Atmos. Chem. Phys. Discuss., 11, 18319–18347, 2011
www.atmos-chem-phys-discuss.net/11/18319/2011/
doi:10.5194/acpd-11-18319-2011

Atmospheric Chemistry and Physics Discussions

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

Y. Tan[1,*], **Y. B. Lim**[1], **K. E. Altieri**[2], **S. P. Seitzinger**[3], **and B. J. Turpin**[1]

[1]Department of Environmental Sciences, Rutgers University, 14 College Farm Road, New Brunswick, NJ 08901, USA
[2]Department of Geosciences, Princeton University, B80 Guyot Hall, Princeton, NJ 08544, USA
[3]International Geosphere-Biosphere Programme (IGBP), Lilla Frescativägen 4a, Stockholm, Sweden
[*]now at: Center for Atmospheric Particle Studies, Carnegie Mellon University, Pittsburgh, 15213, Pennsylvania, USA

Received: 14 June 2011 – Accepted: 14 June 2011 – Published: 28 June 2011

Correspondence to: B. J. Turpin (turpin@envsci.rutgers.edu)

Published by Copernicus Publications on behalf of the European Geosciences Union.

Abstract

Previous experiments have demonstrated that the aqueous OH radical oxidation of methylglyoxal produces low volatility products including 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 is an important intermediate in aqueous methylglyoxal oxidation and a ubiquitous product of gas phase photochemistry, making it a potential "aqueous" SOA precursor in its own right. Altieri et al. (2008) proposed that acetic acid was the precursor of oligoesters observed in methylglyoxal oxidation. However, the fate of acetic acid upon aqueous-phase oxidation is not well understood. In this research, acetic acid at concentrations relevant to atmospheric waters (20 µM–10 mM) was oxidized by OH radical. Products were analyzed by ion chromatography (IC), electrospray ionization mass spectrometry (ESI-MS), and IC-ESI-MS. The formation of glyoxylic, glycolic, and oxalic acids were observed. In contrast to methylglyoxal oxidation, succinic acid and oligomers were not detected. Using results from these and methylglyoxal + OH radical 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 (Hallquist et al., 2009). SOA formation is underestimated by current chemical transport models (Kanakidou et al., 2005; Hallquist et al., 2009). The properties of ambient SOA are also not reproduced in typical smog chamber experiments. Specifically, the oxygen-to-carbon (O/C) ratio of ambient low-volatility oxygenated organic aerosol (LV-OOA) is higher than that formed in traditional smog chamber experiments (Aiken et al., 2008). Longer reaction times, alternate formation mechanisms, and SOA precursors not included in models are considered the most likely explanations (Hallquist et al., 2009). Laboratory and modeling experiments demonstrate that aqueous oxidation of small volatile organic compounds leads to products with high O/C ratios that can effectively contribute to SOA mass (Lim et al., 2005; Carlton et al., 2006; Carlton et al., 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; Lim et al., 2010; Sun et al., 2010; Myriokefalitakis et al., 2011). However, aqueous reaction mechanisms leading to the formation of higher molecular weight compounds (HMWC), including oligomers, are not fully understood.

Organic acids and HMWC are identified products in the aqueous OH radical oxidation of methylglyoxal (Altieri et al., 2008; Tan et al., 2010). A number of these products (e.g., oxalate, pyruvate and succinate) are found predominantly in the particle phase in the atmosphere (Limbeck et al., 2001; Mochida et al., 2003), most likely as salts. Thus the oxidation of methylglyoxal in atmospheric waters is a source of SOA. 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 $\cdot O_2CH_2CO(OH)$ radicals, and by H abstraction at the carboxyl group to a minor extent to form the $CH_3CO_2\cdot$ radicals (Scheme 1) (Schuchmann et al., 1985). The $CH_3CO_2\cdot$ radicals decompose to form $\cdot CH_3$ radicals and are not expected to participate in bimolecular reactions. Dissolved oxygen adds to $\cdot O_2CH_2CO(OH)$ radicals, producing peroxyl radicals ($\cdot O_2CH_2CO(OH)$). Products from the bimolecular reaction of $\cdot O_2CH_2CO(OH)$ include glyoxylic and glycolic acids, formaldehyde and $\cdot KCO_2$, mostly through reactions 1 and 4 in Scheme 1 (Schuchmann et al., 1985; Leitner and Dore, 1997; Benson, 1965; Russell, 1957). 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 oxidation of glycolic acid produces glyoxylic acid and the oxidation of glyoxylic acid produces oxalic acid. 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 concentrations increase from those typically observed in clouds to the higher organic 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 $\cdot CH_2CO_2H$ radicals from acetic acid, based on the work of Wang et al. (2001) who observed succinic acid formation from γ-radiolysis of aqueous acetic acid (2 mM, under N_2O saturated, O_2 depleted conditions) (Wang et al., 2001). 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., $C_3H_4O_2$ from hydracrylic acid) to parent carboxylic acids (e.g., pyruvic, oxalic, and glyoxylic acids) via condensation reactions (esterification) formed series of oligomers. Elemental composition and ion fragmentation 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 predicted reaction components and lactic acid, and 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 IC-ESI-MS (Tan et al., 2010).

HMWC including oligomers have also been hypothesized to form in atmospheric waters via organic radical-radical reactions (e.g., methacrolein, glycoaldehyde, glyoxal, pyruvic acid and phenols) (Guzman et al., 2006; Yao Liu et al., 2009; Lim et al., 2010; Perri et al., 2010; Sun et al., 2010). For example, C_6 and C_7 carboxylic acid formation was observed during the photolysis (320 nm UV) of oxygen-saturated pyruvic acid solutions (Guzman et al., 2006). The formation of these products was explained by radical-radical chemistry (Guzman et al., 2006). Ketyl ($CH_3C(OH)C(O)OH$) and acetyl (CH3C(O)·) radicals are produced when pyruvic acid solution is irradiated by UV light. Guzman et al. (2006) argued that the reactivity of these radicals towards O_2 must be lower than previously believed, making radical recombination and the formation of the observed C_6 and C_7 carboxylic acids possible. Similarly, radical-radical reactions could play an important role in the formation of higher carbon number products from OH radical reaction of methylglyoxal and pyruvic acid.

The fate of acetic acid is critical to understanding the origin of oligomers in the aqueous phase oxidation of methylglyoxal. The OH radical oxidation of methylglyoxal was modeled by Tan et al. (2010) with acetic acid forming only glyoxylic acid and formaldehyde directly, even though additional products (e.g., glycolic and succinic acids) have been proposed. Succinic acid and oligomers should be observed in acetic acid + OH radical experiments if the acid catalyzed esterification pathway proposed by Altieri et al. (2008) is accurate. This work reports the results of batch aqueous acetic acid + OH radical experiments conducted at four concentrations. The products were analyzed by on-line (real-time) mass spectroscopy and by electrospray ionization-mass spectrometry with IC separation (IC-ESI-MS). Interestingly, succinic acid and oligomer formation was not observed. 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. In addition, we demonstrate that acetic acid can effectively form oxalic acid through aqueous phase reactions under atmospherically relevant conditions. Oxalate is largely found in the particle phase in the atmosphere. Thus acetic acid/acetate is an SOA precursor. Acetic

acid/acetate is ubiquitous in atmospheric precipitation, cloud water, fog water and dew (Henry's law constant = 8.8×10^3 M atm^{-1}) (Seinfeld and Pandis, 2006). Concentrations of acetate in cloud water, fog water and dew range from 0.4–245 µM in various field studies (Khare et al., 1999). However, to our knowledge, its contribution to SOA has not been previously considered.

2 Methods

Batch experiments were conducted in a 1 liter glass reaction vessel at 25 ± 2 °C, as described previously (Carlton et al., 2006; Tan et al., 2009). Commercially available acetic acid (Sigma-Aldrich, 99.999 % purity) was diluted to 20 µM, 100 µM, 1 mM, and 10 mM for experiments. Initial H_2O_2 concentrations were 100 µM, 500 µM, 5 mM, and 20 mM, respectively. OH radicals were generated by UV photolysis (254 nm) of H_2O_2 with a mercury lamp (Heraeus Noblelight, Inc. Duluth, GA). The H_2O_2 photolysis rate was $k_1 = (1.1 \pm 0.3) \times 10^{-4}\,s^{-1}$, determined by fitting the simulated H_2O_2 concentration in H_2O_2 + UV control experiments, as described previously (Tan et al., 2010). The concentration of OH radicals was approximately (3–4) × 10^{-12} M for all experiments, according to a dilute aqueous chemistry model which includes acetic acid and H_2O_2 chemistry (Tan et al., 2010). 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, H_2O_2 and NO_3 (Arakaki and Faust, 1998). Dissolved oxygen was measured at the beginning and the end of experiments (YSI ProODO, YSI Inc., Yellow Springs, OH). Solutions remained saturated with oxygen and pH varied from 6.6–3.3 during experiments. The following control experiments were also conducted: acetic acid + UV, acetic acid + H_2O_2, H_2O_2 + UV, mixed standard (250 µM each acetic, formic, glyoxylic, glycolic, succinic, malonic, and oxalic acids) + UV, and mixed standard + H_2O_2. Experiments were also performed with pyruvic acid (1 mM) + OH radical (formed from 5 mM H_2O_2 + UV) and 1 mM pyruvic acid + UV. Note H_2O_2 reacts with glyoxylic and pyruvic acids in the absence of OH radical and pyruvic acid photolyzes in the absence of OH radical. However, H_2O_2 and photolysis reactions are too slow to compete in the presence of OH radical, as explained by 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 0.11 $\mathrm{ml\,min^{-1}}$. 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_2O_2 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 samples were analyzed by IC-ESI-MS, as 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). 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 $\mathrm{\mu l\,min^{-1}}$. The needle voltage was 3.02 kV, the capillary voltage was -9.44 V, the capillary temperature was 260 ˚C, and the tube lens was -57 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 $\cdot O_2CH_2CO_2H$ radical. Glyoxylic and glycolic acids can be effectively oxidized to oxalic acid (m/z^- 89) (Perri et al., 2009; Tan et al., 2009). At the cloud relevant concentration of 20 µM acetic acid, the maximum oxalic acid concentration was ~ 27 % of the acetic acid reacted (Fig. 3, see also Fig. S1). This finding and the high abundance of acetic acid in atmospheric waters suggest that OH radical oxidation of acetic acid could contribute considerably to SOA mass. Interestingly, unlike the oxidation of pyruvic acid and methylglyoxal, neither succinic acid (m/z^- 117) nor HMWC consistent with oligomer series were detected in any acetic acid experiment (Figs. 2, 4). 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 acetic acid + OH radical experiments is at odds with the acid catalyzed esterification mechanism for oligomer formation from methylglyoxal and OH radical proposed previously (Altieri et al., 2008). Also oligomers were not observed when lactic acid was added to the mixed standard containing proposed parent acids. We conclude that acid catalyzed esterification is not fast enough to produce noticeable amounts of oligomers at these concentrations in the presence of OH radical. Interestingly, one of the proposed parent compounds in the Altieri et al. scheme 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 simply 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, radical-radical reactions are proposed below.

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 $C_4H_7O^-$ (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 (Guzman 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), suggesting that the same $C_6H_9O_6^-$ might form in both experiments. (Note, we are confident that $C_6H_9O_6^-$ in the methylglyoxal + OH radical experiment is not explained by pyruvic acid photolysis, because these peaks were not observed in either 1 mM pyruvic acid + OH radical experiment (Fig. S3) nor 3 mM methylglyoxal + UV experiment.) Guzman et al. (2006) proposed that the recombination of ketyl radicals ($CH_3C(OH)C(O)OH$, denoted as ·K) from pyruvic acid photolysis leads to the formation of $C_6H_9O_6^-$. We expect that similar chemistry leads to the formation of $C_6H_9O_6^-$ 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 (·K) proposed by Guzman et al. (2006) which forms $C_6H_9O_6^-$ via recombination. Note that the m/z^- 177 in methylglyoxal + OH radical experiments may have additional structures yet to be understood, because $C_6H_9O_6^-$ 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 $C_9H_{13}O_8^-$ (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 $C_3H_4O_2$. Here we propose an alternative structure for $C_9H_{13}O_8^-$ based on FT-ICR MS/MS analysis (Scheme 4, Fig. 6). Radical-radical reactions could produce this structure of $C_9H_{13}O_8^-$ (Scheme 5). This involves the addition of the ketyl radical (·K) to the carbonyl group of monohydrated methylglyoxal, subsequent radical rearrangement and combination with the ketyl radical (·K). Radical addition to the carbonyl group is endothermic but was suggested by Guzman et al. (2006). Another oligoester, $C_9H_{11}O_7^-$ (m/z^- 231), was proposed to form from pyruvic acid via repeated esterification with hydracrylic acid ($C_3H_6O_3$). Major negatively charged fragments of $C_9H_{12}O_7^-$ 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 $C_9H_{11}O_7^-$ to be similar to that of $C_9H_{13}O_8^-$ except that the rearranged radical (A) associates with the methylglyoxal radical rather than the ketyl radical (·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.

At cloud-relevant concentrations, the total carbon in methylglyoxal + OH radical experiments is explained by low molecular weight organic acid products and CO_2 (Tan et al. 2010). As concentrations in these experiments approach the concentrations of organics found in aerosol water, 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 radical-radical chemistry is capable of explaining their formation (e.g., $C_6H_9O_6^-$, $C_9H_{13}O_8^-$ and $C_9H_{12}O_7^-$). Because the oligoesters formed by acid catalyzed condensation reactions were not identified in the mixed standard plus lactic acid, it appears that these reactions are slower than 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 methylgloxal 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) might stabilize the radical, making the radical less reactive towards dissolved oxygen. The reason for this is not well understood. Acetic acid only forms primary radicals (e.g., $\cdot CH_2CO_2H$) 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_2 aldehydes will form higher molecular weight products through aqueous radical-radical reactions and contribute to SOA. More experimental studies are needed to fully understand the formation of higher molecular weight compounds in wet aerosols.

Supplementary material related to this article is available online at: http://www.atmos-chem-phys-discuss.net/11/18319/2011/ acpd-11-18319-2011-supplement.pdf.

Acknowledgement. This research has been supported by the National Science Foundation (NSF) (ATM-0630298), US Department of Commerce's National Oceanic and Atmospheric Administration (NOAA) (NA07OAR4310279), the US Environmental Protection Agency (EPA) Science to Achieve Results (STAR) program (WDC-RD-833751), the NIEHS sponsored UMDNJ Center for Environmental Exposures and Disease (NIEHS P30ES005022) and the New Jersey Agricultural Experiment Station. We also gratefully acknowledge Melissa Soule, Elizabeth Kujawinski, and the funding sources of the WHOI FT-MS Users' Facility (National Science Foundation OCE-0619608 and the Gordon and Betty Moore Foundation). Any opinions, findings, and conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the NSF, NOAA, or EPA; no official endorsement should be inferred. The authors thank Ron Lauck, Mark J. Perri, Diana Ortiz, Jeffrey Kirkland and Anjuli Ramos for laboratory assistance and invaluable discussions.

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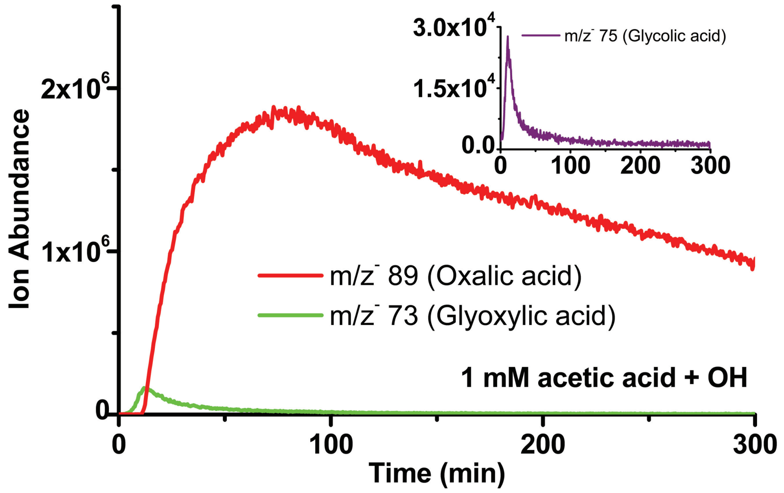


Fig. 1. ESI-MS online analysis of 1 mM acetic acid + OH radical experiment.

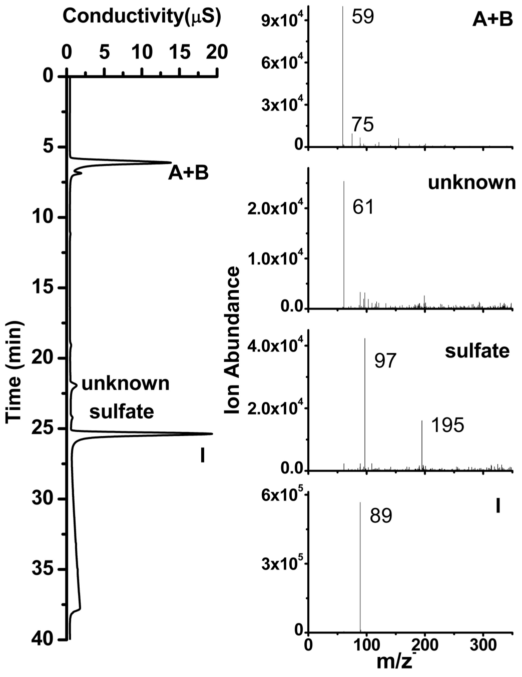


Fig. 2. IC-ESI-MS spectrum of a sample taken from 1 mM acetic acid + OH radical batch reactions (120 min reaction time). (A + B) has the retention time of acetic acid (*m/z*$^-$ 59), glycolic acid (*m/z*$^-$ 75) and formic acid (not an expected product, not detected in ESI-MS because its molecular weight 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).

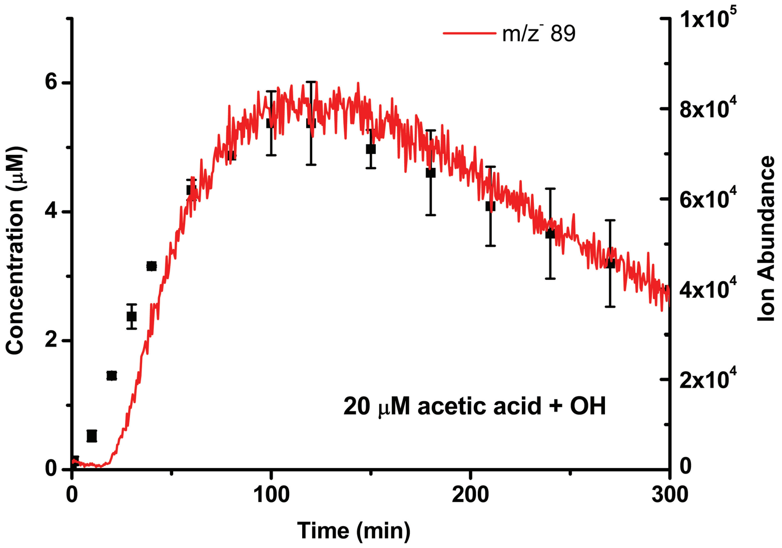


Fig. 3. Oxalic acid production from acetic acid (20 µM) + OH experiments. Ion abundance of oxalic acid (*m/z*$^-$ 89) in negative mode ESI-MS online experiment (red line); oxalic acid concentrations quantified by IC (black squares).

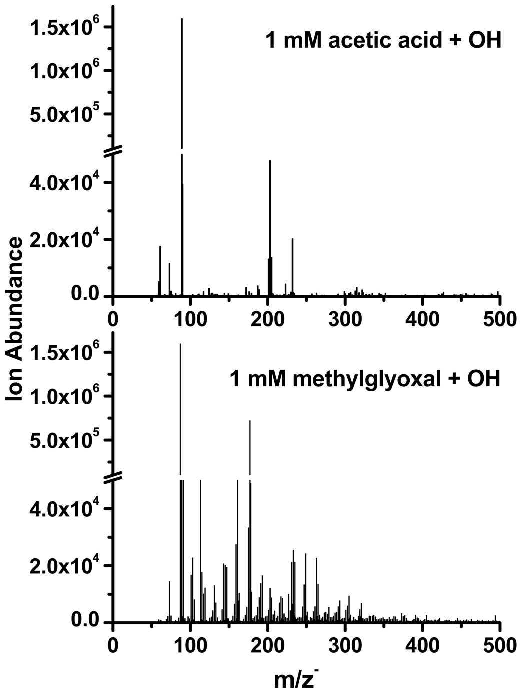


Fig. 4. ESI mass spectra of 1 mM acetic acid + OH radical experiment (120 min reaction time) and 1 mM methylglyoxal + OH radical experiment (120 min reaction time).

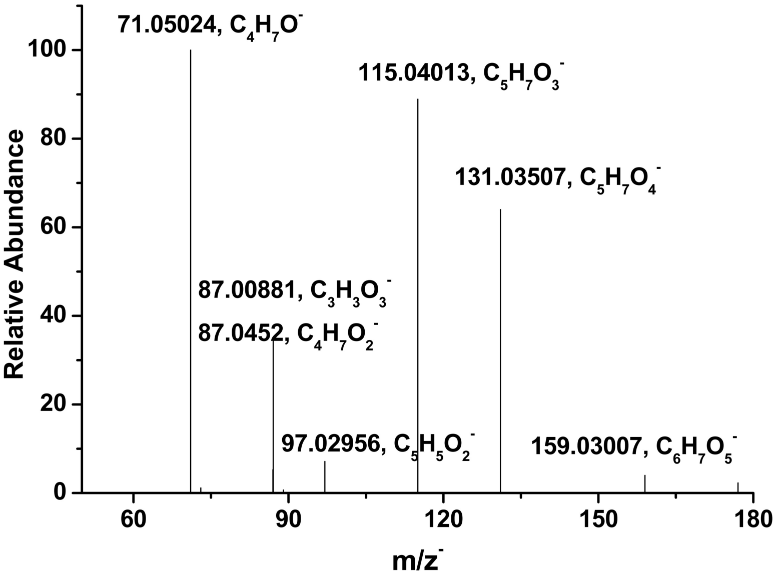


Fig. 5. FT-ICR MS-MS spectra of *m/z*$^-$ 177 from 1 mM methylglyoxal + OH radical experiment (76 min reaction time).

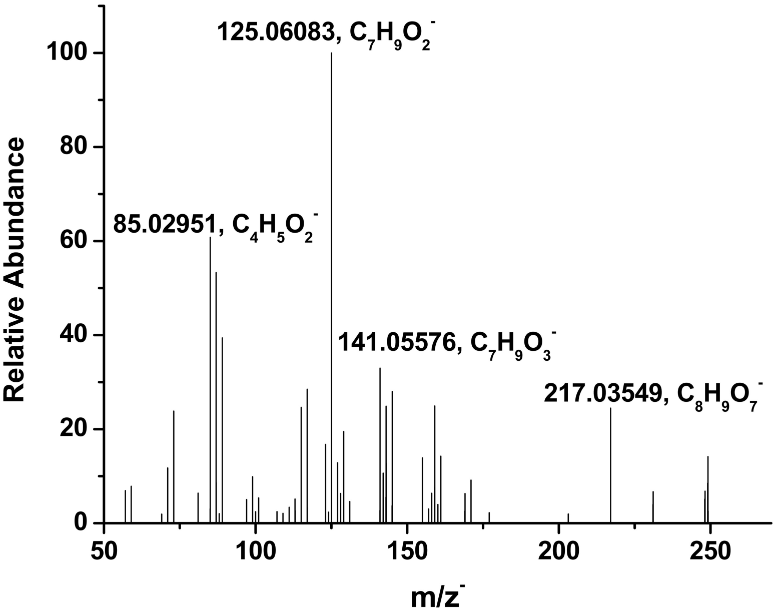
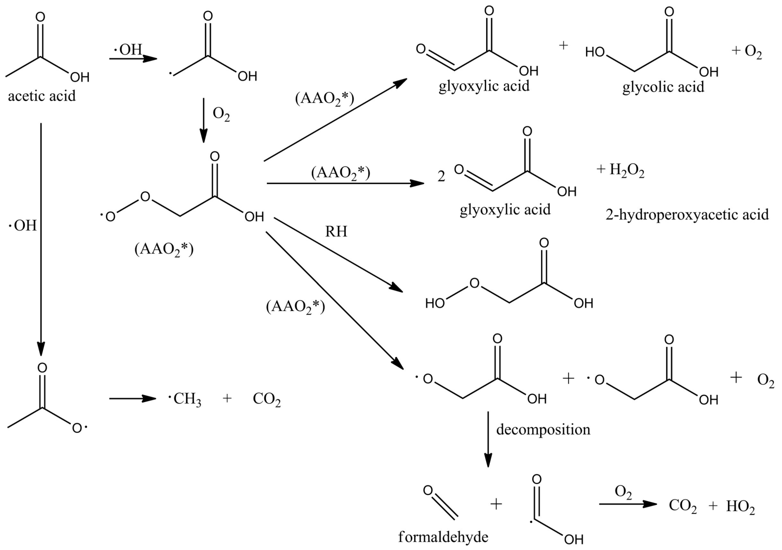
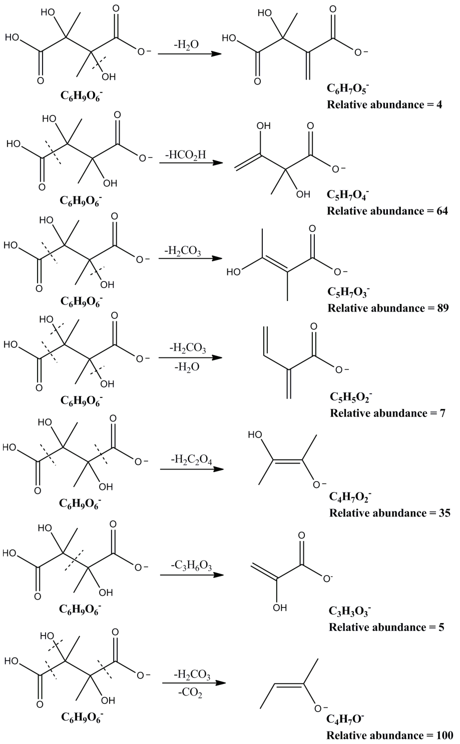


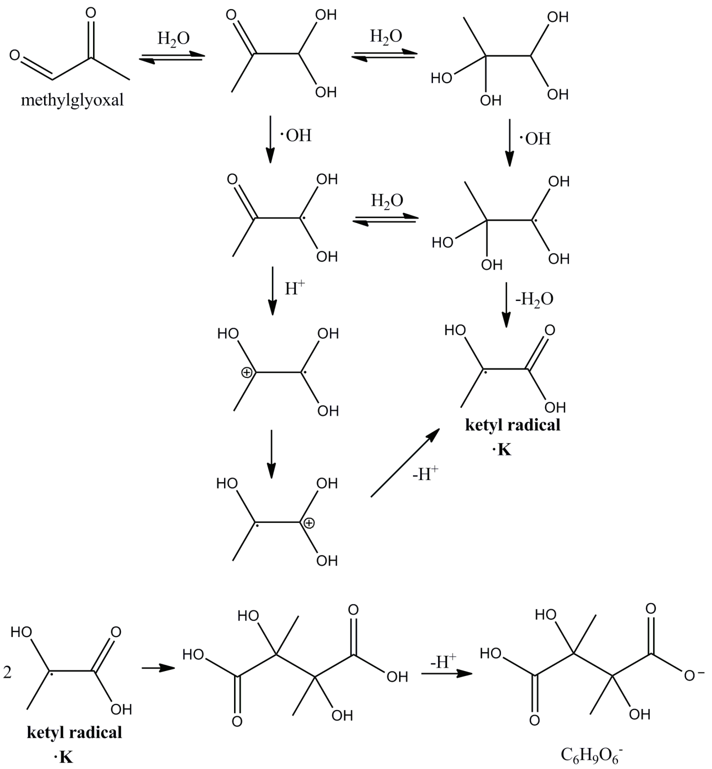
Fig. 6. FT-ICR MS-MS spectra of *m/z*$^-$ 249 from 1 mM methylglyoxal + OH radical experiment (76 min reaction time).



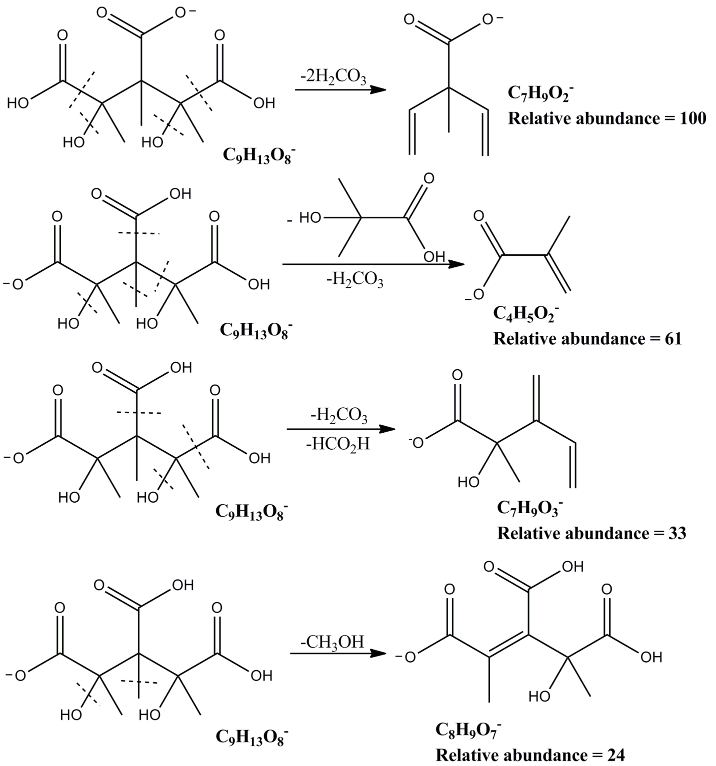
Scheme 1. Oxidation of acetic acid by OH radical (Leitner and Dore, 1997).



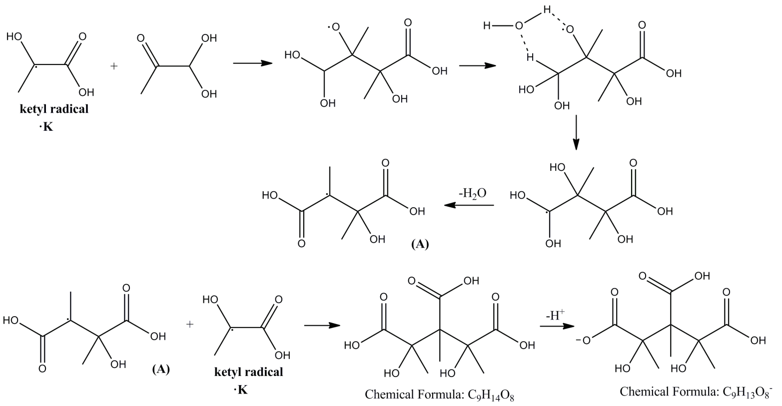
Scheme 2. Proposed structures of $C_6H_9O_6^-$ and fragment ions of $C_6H_9O_6^-$ in FT-ICR MS/MS.



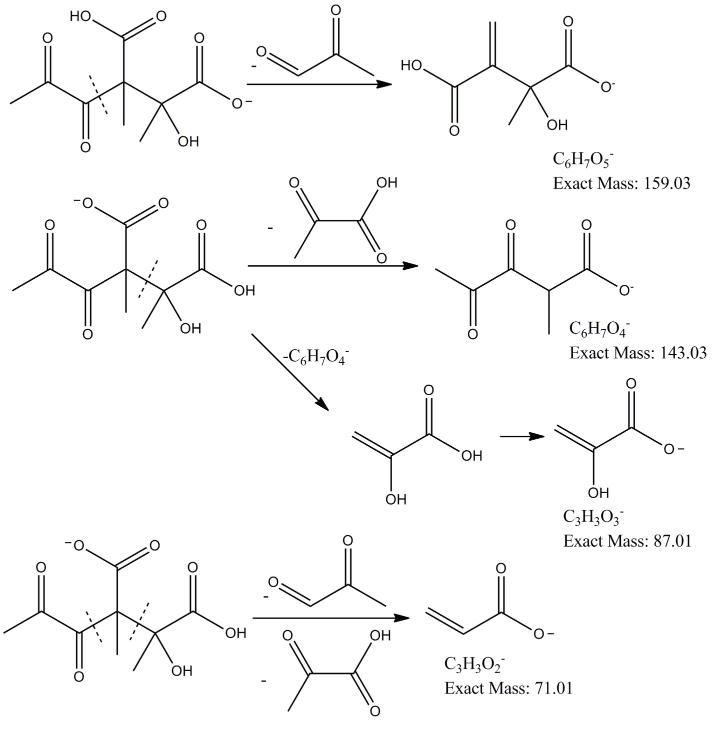
Scheme 3. The formation of ketyl radical (·K) and $C_6H_9O_6^-$ from OH radical oxidation of hydrated methylglyoxal.



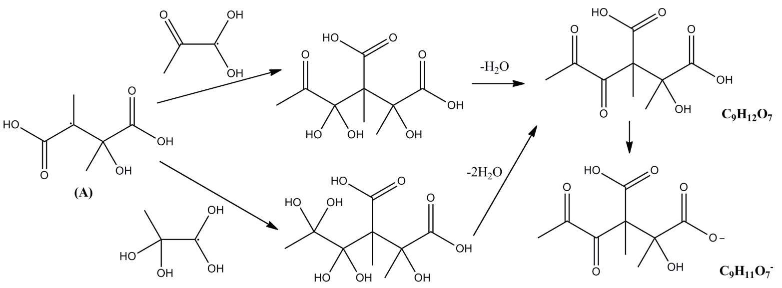
Scheme 4. Proposed structures of $C_9H_{13}O_8^-$ (m/z^- 249.061591 in ESI-MS) and some fragment ions of $C_9H_{13}O_8^-$ in FT-ICR MS/MS.



Scheme 5. The formation of $C_9H_{13}O_8^-$ from radical-radical reactions. Ketyl radical (·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 $C_9H_{13}O_8^-$.



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.



Scheme 7. The formation of $C_9H_{12}O_7^-$ from radical-radical reactions. Formation of (A) is shown in Scheme 5.