aqueous” SOA precursor in its own right. However, the fate of acetic acid upon aqueous-phase oxidation is not well understood. In this research, acetic acid (20  $\mu\text{M}$ –10 mM) was oxidized by OH radicals, and pyruvic acid and methylglyoxal experimental samples were analyzed using new analytical methods, in order to better understand the formation of SOA from acetic acid and methylglyoxal. Glyoxylic, glycolic, and oxalic acids formed from acetic acid and OH radicals. In contrast to the aqueous OH radical oxidation of methylglyoxal, the aqueous OH radical oxidation of acetic acid did not produce succinic acid and oligomers. This suggests that the methylglyoxal-derived oligomers do not form through the acid catalyzed esterification pathway proposed previously. Using results from these experiments, radical mechanisms responsible for oligomer formation from methylglyoxal oxidation in clouds and wet aerosols are proposed. The importance of acetic acid/acetate as an SOA precursor is also discussed. We hypothesize that this and similar chemistry is central to the daytime formation of oligomers in wet aerosols.

## 1 Introduction

Large uncertainties remain in the predicted impact of secondary organic aerosol (SOA) on air quality, climate and human health (Kanakidou et al., 2005; Hallquist et al., 2009). While the refined treatment of intermediate volatility organic compounds (IVOCs) has in some cases brought predicted organic aerosol mass into better alignment with measured mass (Pye et al., 2010; Jathar et al., 2011), formation of SOA through gas phase reactions followed by partitioning into particulate organic matter (from traditional or IVOC precursors) does not account for observed atmospheric SOA properties. Specifically, the oxygen-to-carbon (O/C) ratio of ambient low-volatility oxygenated organic aerosol (LV-OOA, O/C range 0.83–1.02) is higher than that formed in traditional smog chamber experiments (O/C range 0.3–0.4) (Aiken et al., 2008). Liquid water (in clouds and in aerosols) is ubiquitous in the atmosphere. In fact, globally the mass of aerosol water exceeds the sum of all other particle species including organic matter by 2–3 times (Liao and Seinfeld, 2005). Thus, products of gas-phase photochemistry have greater access to liquid water than to particulate organic matter for partitioning. Laboratory and modeling experiments demonstrate that aqueous oxidation of small water-soluble organic compounds forms SOA with high O/C ratios (Lim et al., 2005, 2010; Carlton et al., 2006, 2008; Ervens et al., 2008; Fu et al., 2008; El Haddad et al., 2009; Yao Liu et al., 2009; Perri et al., 2009; Tan et al., 2009; Ervens and Volkamer, 2010; Sun et al., 2010; Zhang et al., 2010; Myriokefalitakis



**Scheme 1.** Oxidation of acetic acid by OH radical (Leitner and Dore, 1997).

et al., 2011). Field measurements show that aerosols are enriched in “aqueous” SOA tracers above clouds, compared to below clouds, and at high relative humidities (Sooroshian et al., 2010). While an understanding of the aqueous chemistry leading to SOA formation is developing, aqueous reaction mechanisms leading to the formation of higher molecular weight compounds (HMWC) including oligomers, are not well understood; and many potential aqueous SOA precursors are not yet recognized.

Laboratory studies suggest that the aqueous OH radical oxidation of methylglyoxal in atmospheric waters is a source of SOA because this chemistry forms several organic acids (e.g., oxalate, pyruvate, glycolate) and HMWC (Altieri et al., 2008; Tan et al., 2010) that are found predominantly in the particle phase in the atmosphere (Limbeck et al., 2001; Mochida et al., 2003), most likely as salts. The formation of simple carboxylic acids is generally well understood. Pyruvic acid is the major first generation product in the aqueous OH radical oxidation of methylglyoxal (Stefan and Bolton, 1999), and the subsequent oxidation of pyruvic acid yields acetic acid (Carlton et al., 2006). Aqueous OH radicals are expected to react with acetic acid primarily by H abstraction at the methyl group to produce  $\cdot\text{CH}_2\text{CO}(\text{OH})$  radicals, and by H abstraction at the carboxyl group to a minor extent to form the  $\text{CH}_3\text{CO}_2\cdot$  radicals (Scheme 1) (Schuchmann et al., 1985). The  $\text{CH}_3\text{CO}_2\cdot$  radicals decompose to form  $\cdot\text{CH}_3$  radicals and are not expected to participate in bimolecular reactions. Dissolved oxygen adds to  $\cdot\text{CH}_2\text{CO}(\text{OH})$  radicals, producing peroxy radicals ( $\cdot\text{O}_2\text{CH}_2\text{CO}(\text{OH})$ ). Products from the bimolecular reaction of  $\cdot\text{O}_2\text{CH}_2\text{CO}(\text{OH})$  in-

clude glyoxylic and glycolic acids, formaldehyde and  $\text{CO}_2$ , mostly through reactions 1 and 4 in Scheme 1 (Schuchmann et al., 1985; Leitner and Dore, 1997; Benson, 1965; Russell, 1957). About 85 % of acetic acid is converted to glyoxylic acid and subsequently to oxalic acid, the remainder is converted to formaldehyde and formic acid. Note the formation of glycolic acid from acetic acid is not included in the Lim et al. (2005) chemical mechanism, nor in the chemical modeling of aqueous OH radical oxidation of methylglyoxal by Tan et al. (2010). The production of oxalic acid from glycolic acid (via glyoxylic acid) is modest. Mechanisms leading to the formation of HMWC remain ambiguous.

Tan et al. (2010) observed that higher-MW products of methylglyoxal and OH radical become increasingly important as organic concentrations increase from those typically observed in clouds to the higher concentrations found in aerosol water. Acid catalyzed esterification was previously proposed to explain the observed oligomer formation from the methylglyoxal and OH radical reaction, and it was proposed that products of acetic acid and OH radicals initiated the esterification process (Altieri et al., 2008). Specifically, Altieri et al. (2008) suggested that succinic acid was produced via the recombination of  $\cdot\text{CH}_2\text{CO}_2\text{H}$  radicals from acetic acid. Altieri et al. (2008) further proposed that succinic acid was oxidized by OH radicals to give hydroxy acids (e.g., lactic or hydracrylic acid), and that repeated addition of monomers from hydroxy acids (e.g.,  $\text{C}_3\text{H}_4\text{O}_2$  from hydracrylic acid) to parent carboxylic acids (e.g., pyruvic, oxalic, and glyoxylic acids) via esterification formed series of oligomers. Elemental composition and ion fragmentation

**Table 1.** Comparison of acetic acid/acetate with previously identified aqueous SOA precursors.

| Precursor           | Atmospheric aqueous phase concentration                 | Aqueous phase reaction rate constant with OH radical ( $\text{M}^{-1} \text{s}^{-1}$ ) |
|---------------------|---|--|
| Acetic acid/Acetate | 0.4–245 $\mu\text{M}$<br>(Khare et al., 1999)           | $1.6 \times 10^7/8.5 \times 10^7$<br>(Lim et al., 2005)                                |
| Glyoxal             | trace–276 $\mu\text{M}$<br>(Munger et al., 1995)        | $1.1 \times 10^9$<br>(Lim et al., 2005)  |
| Methylglyoxal       | 0.02–128 $\mu\text{M}$<br>(Munger et al., 1995)         | $6.44 \times 10^8$<br>(Lim et al., 2005)   |
| Glycolaldehyde      | 1–5 $\mu\text{M}$<br>(Brüggemann et al., 2005)          | $1.5 \times 10^9$<br>(Lim et al., 2005)  |
| Methyl vinyl ketone | 0.02–0.2 $\mu\text{M}$<br>(van Pinxteren et al., 2005)  | $8 \times 10^8$<br>(Zhang et al., 2010)  |
| Methacrolein        | trace–0.5 $\mu\text{M}$<br>(van Pinxteren et al., 2005) | $1.5 \times 10^9$<br>(Gligorovski and Herrmann, 2004)                                  |
| Phenols             | 0.1–30 $\mu\text{M}$<br>(Sagebiel and Seiber, 1993)     | $6.6 \times 10^9$<br>(Field et al., 1982)  |

patterns of a large number of HMWC in methylglyoxal + OH radical experiments are consistent with this proposed mechanism. However, these oligoesters did not form in a mixed standard containing methylglyoxal, pyruvic acid, acetic acid, glyoxylic acid, oxalic acid and lactic acid; they only formed in the presence of OH radical. The pattern of HMWC formed from the OH radical oxidation of methylglyoxal was similar to that formed from the OH radical oxidation of pyruvic acid (10 mM; Altieri et al., 2006). Altieri et al. (2008) implied that oligomer formation in OH radical oxidation of pyruvic acid could be explained by esterification as well. Calculations indeed suggest that esterification is thermodynamically favorable for carboxylic acids under atmospheric conditions (Barsanti and Pankow, 2006), and the formation of succinic acid in methylglyoxal (3 mM) + OH radical experiments has now been confirmed by electrospray ionization-mass spectrometry with IC separation (IC-ESI-MS) (Tan et al., 2010).

HMWC including oligomers have also been hypothesized to form via organic radical-radical reactions in atmospheric waters from OH radical oxidation (methacrolein, glycolaldehyde, glyoxal, phenols) and photolysis (pyruvic acid) of organics (Guzmán et al., 2006; Yao Liu et al., 2009; Rincón et al., 2009; Lim et al., 2010; Perri et al., 2010; Sun et al., 2010). Guzmán et al. (2006) argued that the reactivity of certain organic radicals towards  $\text{O}_2$  must be lower than previously believed, making radical recombination and the formation of HMWC possible. Similarly, organic radical-radical reactions could play an important role in the formation of higher carbon number products from OH radical reaction of methylglyoxal.

Acetic acid is a key intermediate in the aqueous oxidation of methylglyoxal and a potential “aqueous” SOA precursor itself. Recent estimates put the global source of acetic acid at  $\sim 1400 \text{ Gmol yr}^{-1}$  (Paulot et al., 2011). Gas phase oxidation of acetyl peroxy radicals, acetone, and propene are major sources of acetic acid. Direct emissions (e.g., from biomass burning) and aqueous photochemistry also contribute (Paulot et al., 2011; Warneck, 2005). Acetic acid/acetate partitions readily into atmospheric waters (Henry’s law constant =  $8.8 \times 10^3 \text{ M atm}^{-1}$ ) (Seinfeld and Pandis, 2006). Concentrations of acetate in cloud water, fog water and dew range from 0.4–245  $\mu\text{M}$  (Khare et al., 1999). In the aqueous phase, glyoxal and methylglyoxal react with OH radical faster than acetic acid and have comparable concentrations. Other previously studied aqueous SOA precursors (glycolaldehyde, methyl vinyl ketone, methacrolein) have higher OH radical rate constants but are found at much lower concentrations (Table 1). Aqueous acetic acid oxidation is fast enough to compete with these compounds. To our knowledge, the contribution of acetic acid to SOA has not been previously considered.

The fate of acetic acid is critical to understanding the origin of oligomers in the aqueous phase oxidation of methylglyoxal and evaluating its contribution to the global SOA budget. In our dilute aqueous chemistry model (Tan et al., 2010), 100 % of methylglyoxal is oxidized to pyruvic acid and then to acetic acid, and 85 % of acetic acid is oxidized to glyoxylic acid and subsequently to oxalic acid. This work reports the results of batch aqueous acetic acid + OH radical experiments conducted at four concentrations and new analyses conducted with pyruvic acid and methylglyoxal experiment

samples. We demonstrate that acetic acid can effectively form oxalic acid through aqueous phase reactions under atmospherically relevant conditions. However, neither succinic acid nor oligomers form from the OH radical oxidation of acetic acid at any of the concentrations studied. Below we explain how these and previous results suggest that organic radical-radical chemistry is the likely mechanism for oligomer formation from the OH radical oxidation of methylglyoxal and of pyruvic acid.

## 2 Methods

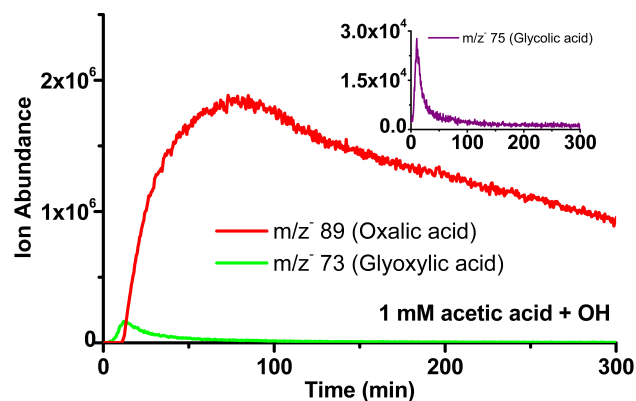
Batch experiments were conducted in a 1 liter glass reaction vessel at  $25 \pm 2$  °C (monitored continuously by thermometer), as described previously (Carlton et al., 2006; Tan et al., 2009). Commercially available acetic acid (Sigma-Aldrich, 99.999% purity) was diluted to 20  $\mu$ M, 100  $\mu$ M, 1 mM, and 10 mM for experiments. OH radicals were generated by UV photolysis (254 nm) of H<sub>2</sub>O<sub>2</sub> with a mercury lamp (Heraeus Noblelight, Inc. Duluth, GA). Initial H<sub>2</sub>O<sub>2</sub> concentrations were 100  $\mu$ M, 500  $\mu$ M, 5 mM, and 20 mM, respectively. Note that a single wavelength light was used rather than a solar spectrum lamp because our goal was to study OH radical reactions rather than photolysis. This lamp and these H<sub>2</sub>O<sub>2</sub> concentrations were needed to generate atmospherically relevant OH radical concentrations which, in the atmosphere are formed instead mostly through gas phase chemistry. The H<sub>2</sub>O<sub>2</sub> photolysis rate was  $k_1 = (1.1 \pm 0.3) \times 10^{-4} \text{ s}^{-1}$ , determined by fitting the simulated H<sub>2</sub>O<sub>2</sub> concentration in H<sub>2</sub>O<sub>2</sub> + UV control experiments, as described previously (Tan et al., 2010). The concentration of OH radicals was approximately  $3 \times 10^{-12}$  M for 20  $\mu$ M, 100  $\mu$ M and 1 mM experiments and a factor of two lower for 10 mM experiments, according to a dilute aqueous chemistry model which includes acetic acid and H<sub>2</sub>O<sub>2</sub> chemistry (Tan et al., 2010). Acetic acid concentrations were depleted during experiments, whereas OH radicals were formed continuously throughout the experiments. Note OH radical concentrations in cloud droplets are believed to be on the order of  $10^{-12}$ – $10^{-14}$  M; the majority coming from the gas phase but with sizeable contributions from aqueous reactions involving Fe(II) (ferrous ion), H<sub>2</sub>O<sub>2</sub> and NO<sub>3</sub><sup>-</sup> (Arakaki and Faust, 1998). The 20 and 100  $\mu$ M experiments reflect acetic acid concentrations observed in cloud and fog water. Higher concentration experiments were designed to better understand oligomer formation from the OH radical oxidation of methylglyoxal (acetic acid is an intermediate). Dissolved oxygen and pH were measured at the beginning and end of experiments (YSI ProODO, YSI Inc., Yellow Springs, OH). Solutions remained saturated with oxygen. pH varied little within experiments, with a pH of 6.6 for the lowest concentration and 3.3 for the highest concentration experiments. At the lowest experimental concentrations (highest pH) acetic acid reacts with OH radicals approximately two times faster

than oxalic acid does. At the highest concentrations (low pH) acetic acid reacts about ten times faster. Experiments were also performed with pyruvic acid (1 mM)+OH radical (formed from 5 mM H<sub>2</sub>O<sub>2</sub>+UV) and 1 mM pyruvic acid+UV. While aqueous pyruvic acid oxidation has been previously reported (Carlton et al., 2006), the analyses of these samples by IC-ESI-MS provide critical new insights.

To investigate the possibility that the presence of H<sub>2</sub>O<sub>2</sub> or UV affects the experimental results, the following control experiments were also conducted: acetic acid+UV, acetic acid+H<sub>2</sub>O<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>+UV, mixed standard (250  $\mu$ M each acetic, formic, glyoxylic, glycolic, succinic, malonic, and oxalic acids)+UV, and mixed standard+H<sub>2</sub>O<sub>2</sub>. Methylglyoxal control experiments have been conducted previously (Tan et al., 2010). Note H<sub>2</sub>O<sub>2</sub> reacts with glyoxylic and pyruvic acids in the absence of OH radical. Methylglyoxal and pyruvic acid photolyze in the absence of OH radical. However, in this and our previous experiments we have found that H<sub>2</sub>O<sub>2</sub> and photolysis reactions are too slow to compete in the presence of OH radical (Tan et al., 2010).

Batch aqueous reactions were monitored in real-time by electrospray ionization mass spectrometry (ESI-MS; HP-Agilent 1100), as described previously (Perri et al., 2009; Tan et al., 2009, 2010). Briefly, solution and mobile phase (40% of 0.05% formic acid in water and 60% methanol) were both continuously delivered from the reaction vessel into the ESI-MS at identical flow rates (0.11 ml min<sup>-1</sup>). Experiments were analyzed in the negative ionization mode with a fragmentor voltage of 40 V and capillary voltage of 3000 V. Discrete samples were collected for analysis by ion chromatography (IC; ICS-3000, Dionex, Sunnyvale, CA; IonPac AS11-HC column with AG11-HC guard column, 30 °C), as described by Tan et al. (2009). Formic, glyoxylic, glycolic, oxalic and mesoxalic acids were identified and quantified with authentic standards and Chromeleon software (version 6.80 SP2, Dionex). Acetic and glycolic acids were not quantified due to coelution. Whether or not it is present, glyoxylic acid cannot be detected in discrete samples because it reacts with residual H<sub>2</sub>O<sub>2</sub> while awaiting analysis. This reaction is not expected to affect concentrations and chemistry in the reaction vessel as it is slow compared to OH radical reactions (Tan et al., 2009). Selected acetic acid and pyruvic acid experiment samples were analyzed by IC-ESI-MS for the first time, via a method described by Tan et al. (2010).

A 1 mM methylglyoxal+OH radical experimental sample taken at 76 min was analyzed by ultra high resolution Fourier transform ion cyclotron resonance electrospray ionization mass spectrometry (ESI FT-ICR MS; Thermo-Finnigan LTQ-XL, Woods Hole Oceanographic Institute Mass Spectrometer Facility; negative ionization mode, variable mass resolution 100 000–750 000) to determine the elemental formulas of products from 50–500 amu, as described previously (Altieri et al., 2009; Perri et al., 2009). FT-ICR MS analyses of methylglyoxal experiments reported previously were limited to >300 amu (Altieri et al., 2008). This



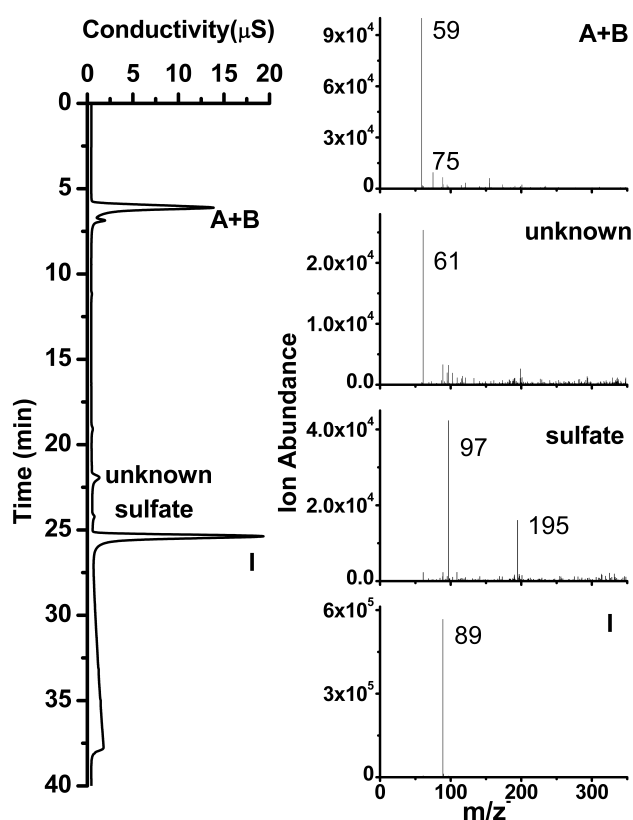
**Fig. 1.** ESI-MS online analysis of 1 mM acetic acid + OH radical experiment.

new analysis yields new insights concerning a key intermediate with  $m/z^-$  177. The sample was diluted with methanol 50:50 v/v and immediately introduced into the ESI source by direct infusion with a flow rate of  $5 \mu\text{l min}^{-1}$ . The needle voltage was 3.02 kV, the capillary voltage was  $-9.44 \text{ V}$ , the capillary temperature was  $260^\circ\text{C}$ , and the tube lens was  $-57 \text{ V}$ . The spectra were mass calibrated using an external calibrant (G2421A Agilent “tuning mix”). The mass lists were processed and exported using Xcalibur v2.0 SR2 (ThermoFisher Scientific). MS/MS analysis was performed on selected ions.

### 3 Results and discussion

#### 3.1 Aqueous phase oxidation of acetic acid by OH radical

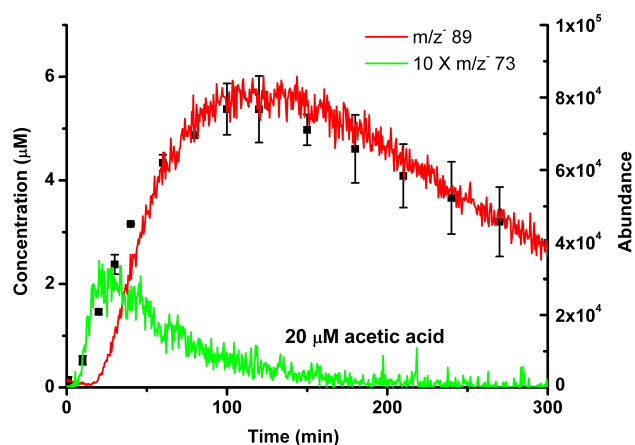
The formation of glyoxylic, glycolic and oxalic acid is supported by the existence of products with  $m/z^-$  of 73, 75 and 89 in the online ESI-MS analysis of the aqueous OH radical oxidation of acetic acid (Fig. 1), and was further verified by IC-ESI-MS analysis (Fig. 2). Glyoxylic acid ( $m/z^-$  73) and glycolic acid ( $m/z^-$  75) both increased rapidly when the experiment started, in agreement with the bimolecular decay of  $\cdot\text{O}_2\text{CH}_2\text{CO}_2\text{H}$  radical. Glyoxylic and glycolic acids are effectively oxidized to oxalic acid ( $m/z^-$  89) (Perri et al., 2009; Tan et al., 2009). Note, with the exception of glycolic acid, this dilute aqueous acetic acid chemistry is contained in the methylglyoxal plus OH radical chemical model published by Tan et al. (2010). Oxalic acid was measured in all experiments containing acetic acid ( $20 \mu\text{M}$ – $10 \text{ mM}$ ) and OH radicals. At the cloud relevant concentration of  $20 \mu\text{M}$  acetic acid, the oxalic acid concentration was 20 % of the acetic acid reacted after 10 min (a typical cloud contact time) and 40 % after 100 min (Fig. 3; Fig. S1). As air parcels encounter clouds multiple times, these longer reaction times are still atmospherically relevant. Note these yields were calcu-



**Fig. 2.** IC-ESI-MS spectrum of a sample taken from 1 mM acetic acid + OH radical batch reactions (120 min reaction time). A + B has the retention time of acetic acid ( $m/z^-$  59), glycolic acid ( $m/z^-$  75) and formic acid (not an expected product, not detected in ESI-MS because its molecular weight is smaller than 50).  $m/z^-$  61 labeled “unknown” is probably carbonate.  $m/z^-$  97 and 195 with the IC retention time of sulfate suggests that sulfate is a low-concentration contaminant; the area of this peak does not change over the course of the experiment. (I) oxalic acid ( $m/z^-$  89).

lated by making use of acetic acid concentrations predicted for the reaction vessel by the aqueous chemistry model in Tan et al. (2010). Given the ubiquitous presence and abundance of acetic acid in the atmosphere, OH radical oxidation of acetic acid could be an important contributor to SOA formed through cloud processing.

Below we compare results from 1 mM acetic acid experiments to results from 1 mM pyruvic acid and 1 mM methylglyoxal experiments in order to better understand the formation of oligomers from the OH radical oxidation of methylglyoxal. These experiments are relevant to chemistry in wet aerosols, where the concentrations of total dissolved organics are 1–10 M. Interestingly, unlike the oxidation of pyruvic acid and methylglyoxal, neither succinic acid ( $m/z^-$  117) nor HMWC/oligomers were detected in any acetic acid experiment (Figs. 2, 4) despite the fact that acetic acid is an intermediate product of methylglyoxal and pyruvic acid and OH radical concentrations in these experiments were



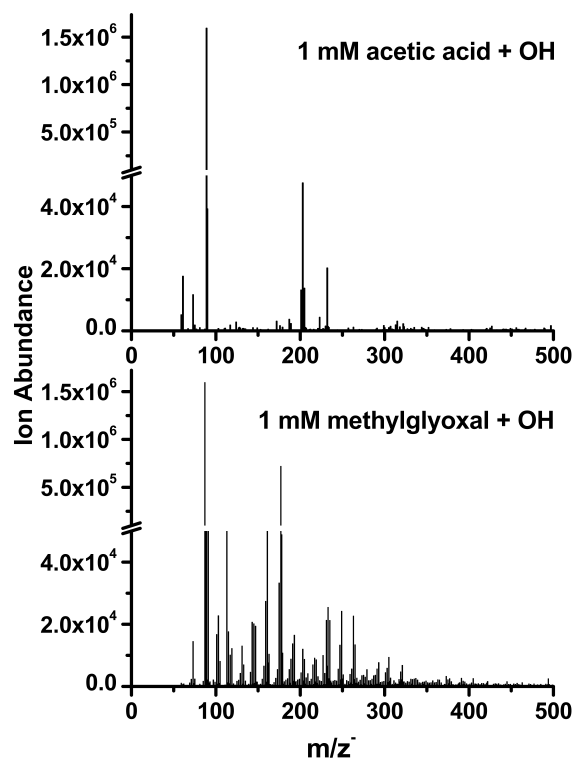
**Fig. 3.** Oxalic and glyoxylic acid production from acetic acid ( $20\ \mu\text{M}$ ) + OH experiments. Ion abundance of oxalic acid ( $m/z^- 89$ , red line) and glyoxylic acid ( $m/z^- 73$ , green line) in negative mode ESI-MS online experiment; oxalic acid concentrations quantified by IC (black squares). Difference between IC and ESI-MS oxalic acid might be due to ionization competition.

comparable. Acetic acid oxidation does not seem to explain the formation of oligomers and other higher carbon number products ( $\geq C_4$ ) from methylglyoxal.

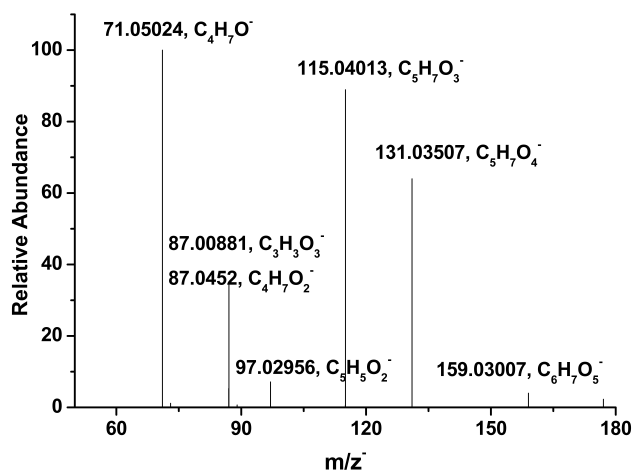
### 3.2 HMWC from methylglyoxal + OH radical experiments

The absence of succinic acid and HMWC in 1 mM acetic acid + OH radical experiments is at odds with the mechanism for oligomer formation from 1 mM methylglyoxal and OH radical proposed previously (Altieri et al., 2008). OH radical concentrations in acetic acid experiments were comparable with those in methylglyoxal experiments, suggesting that the lack of HMWC was not due to OH radical availability. The formation of glyoxylic and oxalic acids from acetic acid, as predicted (Tan et al., 2010), confirms that acetic acid oxidation occurred in these experiments. Thus the methylglyoxal + OH radical oligomers must form through an alternate mechanism that does not involve acetic acid. Oligomers were also not observed when lactic acid was added to the mixed standard containing proposed parent acids, an observation that is also inconsistent with the proposed esterification mechanism. Certainly it is possible that oligomers could form in these mixed standards if the concentrations were even higher or the pH (3.3) was even lower.

Interestingly, one of the parent compounds in the oligomer formation scheme proposed by Altieri et al. (2008) is  $m/z^- 177$ , which is a prominent peak in 3 mM methylglyoxal + OH radical experiments (Tan et al., 2010). Altieri et al. (2008) noted that the unit mass ESI-MS/MS analysis of  $m/z^- 177$  is consistent with an oxalic acid-pyruvic acid dimer ( $C_5H_5O_7^-$ ), although  $C_6H_9O_6^-$  also corresponds to  $m/z^- 177$ .  $m/z^- 177$  does form when oxalic and pyruvic acids are sim-

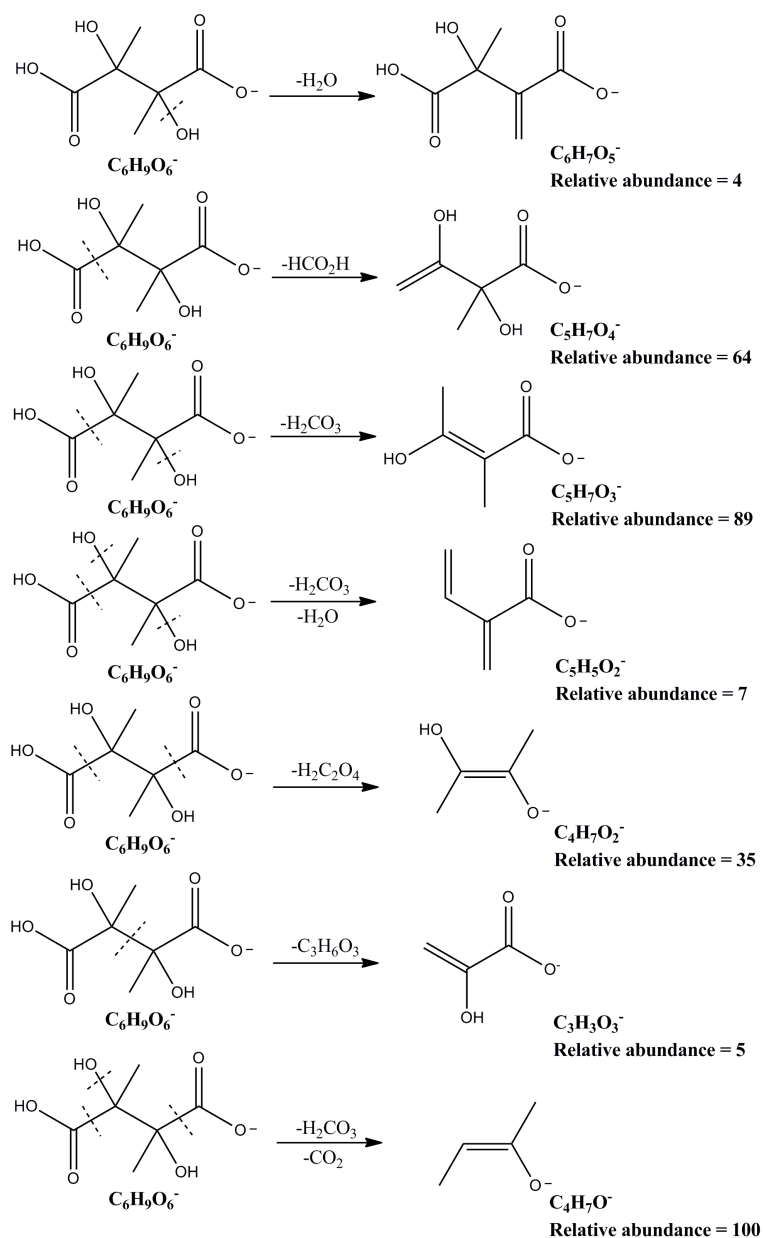


**Fig. 4.** ESI mass spectra of 1 mM acetic acid + OH radical experiment (120 min reaction time) and 1 mM methylglyoxal + OH radical experiment (120 min reaction time).



**Fig. 5.** FT-ICR MS-MS spectra of  $m/z^- 177$  from 1 mM methylglyoxal + OH radical experiment (76 min reaction time).

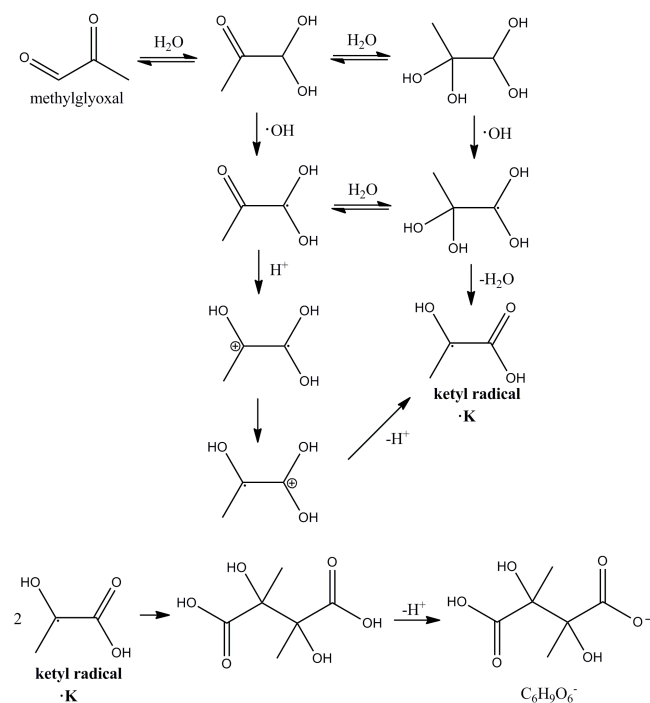
ply mixed together (Tan et al., 2010). However, the IC retention time of  $m/z^- 177$  from the mixed standard is different from that of  $m/z^- 177$  formed in 3 mM methylglyoxal + OH radical experiments, suggesting that the oxalic acid-pyruvic acid dimer was negligible in methylglyoxal + OH radical experiments (Tan et al., 2010). To resolve these discrepancies, organic radical-radical reactions are proposed below.



**Scheme 2.** Proposed structures of  $C_6H_9O_6^-$  and fragment ions of  $C_6H_9O_6^-$  in FT-ICR MS/MS.

In the FT-ICR MS analysis herein, the  $m/z^-$  177 formed in methylglyoxal + OH radical experiments corresponds to a molecular formula of  $C_6H_9O_6^-$  (177.04029). FT-ICR MS/MS analysis of  $m/z^-$  177 showed major negatively charged fragments of  $C_4H_7O_2^-$  (71.05024),  $C_3H_3O_3^-$  (87.00881),  $C_4H_7O_2^-$  (87.04520),  $C_5H_5O_2^-$  (97.02956),  $C_5H_7O_3^-$  (115.04013),  $C_5H_7O_4^-$  (131.03507), and  $C_6H_7O_5^-$  (159.03007) (Fig. 5). We propose a structure for  $C_6H_9O_6^-$  based on these fragment ions (Scheme 2). The proposed structure of  $C_6H_9O_6^-$  is the same as that of a  $C_6$  dicarboxylic acid observed in the photolysis of aqueous pyruvic acid (Guzmán et al., 2006). In fact, similar IC peaks with  $m/z^-$

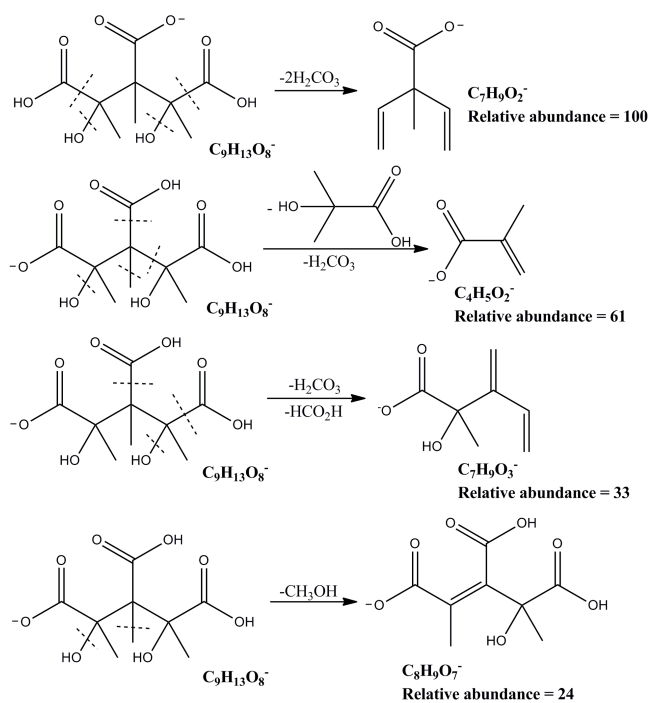
177 were found when comparing the IC-ESI-MS spectrum of a 1 mM pyruvic acid + UV experiment sample (Fig. S2) with that of a 3 mM methylglyoxal + OH radical experiment sample in the study of Tan et al. (2010). This suggests that the same  $C_6H_9O_6^-$  forms in both experiments. The fact that this ion is observed in the ESI-MS after pre-separation by IC confirms that it is not an artifact of electrospray ionization. We argue that  $C_6H_9O_6^-$  forms through different mechanisms in pyruvic acid + UV and methylglyoxal + OH. This is because, while we see this compound in 1 mM pyruvic acid photolysis experiments, we do not see it in 1 mM pyruvic acid + OH radical experiments (Fig. S3). We think this is because OH



**Scheme 3.** The formation of ketyl radical ( $\bullet\text{K}$ ) and  $\text{C}_6\text{H}_9\text{O}_6^-$  from OH radical oxidation of hydrated methylglyoxal.

radical reactions are faster than photolysis reactions and produce different products. If pyruvic acid photolysis were the source of  $\text{C}_6\text{H}_9\text{O}_6^-$  in the methylglyoxal + OH radical experiment, then we would also see the formation of  $\text{C}_6\text{H}_9\text{O}_6^-$  in the pyruvic acid + OH radical experiment, since pyruvic acid is the first generation product of methylglyoxal + OH radical. This compound was also not found in the 3 mM methylglyoxal + UV experiment. Thus,  $\text{C}_6\text{H}_9\text{O}_6^-$  in the methylglyoxal + OH radical experiment must form through a different pathway. Guzmán et al. (2006) proposed that the recombination of ketyl radicals ( $\text{CH}_3\text{C}(\text{OH})\text{C}(\text{O})\text{OH}$ , denoted as  $\bullet\text{K}$ ) from pyruvic acid photolysis leads to the formation of  $\text{C}_6\text{H}_9\text{O}_6^-$ .

We expect that similar chemistry leads to the formation of  $\text{C}_6\text{H}_9\text{O}_6^-$  in the OH radical oxidation of methylglyoxal, except that the ketyl radicals form differently (Scheme 3). Experimental observations (Nemet et al., 2004) and theoretical calculations (Krizner et al., 2009) indicate that methylglyoxal immediately transforms to monohydrate (~60%) and dihydrate (~40%) forms in aqueous solutions. The enol form of methylglyoxal should be negligible (<0.01%) based on thermodynamic calculations. OH radicals react with mono- and dihydrated methylglyoxal via H-abstraction to give corresponding radicals. The proton coupled electron transfer in monohydrated methylglyoxal radical (Livingston and Zeldes, 1966) and the dehydration of dihydrated methylglyoxal radical (Buley et al., 1966) readily produce the ketyl radical ( $\bullet\text{K}$ ) which forms  $\text{C}_6\text{H}_9\text{O}_6^-$  via recombination

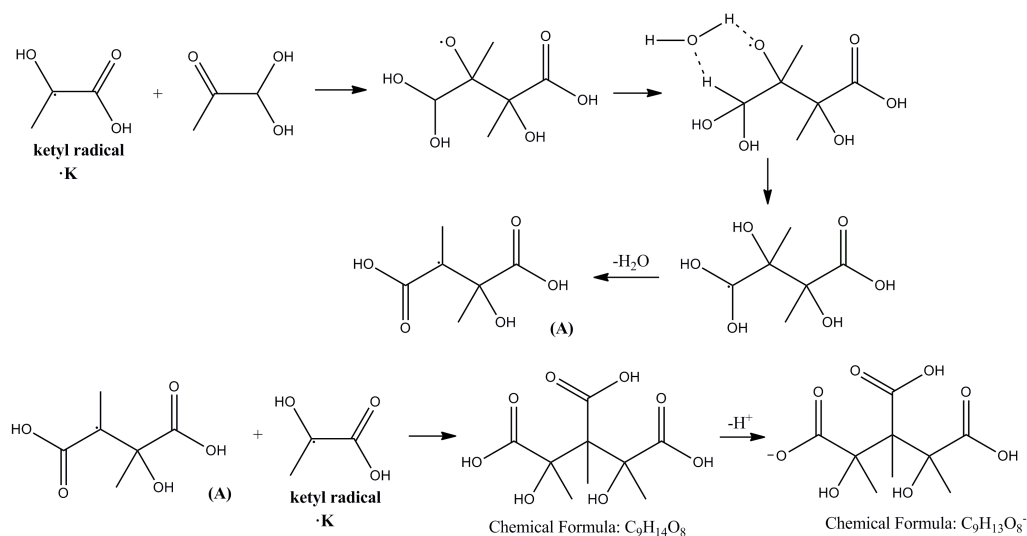


**Scheme 4.** Proposed structures of  $\text{C}_9\text{H}_{13}\text{O}_8^-$  ( $m/z^-$  249.061591 in ESI-MS) and some fragment ions of  $\text{C}_9\text{H}_{13}\text{O}_8^-$  in FT-ICR MS/MS.

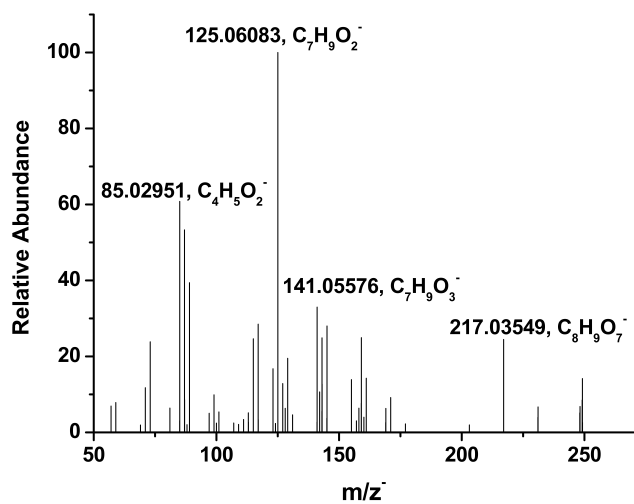
nation (Guzmán et al., 2006; Rincón et al., 2009). Note that the  $m/z^-$  177 in methylglyoxal + OH radical experiments may have additional structures yet to be understood, because  $\text{C}_6\text{H}_9\text{O}_6^-$  was observed in four distinct IC peaks and chiral isomers are not separated by the IC column.

The structures of previously observed oligomers can also be explained by radical-radical reactions. For example, Altieri et al. (2008) proposed that  $\text{C}_9\text{H}_{13}\text{O}_8^-$  ( $m/z^-$  249.061591, observed via ultra-high resolution FT-ICR MS) is an oligoester formed via condensation between  $m/z^-$  177 and hydracrylic acid, adding  $\text{C}_3\text{H}_4\text{O}_2$ . Here we propose an alternative structure for  $\text{C}_9\text{H}_{13}\text{O}_8^-$  based on FT-ICR MS/MS analysis (Scheme 4, Fig. 6). Radical-radical reactions could produce this structure of  $\text{C}_9\text{H}_{13}\text{O}_8^-$  (Scheme 5). This involves the addition of the ketyl radical ( $\bullet\text{K}$ ) to the carbonyl group of monohydrated methylglyoxal, subsequent radical rearrangement and combination with the ketyl radical ( $\bullet\text{K}$ ). Radical addition to the carbonyl group is endothermic but was suggested by Guzmán et al. (2006). Another oligoester,  $\text{C}_9\text{H}_{11}\text{O}_7^-$  ( $m/z^-$  231), was proposed to form from pyruvic acid via repeated esterification with hydracrylic acid ( $\text{C}_3\text{H}_6\text{O}_3$ ). Major negatively charged fragments of  $\text{C}_9\text{H}_{12}\text{O}_7^-$  in previous unit mass ESI-MS/MS analysis included  $m/z^-$  159, 143, 87 and 71; these fragments can also be explained by the structure proposed in Scheme 6. We expect the formation of  $\text{C}_9\text{H}_{11}\text{O}_7^-$  to be similar to that of  $\text{C}_9\text{H}_{13}\text{O}_8^-$  except that the rearranged radical (A) associates with the methylglyoxal radical rather than the ketyl radical





**Scheme 5.** The formation of  $C_9H_{13}O_8^-$  from radical-radical reactions. Ketyl radical ( $\bullet K$ ) adds to the carbonyl group of monohydrated methylglyoxal, and the product isomerizes. The water assisted 1,3 H-shift is likely to happen because the product is a more stable tertiary radical. The resulting radical dehydrates and forms intermediate radical (A). (A) recombines with the ketyl radical and forms  $C_9H_{13}O_8^-$ .



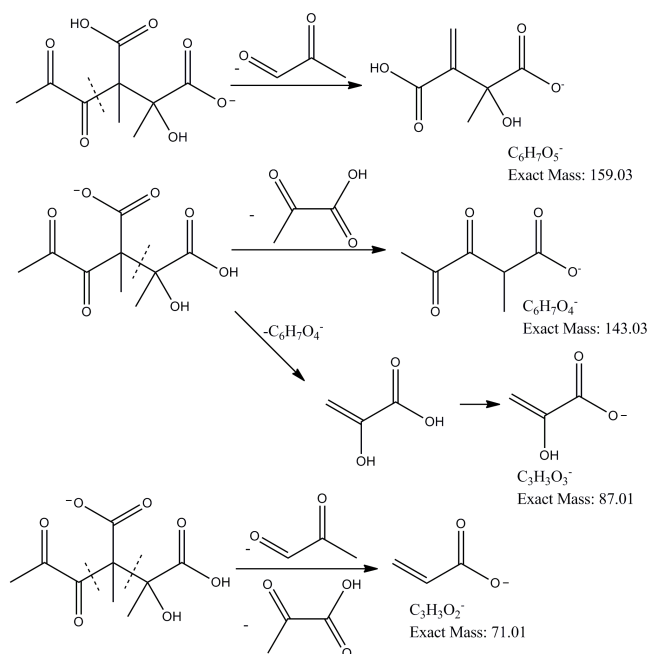
**Fig. 6.** FT-ICR MS-MS spectra of  $m/z^-$  249 from 1 mM methylglyoxal + OH radical experiment (76 min reaction time).

( $\bullet K$ ) in the last step (Scheme 7). Other structures and mechanisms are possible.

#### 4 Conclusions and atmospheric implications

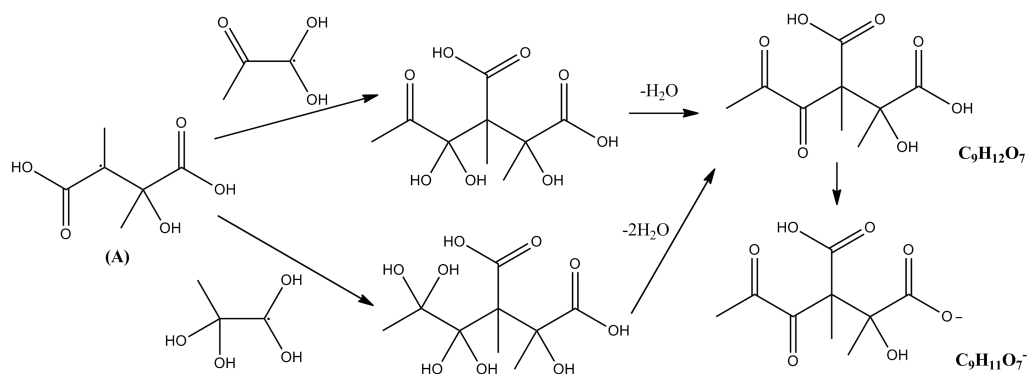
Oxalic acid production from aqueous acetic acid oxidation, suggested by Warneck et al. (2005), is confirmed by this work. We expect SOA production from the aqueous photooxidation of acetate to impact the global distribution of SOA, because the atmospheric burden of acetate is substantial.

Our previous OH radical oxidation experiments conducted with pyruvic acid, glyoxal, methylglyoxal, glycolaldehyde



**Scheme 6.** Possible structures of  $C_9H_{11}O_7^-$  ( $m/z^-$  231 in ESI-MS) and major fragment ions of  $m/z^-$  231 in ESI-MS/MS. Note that chemical formulas of fragment ions were not determined by unit mass ESI-MS/MS.

and this work with acetic acid validate, in large part, the dilute aqueous chemical mechanism which we documented in our previous publications (Lim et al., 2005; Perri et al., 2009; Tan et al., 2009, 2010). This dilute aqueous chemistry model reproduces well the concentrations of total carbon, pyruvic



**Scheme 7.** The formation of C<sub>9</sub>H<sub>12</sub>O<sub>7</sub><sup>-</sup> from radical-radical reactions. Formation of (A) is shown in Scheme 5.

acid and oxalic acid in laboratory experiments conducted with glyoxal or methylglyoxal and OH radical at cloud relevant concentrations in the presence and absence of acidic sulfate (i.e., 30 μM; Tan et al., 2009, 2010). However, this dilute chemistry model is not appropriate for prediction of SOA formed in wet aerosols where the concentrations of dissolved organics are quite high. In order to better understand how the chemistry differs at the high organic concentrations found in aerosol water we have conducted experiments at increasing concentrations and found that high molecular weight organics are increasingly formed. We found that the high molecular weight products formed from methylglyoxal + OH (Tan et al., 2010; Altieri et al., 2008) did not form as a result of acetic acid chemistry, and that organic radical-radical chemistry is capable of explaining their formation (e.g., C<sub>6</sub>H<sub>9</sub>O<sub>6</sub><sup>-</sup>, C<sub>9</sub>H<sub>13</sub>O<sub>8</sub><sup>-</sup> and C<sub>9</sub>H<sub>12</sub>O<sub>7</sub><sup>-</sup>). Because the oligoesters formed by acid catalyzed condensation (esterification) reactions were not identified in the mixed standard plus lactic acid, it appears that these reactions are slower than organic radical-radical reactions, and radical chemistry is the major mechanism leading to oligomer formation from methylglyoxal in the presence of OH radical.

The observation that methylglyoxal but not acetic acid oxidation produces oligomers suggests that having the hydroxyl group on the same carbon (as the case for ketyl radical in Scheme 3) stabilizes the radical making the radical less reactive towards dissolved oxygen. In fact, Guzmán et al. (2006) argued that ketyl radicals form organic radical-radical products rather than peroxy radical products because hydrogen bonding stabilizes the ketyl radical and the formation of the peroxy radical is endothermic. This has been confirmed in low temperature experiments, and the major peak is C<sub>6</sub>H<sub>9</sub>O<sub>6</sub><sup>-</sup> (Rincón et al., 2009). Acetic acid only forms primary radicals (e.g., •CH<sub>2</sub>CO<sub>2</sub>H) which are not stabilized by hydroxyl groups (as shown in Scheme 1). Aldehydes usually hydrate in aqueous solutions, and their oxidation by OH radical produces potentially stable tertiary radicals with hydroxyl groups, except in the case of formaldehyde. It is likely that other ≥C<sub>2</sub> aldehydes will form higher molecular weight

products through aqueous radical-radical reactions and contribute to SOA, although clearly more experimental studies are needed to fully understand the formation of higher molecular weight compounds in wet aerosols.

In this paper we show that the oligomer formation mechanism (esterification) proposed by Altieri et al. (2008) is not viable, and provide evidence suggesting that, as for glyoxal (Lim et al., 2010), methylglyoxal oligomers form through organic radical-radical reactions. Organic radical-radical reactions have also been implicated in the formation of oligomers from other precursors (e.g., Yao Liu et al., 2009; Sun et al., 2010). It seems that there is a growing consensus that oligomers formed through photolysis or OH radical reactions are formed in this way. Organic radical-radical reactions are faster than non-radical reactions and produce oligomers irreversibly. However, high molecular weight products clearly also form through dark (non-radical) reactions, and the relative importance of radical and non-radical pathways to SOA formation in wet aerosols is not yet well understood (e.g., Ervens and Volkamer, 2010; Lim et al., 2010 and references therein). When organic radical-radical reactions are included in our aqueous chemistry model, the model predicts that oligomers will be the dominant products of glyoxal + OH radical at aerosol-relevant organic concentrations, whereas organic acids will be the dominant products at cloud-relevant concentrations (Lim et al., 2010). We are currently expanding the methylglyoxal chemistry to account for organic radical-radical reactions that lead to the formation of oligomers at high concentrations. This paper provides important insights needed to develop this expanded model.

**Supplementary material related to this article is available online at:**  
<http://www.atmos-chem-phys.net/12/801/2012/acp-12-801-2012-supplement.pdf>.

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