Laboratory study of the effect of oxalic acid on the cloud condensation nuclei activity of mineral dust aerosol

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ABSTRACT

Dicarboxylic acids, which make up a significant portion of the atmospheric organic aerosol, are emitted directly through biomass burning as well as produced through the oxidation of volatile organic compounds. Oxalic acid, the most abundant of the dicarboxylic acids, has been shown by recent field studies to be present in mineral dust aerosol particles. The presence of these internally mixed organic compounds can alter the water absorption and cloud condensation nuclei (CCN) abilities of mineral particles in the Earth's atmosphere. The University of Iowa's Multi-Analysis Aerosol Reactor System (MAARS) was used to measure the CCN activity of internally mixed particles that were generated from a mixture of either calcite or polystyrene latex spheres (PSLs) in an aqueous solution of oxalic acid. Although PSL is not a mineral dust component, it is used here as a non-reactive, insoluble particle. CCN measurements indicate that the internally mixed oxalate/calcite particles showed nearly identical CCN activity compared to the original calcite particles whereas oxalic acid/PSL internally mixed particles showed much greater CCN activity compared to PSL particles alone. This difference is due to the reaction of calcite with oxalic acid, which produces a relatively insoluble calcium oxalate coating on the particle surface and not a soluble coating as it does on the PSL particle. Our results suggest that atmospheric processing of mineral dust aerosol through heterogeneous processes will likely depend on the mineralogy and the specific chemistry involved. Increase in the CCN activity by incorporation of oxalic acid are only expected for unreactive insoluble dust particles that form a soluble coating.

1. Introduction

Dicarboxylic acids (DCAs) are a significant portion of the organic aerosol mass concentration, with oxalic acid being the most abundant (Legrand et al., 2005; Sorooshian et al., 2006; Martinelango et al., 2007; Hsieh et al., 2009; Hsu and Ding, 2009; Miyazaki et al., 2009; Kundu et al., 2010) having concentrations measured as high as 1.43 µg m^{-3} (Miyazaki et al., 2009). This accounts for as much as 84% of the total DCAs in the atmosphere (Hsieh et al., 2009). Formation pathways for oxalic acid are still being investigated, but one primary source is known to be biomass burning (Li et al., 2009; Yang et al., 2009). Secondary production of oxalic acid occurs through oxidation of gaseous glyoxal (Rinaldi et al., 2011) and photooxidation of longer-chain DCAs (Yang et al., 2008a, 2008b; Kundu et al., 2010) which is enhanced in aqueous-phase reactions in cloud droplets (Carlton et al., 2007; Chen et al., 2007; Ervens et al., 2008). Field measurements by Hsieh et al. of suburban aerosol in

southern Taiwan reported that peak concentrations of oxalic acid occurred in the droplet mode, indicating an association with cloud processing (Hsieh et al., 2009). Model simulations (Ervens et al., 2004; Chen et al., 2007) and field studies (Tan et al., 2009) and have shown the production of secondary organic aerosols (SOAs), including oxalic acid, to be enhanced in the presence of clouds. Additionally, measurements of the contribution of oxalic acid to the total water soluble organic concentrations in New Delhi showed higher mass fractions of oxalate during nighttime compared to daytime, suggesting the production of oxalate via the oxidation of longer-chain DCAs in aqueous aerosols which were more abundant under higher relative humidity conditions present during the nighttime (Miyazaki et al., 2009). Similarly, sulfate which has been long recognized to form during cloud processing has been shown to have concentrations highly correlated with those of oxalate, suggesting oxalate is also produced via cloud processing (Yu et al., 2005; Sorooshian et al., 2006; Yang et al., 2009).

Along with heterogeneous gas-phase reactions (Usher et al., 2003; Krueger et al., 2004; Sullivan and Prather, 2007; Sullivan et al., 2009b), cloud processing has also been shown to be an important pathway for the formation of coated or internally mixed

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mineral dust aerosol (Liu et al., 2005; Matsuki et al., 2010). Generated from windblown soil, mineral dust can be transported globally with atmospheric lifetimes of days to weeks, during which time it can impact the Earth's climate as well as the chemical balance of the atmosphere (Bauer et al., 2004). Coating of the mineral dust particles can occur through cloud processing as the particles are collected by existing cloud droplets which were nucleated by soluble particles and that dissolved soluble material is redistributed until evaporation leaves internally mixed particles. On a global average it has been estimated that any particular atmospheric aerosol has undergone the evaporation/condensation cycle three times, (Pruppacher and Jaenicke, 1995) and repetition of this cycle has been shown to significantly increase the mass of soluble material incorporated into dust particles (Wurzler et al., 2000). Freshly emitted dust and mineral aerosols can have a significant hygroscopicity and CCN activity (Kumar et al., 2011) which has been shown to increase due to the cloud processing of dust aerosols (Crumeyrolle et al., 2008) as well as impact the deposition of dust (Fan et al., 2004). Conversely, the association of hygroscopic and CCN active substances like diacids can be decreased due to their incorporation into mineral dust (Sullivan and Prather, 2007).

Carbonates, a significant and reactive component of mineral dust aerosol, have been found enriched in some cloud residual samples (Matsuki et al., 2010) providing evidence that there is potential for these coatings or aqueous reactions to occur. In a study of Asian aerosol by Sullivan et al. 10.2% of the mineral dust particles contained oxalic acid which was only detected in the dust particles (Sullivan and Prather, 2007). They hypothesized that DCAs may be found in increased amounts in mineral dust due to their ability to chelate divalent cations such as Ca^{2+} and Mg^{2+} (Sullivan and Prather, 2007). The presence of internally mixed oxalate has also been measured in another Asian dust aerosol, as well as a Saharan dust aerosol (Falkovich et al., 2004; Yang et al., 2009). It is also possible for calcite to react with oxalic acid to form calcium oxalate, according to:

$$CaCO_3 + H_2C_2O_4 \leftrightarrow CaC_2O_4 + CO_2 + H_2O \qquad (1)$$

Although the hygroscopicity (Prenni et al., 2001; Fan et al., 2004; Svenningsson et al., 2006) and CCN activity (Sullivan et al., 2009a; Falkovich et al., 2004; Kumar et al., 2003; Giebl et al., 2002; Hori et al., 2003; Sun and Ariya, 2006) of dicarboxylic acids such as oxalic acid has been measured previously and oxalic acid has been shown to act as heterogeneous ice nucleus (Zobrist et al., 2006), it is still not clear how internally mixed DCAs may impact the climate forcing properties of mineral dust. Xue et al. reported increased light scattering and absorption of soot aggregates with thin coatings of dicarboxylic acids, which was further enhanced when the coated soot was exposed to high relative humidity (Xue et al., 2009) and increases in hygroscopicity and CCN activity have been measured when calcite was internally mixed with organic humic substances (Hatch et al., 2008, 2009). In this study, measurements of the CCN activity of internally mixed particles generated from mixtures of either calcite ($CaCO_3$) or PSLs in an aqueous solution of oxalic acid were made. $CaCO_3$ and PSLs were used as models for mineral dust aerosol with one being a reactive component and the other an unreactive, insoluble component. PSLs were used widely in earlier studies to investigate atmospheric processes. Internally mixed aerosol particles consisting of PSLs and soluble components were used before to study the impact of heterogeneous processing of mineral dust aerosol on climate (Gibson et al., 2007). The CCN activity of coated PSLs was also used to explore the effectiveness of humic coatings on insoluble particles (Hatch et al., 2008). In addition, coated PSL spheres were used to study products and mechanisms of ozone reactions with oleic acid for aerosol particles (Katrib et al., 2004). Besides CCN measurements, Fourier transform infrared

(FT-IR) extinction measurements were performed to confirm speciation of oxalate in the internally mixed calcite particles.

2. Experimental methods

2.1. Materials

All of the chemicals used in this study were commercially available and used as received. Oxalic acid (99.999%) was purchased from Aldrich, and aerosols were generated from a 0.2-wt% solution using Optima water (Fisher Scientific). Calcite (OMYA) and PSLs (Polysciences, Inc., Cat. #07304) were atomized from suspensions in Optima water. Internally mixed particles were generated by atomizing a suspension of insoluble powder in an aqueous solution of soluble material. Calcium oxalate monohydrate (99.9985%) was purchased from Alfa Aesar.

2.2. Size distribution and cloud condensation nuclei activity measurements and Fourier transform infrared extinction spectra

Size distributions and cloud droplet activation measurements were obtained using the University of Iowa's Multi-Analysis Aerosol Reactor System (MAARS), which has been described in detail elsewhere (Gibson et al., 2006). Aerosols were generated by a constant output atomizer (Model 3076, TSI, Inc.) from an aqueous solution or suspension as described above. The aerosol was then passed through two diffusion dryers (Model 3062, TSI, Inc.) and dried to a low relative humidity (RH ≤ 10%). The particles follow a flow stream from the aerosol generator through the path of the IR beam by a combination of conductive tubing and glass flow tubes. The glass flow tube system consists of an initial conditioning tube and an observation cell that is collinear with the IR beam. For the CCN measurements the aerosol was passed through a differential mobility analyzer (DMA_1; Model 3080, TSI, Inc.) in order to size select 200 nm particles. The sheath and aerosol flows of the DMA_1 were set to be 3 lpm and 0.3 lpm, respectively. This monodisperse aerosol was then split between a continuous flow streamwise thermal-gradient cloud condensation nuclei counter (Droplet Measurement Technologies; Model CCN-2) (Roberts and Nenes, 2005) and a condensation particle counter (CPC; Model 3025A, TSI, Inc.). For a given diameter and supersaturation, the CCN activity is reported as the ratio of particles that act as a cloud condensation nuclei (#CCN) to the number of particles counted by the CPC (#CN). The ammonium sulfate activity data presented by Tang and Munkelwitz was used to calibrate the supersaturation generated in the CCN counter to the thermal gradient of the diffusion chamber (Tang and Munkelwitz, 1994). This is useful so as to compare to other measurements made previously in our laboratory. Full size distributions were measured by bypassing DMA_1 and directing the dry polydisperse aerosol into a scanning mobility particle sizer (SMPS; Model 3936, TSI, Inc.), which consists of a second DMA (DMA_2) (flow rates are 3.0 (sheath) and 0.3 (sample) lpm) coupled to the CPC. The FT-IR extinction spectra were measured using a Fourier-transform infrared (FT-IR) spectrometer (Thermo Nicolet Nexus Model 670) with a liquid nitrogen cooled external MCT-A detector. The IR spectra were acquired from 740 to 4000 cm^{-1} using 8 cm^{-1} resolution by co-adding 256 scans. All FT-IR spectra were referenced to the background signal collected under dry conditions.

2.3. Theoretical methods

A single hygroscopicity parameter, κ, has recently been developed using "κ-Köhler theory" (Petters and Kreidenweis, 2007, 2008) in order to determine a single parameter which can be