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How do components of real cloud water affect aqueous pyruvate oxidation?

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ABSTRACT

Chemical oxidation of dissolved volatile or semi-volatile organic compounds within fog and cloud droplets in the atmosphere could be a major pathway for secondary organic aerosol (SOA) formation. This proposed pathway consists of: (1) dissolution of organic chemicals from the gas phase into a droplet; (2) reaction with an aqueous phase oxidant to yield low volatility products; and (3) formation of particle phase organic matter as the droplet evaporates. The common approach to simulating aqueous SOA (aqSOA) reactions is photo-oxidation of laboratory standards in pure water. Reactions leading to aqSOA formation should be studied within real cloud and fog water to determine whether additional competing processes might alter apparent rates of reaction as indicated by rates of reactant loss or product formation. To evaluate and identify the origin of any cloud water matrix effects on one example of observed aqSOA production, pyruvate oxidation experiments simulating aqSOA formation were monitored within pure water, real cloud water samples, and an aqueous solution of inorganic salts. Two analysis methods were used: online electrospray ionization high-resolution time-of-flight mass spectrometry (ESI-HR-ToF-MS), and offline anion exchange chromatography (IC) with quantitative conductivity and qualitative ESI-HR-ToF-MS detection. The apparent rate of oxidation of pyruvate was slowed in cloud water matrices: overall measured degradation rates of pyruvate were lower than in pure water. This can be at least partially accounted for by the observed formation of pyruvate from reactions of other cloud water components. Organic constituents of cloud water also compete for oxidants and/or UV light, contributing to the observed slowed degradation rates of pyruvate. The oxidation of pyruvate was not significantly affected by the presence of inorganic anions (nitrate and sulfate) at cloud-relevant concentrations. Future bulk studies of aqSOA formation reactions using simplified simulated cloud solutions and model estimates of generated aqSOA mass should take into account possible generation of, or competition for, oxidant molecules by organic components found in the complex matrices typically associated with real atmospheric water droplets. Additionally, it is likely that some components of real atmospheric waters have not yet been identified as aqSOA precursors, but could be distinguished through further simplified bulk oxidations of known atmospheric water components.

1. Introduction

Reactions of organic chemicals occurring within liquid water in the atmosphere, such as cloud or fog droplets, can form low volatility products that add particle-phase mass to the atmosphere after the droplets evaporate. This additional particle mass (called aqueous secondary organic aerosol, or aqSOA) is postulated to be formed primarily through the oxidation of dissolved "precursor" molecules by hydroxyl radical ($^{\bullet}OH$) in cloud and fog droplets, and through non-radical mechanisms in wet aerosol particles (which contain aqSOA higher precursor concentrations) and during droplet evaporation (Ervens et al., 2011, 2013; Loeffler et al., 2006). Formation of

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aqSOA has been supported by thermodynamic calculations of high molecular mass (HMM) compound production from aqueous reactions (Barsanti and Pankow, 2006), laboratory studies of simulated cloud droplet bulk-phase reactions (Carlton et al., 2006; Lee et al., 2011b), and comparison of products of laboratory bulk-phase reactions with components of real cloud water (Altieri et al., 2008). Particle mass formed through atmospheric aqueous reactions is particularly important because the added mass can shift the geometric mean diameter of particles released from evaporating droplets to larger sizes, making them more effective visible light scatterers (Hegg et al., 2004) and better cloud condensation nuclei (Feingold and Kreidenweis, 2000). The droplet particle size mode, formed through atmospheric aqueous reactions, often contains chemical species that are known or likely products of aqueous reactions, including sulfate, oxalate, glyoxylate, and other low molecular mass (LMM) organic acids (Crahan et al., 2004; John et al., 1990). Such compounds are commonly observed in ambient fogs and clouds (Herckes et al., 2013 and references therein).

The most commonly employed method for experimentally studying aqSOA formation reactions is to simulate oxidations occurring within the bulk phase of atmospheric water droplets. Simplified bulk aqueous oxidation experiments are generally carried out using a glass or quartz photoreactor containing the simulated cloud or fog solution and oxidant, and monitoring composition using offline and online analytical techniques such as chromatographic separation and/or mass spectral detection. A simulated atmospheric water solution generally contains only a few chemical constituents: for example, methylglyoxal or glyoxal with sulfate, nitrate, ammonium, or amines added (De Haan et al., 2011; Kirkland et al., 2013; Tan et al., 2009). Research has also been carried out to show oxidation within real cloud water solutions (Lee et al., 2012), within solutions of atmospherically relevant aromatic compounds in the presence of inorganic radicals or ions (Anastasio et al., 1997; Herrmann et al., 1995; Sun et al., 2010), and on inorganic particles at high relative humidity using various organic aqSOA precursors (Chan et al., 2013; Galloway et al., 2009; Zhang et al., 2011). It is understood that bulk reactions do not capture the dynamics or heterogeneous chemical interactions that occur at the surface of a droplet (Donaldson and Valsaraj, 2010), but instead are intended to reproduce bulk aqueous chemical reactions. The assumption is also made that the conditions of the reaction provided by the oxidant and simulated atmospheric water solution are chemically relevant for various suspended atmospheric water droplet systems such as cloud, fog, or wet aerosol water. It is possible that additional reactions occur within real atmospheric waters that differ from those proposed for simplified oxidation reactions, and that would alter the kinetics and contributions of particle mass by aqSOA formation processes under real cloud water conditions.

Many interactions of aqSOA precursor and oxidant molecules with trace atmospheric water components are possible, leading to multiple potential effects on observed product formation. Acidity and ionic strength are known to affect the extent of protonation and thus reactivities and photochemical properties of organic molecules and the partitioning of VOCs to atmospheric water (Ervens and Volkamer, 2010). Recently it has been found that very high concentrations of inorganic species are most likely needed for organic–inorganic interactions: sulfuric acid at cloud and fog droplet relevant concentrations (0.2–0.8 mM) does not impact glyoxal or methylglyoxal (0.03–3 mM) aqueous oxidation (Tan et al., 2009, 2010), and only a small decrease in product formation is observed when glyoxal is oxidized in the presence of nitric acid (1 mM glyoxal; Kirkland et al., 2013). At concentrations found in wet aerosol particles, however, aqueous inorganic salts (1–24 M) can react with methylglyoxal (1.6 M) and glyoxal (0.01–2.2 M) to form sulfur and nitrogen-containing organic products with light absorbing properties (Kampf et al., 2012; Sareen et al., 2010; Shapiro et al., 2009). Organic species with nitrogen and sulfur-containing moieties have been observed in fog water samples collected in Fresno, California (Mazzoleni et al., 2010), showing that complex interactions do occur within polluted atmospheric water droplets. Components of real cloud water could inhibit or speed aqueous oxidation reactions (and thus aqSOA formation) by effectively competing for light and/or oxidant molecules (Zhang et al., 2003), or by generating oxidant molecules (Arakaki and Faust, 1998). Such components include inorganic species and a wide range of organic molecules commonly found in cloud droplets (as listed in Herckes et al., 2013). Strong light absorption in the visible range by "brown carbon" species was recently reported, for example, from various organic nitrogen compounds identified in cloud water collected in Eastern China (Desyaterik et al., 2013). An apparent inhibition of organic species aqueous oxidation was observed due to chemical reduction with humic-like substances (HULIS) (Canonica and Laubscher, 2008), suggesting that oxidation reactions within atmospheric waters may be slowed in solutions where high molecular mass (HMM) organic components are present. Formation of reactive oxygen species from reactions of photosensitizers or formation of excited state phenols or HULIS could alternatively increase aqSOA formation reaction rates (Anastasio et al., 1997; Lin and Yu, 2011; Page et al., 2011). Metal–organic charge transfer reactions can also enhance organic radical formation (Zuo and Hoigné, 1994). It is proposed here that oxidants or other radical species (organic or inorganic) found or generated by UV photolysis within atmospheric water samples could enhance oxidation of aqSOA precursor species, or alternatively, that atmospheric water components could compete for oxidant molecules and/or UV light in sufficient amounts to effectively slow the rate of aqSOA product formation. The interactions of different reactants and oxidants within cloud water as compared to chemical standard solutions could also result in different chemical products. For example, if organic radicals are formed through photolysis or $^{\bullet}OH$ oxidation of cloud components, radical–radical reactions forming unique HMM products may occur. As Lim et al. (2013) have suggested, such formation of HMM products could compete with production of LMM organic acids such as oxalate.

Pyruvic acid is the most abundant aqueous reaction product of methylglyoxal (a gas-phase product of the oxidation of isoprene and many anthropogenic volatile organic compounds), and is a chemical intermediate in aqSOA formation pathways (Fig. 1; Lim et al., 2013). The mechanism of aqueous phase oxidation of pyruvic acid was proposed by Stefan et al. (1996) and later revised by Lim et al. (2013); it has been verified using simple photoreactions at high pyruvic acid concentration (1 mM), showing the production of glyoxylic acid followed by oxalic acid (Carlton et al., 2006; Tan et al., 2010). Here we report on experiments to examine real cloud water component