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SOA from methylglyoxal in clouds and wet aerosols: Measurement and prediction of key products

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ABSTRACT

Aqueous OH radical oxidation of methylglyoxal in clouds and wet aerosols is a potentially important global and regional source of secondary organic aerosol (SOA). We quantify organic acid products of the aqueous reaction of methylglyoxal (30–3000 μM) and OH radical (approx. 4×10^{-12} M), model their formation in the reaction vessel and investigate how the starting concentrations of precursors and the presence of acidic sulfate (0–840 μM) affect product formation. Predicted products were observed. The predicted temporal evolution of oxalic acid, pyruvic acid and total organic carbon matched observations at cloud relevant concentrations (30 μM), validating this methylglyoxal cloud chemistry, which is currently being implemented in some atmospheric models of SOA formation. The addition of sulfuric acid at cloud relevant concentrations had little effect on oxalic acid yields. At higher concentrations (3000 μM), predictions deviate from observations. Larger carboxylic acids ($\geq C_4$) and other high molecular weight products become increasingly important as concentration increases, suggesting that small carboxylic acids are the major products in clouds while larger carboxylic acids and oligomers are important products in wet aerosols.

1. Introduction

Fog and cloud processing, a major source of atmospheric sulfate, has been hypothesized to be a substantial source of secondary organic aerosol (SOA) (Blando and Turpin, 2000; Gelencser and Varga, 2005; Carlton et al., 2009). Observations provide support for in-cloud SOA production (Yu et al., 2005; Heald et al., 2006; Sorooshian et al., 2007a,b). Modeling studies estimate that SOA formed through aqueous reactions in clouds and wet aerosols is comparable in magnitude to “traditional SOA” (Chen et al., 2007; Carlton et al., 2008; Fu et al., 2008; Fu et al., 2009). However, the uncertainties in these estimates are quite large, in part because the aqueous chemical mechanisms are largely unvalidated.

Methylglyoxal is a common α-dicarbonyl formed in atmospheric oxidation of both biogenic and anthropogenic precursors, including isoprene, acetone, and xylenes (Fu et al., 2008 and reference therein). Methylglyoxal has a global source of 140 Tg a^{-1} (Fu et al., 2008). UV photolysis and reaction with hydroxyl radical are the main gas phase loss processes for methylglyoxal (Koch and Moortgat, 1998) and yield carbon monoxide, acetaldehyde, and formaldehyde. Methylglyoxal enters droplets readily due to its high effective Henry’s law constant ($H_{eff} = 3.71 \times 10^3$ M atm^{-1} at 25 °C) and fast uptake rate (Betterton and Hoffmann, 1988; Zhou and Mopper, 1990). Reactive uptake of methylglyoxal on sulfuric acid (55–85 wt%) has an effective Henry’s law constant of 4.0×10^3–5.9×10^3 M atm^{-1} at 10 °C, decreasing with increasing acidity (Zhao et al., 2006). Typical aqueous methylglyoxal concentrations vary from a few μM in rain water to >100 μM in fog water (Munger et al., 1995). Methylglyoxal could reach very high concentrations in aerosol water (0.7–7 mM; Sareen et al., 2010) and during cloud evaporation. Aqueous methylglyoxal oxidation leads to the formation of oxalic acid and high molecular weight products (Altieri et al., 2006, 2008; Carlton et al., 2006). When this chemistry takes place in clouds and fogs followed by droplet evaporation (or if this chemistry occurs in aerosol water) then the lower volatility products will remain in part in the particle phase, forming SOA. In addition, evaporation of droplets containing methylglyoxal induces formation of methylglyoxal oligomers, which could contribute to SOA (Loeffler et al., 2006; De Haan et al., 2009).

Several laboratory studies provide insights into the aqueous OH radical chemistry of methylglyoxal, illustrated in part by Fig. 1. In the aqueous phase, methylglyoxal hydrates (Nemet et al., 2004). Rate constants for reaction between OH radical and methylglyoxal

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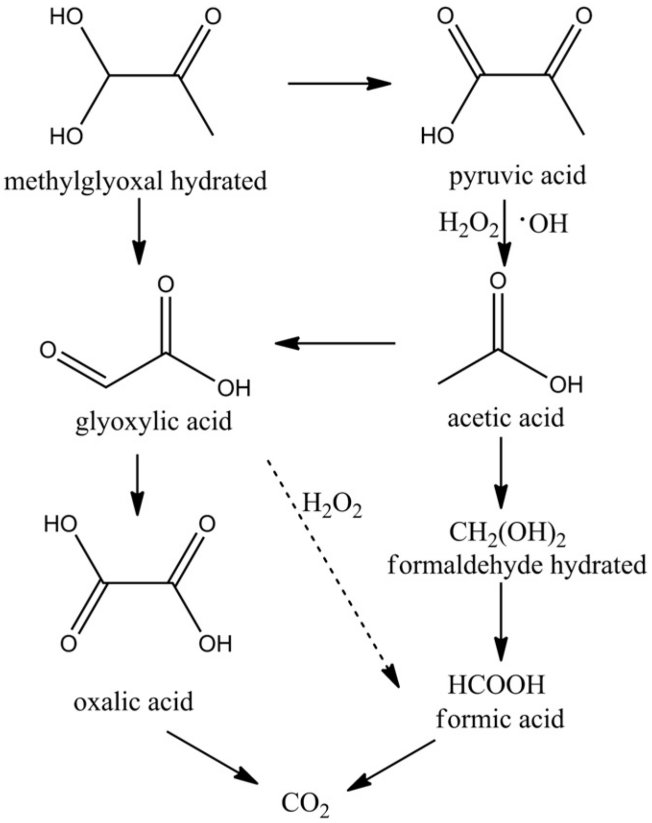

Fig. 1. Reactions included in kinetic modeling (Table 1) for aqueous OH radical oxidation of methyglyoxal (Lim et al., 2005).

have been measured (Ervens et al., 2003; Monod et al., 2005). The aqueous OH radical oxidation product of methylglyoxal is pyruvic acid (Stefan and Bolton, 1999). Acetic, formic, glyoxylic, and oxalic acids were measured in aqueous pyruvic acid (5–10 mM) plus OH radical oxidation experiments (Carlton et al., 2006). These experiments verified that glyoxylic and oxalic acids formed from the OH radical oxidation of pyruvic acid (they did not form in control experiments), whereas acetic and formic acids could have been formed via OH radical and/or H_2O_2 oxidation. Formation of methylglyoxal, pyruvic and oxalic acids from methacrolein (0.4–5 mM) has also been documented (Liu et al., 2009). Ambient measurements suggest that a majority of pyruvate, oxalate, and glyoxylate exist in the particle phase under typical atmospheric conditions (Limbeck et al., 2001). Formation of additional carboxylic acids (i.e., glycolic, succinic and hydracrylic acids) and oligomers from aqueous methylglyoxal (2 mM) photooxidation has also been reported (Altieri et al., 2008). Moreover, oligomer production has been observed in OH radical oxidation, O_3 oxidation and direct photolysis of pyruvic acid (5–100 mM) (Altieri et al., 2006; Guzman et al., 2006; Grgic et al., 2010). Methylglyoxal also interacts with inorganic aerosol constituents (e.g., sulfate, nitrate), forming oligomers via acetal/hemiacetal and aldol condensation in aqueous aerosol mimics (16 mM–2.0 M methylglyoxal; Sareen et al., 2010) and simulated cloud water (1 mM methylglyoxal; Yasmeen et al., 2010). The formation of low volatility acids and oligomers from methylglyoxal suggests that aqueous methylglyoxal chemistry is a source of SOA. However, none of these experiments were performed at cloud-relevant concentrations (1–100 μM).

This paper provides the first measurements of the products of aqueous OH radical oxidation of methylglyoxal at cloud relevant concentrations and the first quantitative validation of dilute aqueous chemistry model predictions against measured product concentrations. The effect of sulfuric acid on cloud processing of methylglyoxal is also reported. Batch aqueous methylglyoxal + OH radical oxidation experiments were performed at three concentrations. Products were measured by on-line (real-time) mass spectroscopy and by ion chromatography-mass spectrometry. The 30 μM experiments are cloud relevant; 300 μM experiments could represent some heavily polluted fogs, and 3000 μM experiments shed light on chemistry in aerosol water. (Methylglyoxal concentrations in aerosols are ~ mM, whereas total organic concentrations in aerosol water are considerably higher.) Examination of the chemistry with increasing precursor concentration provides insights into differences between the aqueous photochemistry of dicarbonyls in clouds and in aerosol water.

2. Approach

2.1. Experiments with real-time ESI-MS

Electrospray ionization mass spectrometry (ESI-MS; HP-Agilent 1100) does not fragment ions. Carboxylic acids are detected in the negative ionization mode as molecular weight minus one. Aldehydes and alcohols are detected in the positive mode.

Experiments with real-time ESI-MS (online experiments, Fig. 2a,b) were performed as previously described (Perri et al., 2009; Tan et al., 2009). 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 mL min^{-1}. Experiments were analyzed in negative or positive ionization mode from 50–1000 amu with a fragmentor voltage of 40 V and capillary voltage of 3000 V. Nitrogen was the drying gas (10 L min^{-1}, 350 °C). Discrete samples were taken for ion chromatography and total organic carbon analysis.

2.2. Batch reactions

Batch aqueous reactions of methylglyoxal (30, 300, 3000 μM) and OH radical ($\sim 4 \times 10^{-12}$ M, estimated) with and without sulfuric acid were conducted in a 1 L glass reaction vessel at 25 ± 2°C, as described previously (Carlton et al., 2006; Tan et al., 2009). Experimental conditions are provided in Table S1. OH radicals were continuously generated by the photolysis of H_2O_2 by UV (254 nm) light from a monochromatic mercury lamp (Heraeus Noblelight, Inc. Duluth, GA). The pH varied from 6.7 to 2.1, decreasing with increasing H_2SO_4 and increasing reaction time. At least two experiments were conducted for each of the nine treatment combinations. Reaction samples and duplicates (10% of samples) were analyzed within 12 hours of collection for organic acids by ion chromatography (IC; ICS-3000, Dionex, Sunnyvale, CA; IonPac AS11-HC column with AG11-HC guard column, 30 °C), as described in detail by Tan et al. (2009). Pyruvic, acetic, formic, glyoxylic, glycolic, malonic, succinic and oxalic acids were identified and quantified with mixed standards and Chromeleon software (version 6.80 SP2, Dionex). Single standards of mesoxalate (prepared from sodium mesoxalate monohydrate, 98.7%, Sigma–Aldrich) were run separately. Selected samples and control samples were also analyzed by ESI-MS after preseparation in the IC (IC-ESI-MS), as shown in Fig. 3 and discussed in detail below. The conductivity detector effluent (0.4 mL min^{-1}) was directed into the ESI-MS which was operated as described above. Total organic carbon analysis was performed on batch reaction samples as described previously (Perri et al., 2009) using a Shimadzu TOC-5000A Total Carbon Analyzer (TOCAN).