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Secondary organic aerosol production from aqueous photooxidation of glycolaldehyde: Laboratory experiments

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ABSTRACT

Organic particulate matter (PM) formed in the atmosphere (secondary organic aerosol; SOA) is a substantial yet poorly understood contributor to atmospheric PM. Aqueous photooxidation in clouds, fogs and aerosols is a newly recognized SOA formation pathway. This study investigates the potential for aqueous glycolaldehyde oxidation to produce low volatility products that contribute SOA mass. To our knowledge, this is the first confirmation that aqueous oxidation of glycolaldehyde via the hydroxyl radical forms glyoxal and glycolic acid, as previously assumed. Subsequent reactions form formic acid, glyoxylic acid, and oxalic acid as expected. Unexpected products include malonic acid, succinic acid, and higher molecular weight compounds, including oligomers. Due to (1) the large source strength of glycolaldehyde from precursors such as isoprene and ethene, (2) its water solubility, and (3) the aqueous formation of low volatility products (organic acids and oligomers), we predict that aqueous photooxidation of glycolaldehyde and other aldehydes in cloud, fog, and aerosol water is an important source of SOA and that incorporation of this SOA formation pathway in chemical transport models will help explain the current under-prediction of organic PM concentrations.

1. Introduction

The direct and indirect effects of atmospheric aerosols on radiative forcing introduce large uncertainties in climate change predictions (Kanakidou et al., 2005). Aerosols also contribute to poor air quality and adverse health effects (Poschl, 2005). Organic matter is a major component of atmospheric aerosol; however, the current understanding of the sources and atmospheric formation of organic particulate matter is insufficient to explain its atmospheric abundance (Heald et al., 2005).

It has been hypothesized (Blando and Turpin, 2000) that cloud and fog processing forms secondary organic aerosol (SOA) through aqueous reactions, similar to the formation of sulfate aerosol. Briefly, primary gas emissions such as alkenes and aromatics are oxidized in the gas phase to form water-soluble products. These water-soluble gases dissolve into cloud droplets and react in the aqueous phase to form low volatility products. Upon cloud droplet evaporation, these low volatility products remain at least in part in the particle phase, contributing SOA. This in-cloud SOA formation mechanism is supported by recent field evidence (Heald et al., 2006; Sorooshian et al., 2007a,b), laboratory studies of glyoxal, methylglyoxal, and pyruvic acid (Altieri et al., 2006, 2008; Carlton et al., 2006, 2007), and modeling studies (Chen et al., 2007; Ervens et al., 2004; Lim et al., 2005). Similar aqueous reactions in aerosol water have also been shown to form SOA in smog chamber experiments (Volkamer et al., 2008).

Glycolaldehyde is a water-soluble compound, $k_{H,298} > 3 \times 10^5$ M atm^{-1} (Betterton and Hoffmann, 1988), that is potentially important to SOA formation through aqueous phase reactions. Glycolaldehyde is produced in the gas phase from terpenes such as isoprene (Lee et al., 2006), from ethene (Niki et al., 1981), and it has been measured in biomass burning plumes (Bertschi et al., 2003). Because of isoprene's large global flux (468 Tg C year^{-1}) (Spaulding et al., 2003), the contribution of isoprene to the global burden of SOA will be substantial even if SOA yields are modest (Henze and Seinfeld, 2006). In the gas phase, 32% of isoprene is oxidized via hydroxyl radical ($\cdot$OH) to methyl vinyl ketone (MVK), and 70% of MVK is oxidized to glycolaldehyde via $\cdot$OH (Atkinson and Arey,

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1998; Spaulding et al., 2003), yielding a global glycolaldehyde flux of approximately 42 Tg C year^{-1} from isoprene and ·OH alone. Ethene is produced from automobile emissions and may contribute substantially to glycolaldehyde production in urban areas (Doskey et al., 1992; Niki et al., 1981). Comparable gas phase isoprene and glycolaldehyde mixing ratios were measured during the summer in rural Germany (Grossmann et al., 2003), with peak mixing ratios as high as 840 ppt in September in California (Spaulding et al., 1999) and 1.3 ppb in an August pollutant transport episode in Nova Scotia (Lee et al., 1996). Aqueous glycolaldehyde concentrations of 1 –5 μM were measured in cloud water during the FEBUKO experiment during fall in Germany (Bruggemann et al., 2005; Valverde-Canossa et al., 2005). Gas phase lifetimes (τ_{OH}) of isoprene, MVK, and glycolaldehyde are estimated to be 1.4 h (Atkinson and Arey, 2003; Kuhn et al., 2007), 6.9 h (Atkinson and Arey, 2003; Kuhn et al., 2007), and 1 day (Bacher et al., 2001; Niki et al., 1987), respectively, providing time needed for gas phase glycolaldehyde to reach clouds, fogs, or aerosols.

Gas phase oxidation of glycolaldehyde forms CO, CO_2, formic acid, formaldehyde, and glyoxal (Bacher et al., 2001; Butkovskaya et al., 2006; Karunanandan et al., 2007; Magneron et al., 2005). In the aqueous phase (Fig. 1) glycolaldehyde is expected to oxidize to form glyoxal and glycolic acid, which can both oxidize further to form glyoxylic acid and oxalic acid (Warneck, 2003). Glycolate, glyoxylate, and oxalate are found in the particle phase in the atmosphere (Jaffrezo et al., 1998; Lewandowski et al., 2007; Sorooshian et al., 2007b), typically with ammonium as the counter-ion. Thus the organic acids formed from aqueous glycolaldehyde oxidation are expected to partition with high efficiency into the particle phase (after formation in aerosol water and after cloud/fog droplet evaporation), contributing atmospheric SOA (Lim et al., 2005). Including this process in atmospheric models should help to close the gap between measured and modeled atmospheric particulate matter.

To our knowledge, the aqueous oxidation of glycolaldehyde via ·OH radicals has not been studied experimentally, but, as indicated above, has two possible reaction channels: formation of glycolic acid and glyoxal. The aqueous rate constants for formation of glycolic acid and glyoxal from glycolaldehyde used in current models are estimated based on the rate constant for formaldehyde oxidation and an assumed branching ratio (Warneck, 2003). Oxidation of glycolic acid via ·OH has been observed to form glyoxylic acid, oxalic acid, and formic acid in laboratory experiments (Vel Leitner and Dore, 1997). Oxidation of glyoxal has been shown to produce glyoxylic acid (Buxton et al., 1997), oxalic acid and formic acid, as well as uncharacterized higher molecular weight products (Carlton et al., 2007). Rate constants based on the disappearance of glyoxylic acid, oxalic acid, and formic acid upon reaction with ·OH have been measured (Ervens et al., 2003b). The glycolaldehyde chemical mechanism described above is currently in use in several atmospheric models (Chen et al., 2007; Ervens et al., 2008; Lim et al., 2005; Warneck, 2005).

In order to verify the fate of glycolaldehyde and to understand the role that the atmospheric aqueous photochemistry of glycolaldehyde plays in SOA production, bulk aqueous ·OH + glycolaldehyde experiments were performed, and products were measured by ion chromatography and on-line (real-time) mass spectrometry. Measured concentration dynamics were compared with those predicted by the chemical mechanism described above (Fig. 1). We verified that glyoxal and glycolic acid are produced and oxidize further to form glyoxylic acid, formic acid, and oxalic acid. Additional unpredicted products were identified and characterized, including malonic acid, succinic acid, and higher molecular weight species. The rate of glycolaldehyde disappearance and the formation of glyoxal are consistent with model predictions. The model over-predicts oxalic acid production by more than a factor of two relative to the experimentally observed concentrations and under-predicts glycolic acid by a similar amount. A better understanding of the chemical mechanism for production of the additional products is needed to improve model performance.

2. Methods

2.1. Reaction vessel experiment

To simulate the atmospheric aqueous phase photochemistry of glycolaldehyde, oxidation reactions via hydroxyl radical (·OH) were conducted in a 1 L glass reaction vessel (Ace glass 7841-16). Glycolaldehyde (Pfaltz & Bauer) was dissolved in 18 MOhm milli-Q water, filtered through a 0.45 μm filter, and diluted to 1 mM in the 1 L reaction vessel. H_2O_2 (5 mM, diluted from 30% H_2O_2, Sigma–Aldrich) was added to the reaction vessel and photolyzed in-situ using a 254 nm Hg lamp (Strahler) contained in a quartz immersion

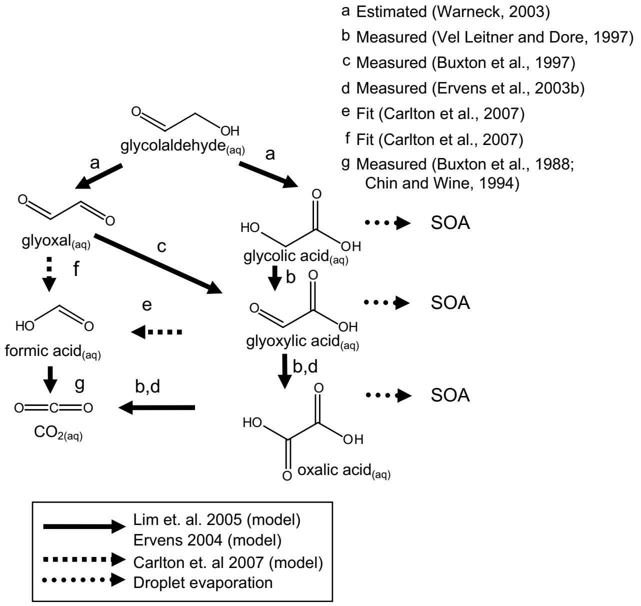

Fig. 1. Expected reaction scheme for glycolaldehyde oxidation based on works shown. Carlton et al. (2007) also includes reaction of glyoxal + ·OH to form large multi-functional compounds, which react further to form oxalic acid. All reactions are with ·OH except for (f), which is with H_2O_2.