Synergistic effect in the humidifying process of atmospheric relevant calcium nitrate, calcite and oxalic acid mixtures

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ABSTRACT

Hygroscopicity is a critical property for evaluating aerosol’s environmental and climate impacts. Traditional view always considered hygroscopic behavior of aerosol as a water adsorption/absorption—desorption cycle in which the size, water content and morphology etc. are well characterized. However, the chemical reactions between coexisting components in mixed particles during humidifying-dehumidifying process are almost neglected. In this study, we found that there exists synergistic effect among Ca(NO$_3$)$_2$, CaCO$_3$ and H$_2$C$_2$O$_4$ mixtures during humidifying process. Substitution of strong acid (HNO$_3$) by medium acid (H$_2$C$_2$O$_4$) take place during vapor absorption on Ca(NO$_3$)$_2$/H$_2$C$_2$O$_4$ mixture. Moreover, the presence of nitrate exhibits a promotive effect to the reaction between H$_2$C$_2$O$_4$ and CaCO$_3$ under ambient condition. These results provoke us to rethink the hygroscopic behavior of mixed aerosol in which chemical reaction can greatly change the chemical composition, mixing state and consequently environmental and climate impacts.

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1. Introduction

Dicarboxylic acids (DCAs, or diacids) are ubiquitous in the atmosphere and represent a significant portion of the organic fraction of aerosols (Chebbi and Carlier, 1996). Due to their strong hydrophilic and hygroscopic properties, dicarboxylic acids are able to reduce surface tension of cloud condensation nuclei (CCN), which consequently affect the cloud formation and the global radiation balance (Facchini et al., 1999; Yu, 2000). Oxalic acid (H$_2$C$_2$O$_4$, or HOx) is the most abundant contributor to the total dicarboxylic acid mass in ambient organic aerosol particles, which has been detected in aqueous phase (fog, cloud, and precipitation) and particulate phases (Chebbi and Carlier, 1996; Kawamura et al., 2010; Yao et al., 2002; Yu, 2000). The primary sources of HOx include fossil fuel combustion, biomass burning and vehicle exhaust while the secondary formation pathways include photo-oxidation of volatile organic compounds (VOC) in gas-phase, aqueous phase, and heterogeneous processes (Carlton et al., 2007; Chebbi and Carlier, 1996; Warneck, 2003; Yu, 2000). There also observed a high correlation between sulfate and oxalate in aerosol collected at various locations, which was likely a result of the potential importance of the in-cloud formation pathway for both sulfate and oxalate (Yu et al., 2005).

Recently, field measurement results of analyzing Asian dust by single particle mass spectrometry (ATOFMS) showed that HOx was predominantly mixed with mineral dust during transportation in the atmosphere (Sullivan and Prather, 2007; Yang et al., 2009). In these studies, oxalic acid were typically detected as the conjugate anion, [H$_2$C$_2$O$_4$]$^-$ (m/z –89), in the ATOFMS. Sullivan and Prather (2007) proposed a mechanism to explain these observations. The diacids and their precursors which were produced from the photochemical oxidation of volatile organic compounds were partitioned to the alkaline Asian dust, subsequently the precursors underwent heterogeneous and aqueous oxidation. It indicates that there exists affinity interaction between HOx and dust particles, especially alkaline constituents. In contrast, by using X-ray absorption fine structure spectroscopy (XAFS), Furukawa and Takahashi found that most of the oxalic acid is present as metal oxalate complexes in the aerosols, especially present as Ca and Zn oxalate complexes (Furukawa and Takahashi, 2011). It seems that there exists a discrepancy between field measurement results and the conversion mechanism of oxalic acid to oxalate complexes has not been well recognized.

On the other hand, calcite (CaCO$_3$) is an important ubiquitous mineral in the atmosphere as well as a reactive component of mineral dust aerosols. Due to its alkalescence, calcite has a significant neutralization effect on atmospheric acidic constituents, such as H$_2$SO$_4$, SO$_2$, HNO$_3$, NO$_2$, and carboxylic acids (Dentener et al., 1996; Prince et al., 2008; Usher et al., 2003). These reactions not only change atmospheric trace gas distributions but also modify the composition and mixing state of particles, and consequently affect the thermodynamic and optical properties of particles. For example, Ca(NO$_3$)$_2$/CaCO$_3$ mixture formed from heterogeneous reaction between nitric acid and calcite has been observed in both field
measurement and laboratory studies (Al-Abadleh et al., 2003; Laskin et al., 2005; Sullivan et al., 2007). Soluble calcium nitrate formed on calcite surface enormously enhanced the hygroscopicity of the mixtures and reactivity to other soluble gases (Al-Abadleh et al., 2003; Liu et al., 2008; Prince et al., 2008). However, little is known about the interaction between calcite and HOx in mixed mineral dust particles.

The hygroscopic behavior of individual components, such as CaCO₃, Ca(NO₃)₂, or H₂C₂O₄, were widely studied (Braban et al., 2003; Gibson et al., 2006; Gustafsson et al., 2005; Peng et al., 2001; Tang and Fung, 1997), while the hygroscopic behavior of these particle mixtures has been paid little attention except the Ca(NO₃)₂/CaCO₃ mixture (Al-Abadleh et al., 2003; Liu et al., 2008). It seems that oxalate may be probably formed from the calcite/oxalic acid mixture under humid condition although it is not clear yet. Here, we present the first laboratory study about the hygroscopic behavior of mixed calcite and HOx particles. A little amount of Ca(NO₃)₂ was added to this mixture to mimic atmospheric aged calcite particles. The aim of this work is to reveal the potential formation mechanism of oxalate complexes in mixed aerosol particles during the atmospheric aging process. It showed that the affinity between oxalic acid and alkaline dust might not be that simple and synergistic effect between different components plays an important role in the humidifying process.

2. Materials and methods

2.1. In situ Raman spectroscopy

Raman spectroscopy has been proven as a powerful tool and widely used to investigate the heterogeneous reactions and hygroscopic behavior of aerosol (Liu et al., 2008; Tang and Fung, 1997). In situ Raman spectra were recorded on a UV resonance Raman spectrometer (UVR DLPC-DL-03), which has been described in a previous article (Liu et al., 2010). Briefly, a continuous diode pumped solid state (DPSS) laser beam (532 nm) was used as the exciting radiation with the source power of 40 mW. The diameter of the laser spot on the sample surface was focused at 25 μm. The spectra resolution was 2.0 cm⁻¹. The instrument was calibrated against the Stokes Raman signal of Teflon at 1378 cm⁻¹. All experiments were conducted at 293 K. Particles were placed in an in situ cell as flow reactor. The relative humidity was controlled by adjusting the ratio of dry and humid nitrogen in the gas flow and it was recorded by a moisture meter (CENTER 314, China) with an accuracy ±2% RH and ±0.1 K. The equilibrium time for each RH point was more than 30 min. A humidifying-dehumidifying (H–D) cycle represents that the relative humidity increased from 0 to 99% and then decreased to 0 step by step.

2.2. Vapor sorption analyzer

Water adsorption isotherms were measured with a modified vapor sorption analyzer at 278 K. The method has been described in a previous article (Ma et al., 2010). The mixed particles were first ground together and then evacuated at room temperature for 3 h with the pressure of 10⁻³ Torr. The evacuated particles were exposed to vapor with different RH to determine its adsorption isotherm by calculating the pressure change during the equilibrium process.

2.3. Chemicals

Externally mixed particles were prepared by grinding different components together and then were placed in a flow reactor. The molar ratio of HOx and calcite was unity according to the stoichiometry. CaCO₃ (AR, Beijing Yili Fine Chemical Co. Ltd.), H₂C₂O₄·2H₂O (AR, Tianjin Jinke Chemical Co. Ltd.) and Ca(NO₃)₂·4H₂O (AR, Beijing Yili Fine Chemical Co. Ltd.) were used as purchased. Distilled H₂O was degassed by heating prior to use.

3. Results

3.1. Raman spectra of oxalic acid dihydrate and anhydrous particles

At first, the Raman spectra of oxalic acid dihydrate and anhydrous particles were measured and the results are shown in Fig. 1. For dihydrate particles, several peaks at 111, 158, 185, 483, 577, 642, 858, 1383, 1494, 1636, 1692, and 1738 cm⁻¹ are observed in the range of 50–2000 cm⁻¹, while two bands at 3445 and 3485 cm⁻¹ are observed in the range of 2400–3800 cm⁻¹. The oxalic acid dihydrate molecular has the C₂ᵥ point group symmetry and eighteen normal modes which were summarized detailedly by Mohacek-Grosev et al. (2009).

According to the assignments in literatures (Ebisuzaki and Angel, 1981; Mohacek-Grosev et al., 2009; Nieminen et al., 1992), we made assignments of these peaks as follows. The peaks at 1636, 3445, and 3485 cm⁻¹ are attributed to the bending mode (ν₁), symmetric (ν₂) and asymmetric (ν₃) stretching modes of hydrated water, respectively. These three peaks disappeared when the dihydrate particles were purged with dry N₂ for 2 h, as seen in the spectrum of anhydrous particles. The peaks at 1738, 1383, 858, and 483 cm⁻¹ are assigned to the stretching mode of C–O, C–OH, C–C, and the out of plane bending mode of C=O, respectively. These peaks shifted to 1712, 1320, 850, and 486 cm⁻¹ in the spectrum of anhydrous particles. The peak at 1692 cm⁻¹ is due to the coupled C=O and C–O stretching modes. The peak at 1494 cm⁻¹ is due to the COH deformation coupled to C–O and C–C stretching, which shifted to 1486 cm⁻¹ for anhydrous particles. The peaks at 642 and 577 cm⁻¹ are attributed to the out of plane bending and in plane deformation of COOH while in the anhydrous particles only the in plane deformation mode at 541 cm⁻¹ is observed. The peaks at 180 and 158 cm⁻¹ have been attributed to the translational lattice vibration of the water molecule (Ebisuzaki and Angel, 1981). However, these peaks can also be seen in the spectrum of anhydrous particles without position shift. Therefore, these peaks may be due to the inter-molecular hydrogen-bonding. Another peak at 111 cm⁻¹ is the characteristic feature of the α-phase of oxalic acid dihydrate (Ebisuzaki and Angel, 1981), which shifts to 120 cm⁻¹ for
anhydrous particles. Three peaks at 2585, 2770, and 2910 cm\(^{-1}\) in the spectrum of anhydrous particles were not reported in literatures which may be due to combination tone.

3.2. Hygroscopic behavior of oxalic acid anhydrous particles

Fig. 2 shows the Raman spectra of water adsorption on anhydrous oxalic acid particles as a function of relative humidity. The peaks at 120, 158, 185, 486, 541, 847, 1320, 1486, and 1707 cm\(^{-1}\) for anhydrous particles are observed in Fig. 2A. When these particles were exposed to vapor, several peaks at 111, 158, 185, 486, 577, 642, 862, 1383, 1494, 1636, and 1738 cm\(^{-1}\) were observed as RH increased. According to the discussion above, these peak position shifts are due to the conversion of anhydrous particles to dihydrate. Moreover, as seen in Fig. 2B, the appearance of peaks at 3445 and 3485 cm\(^{-1}\), which is similar to that of dihydrate oxalic acid particles, is also attributed to formation of hydrate.

The peak at 111 cm\(^{-1}\) as the characteristic feature of the \(\alpha\)-phase of oxalic acid appears at 31.4% RH, indicating the conversion of anhydrous to dihydrate took place in the range of 15.7–31.4% RH, which is consistent with Braban et al. (2003). However, no deliquescence in the range of 0–99% RH was observed. It would be discussed later.

3.3. Hygroscopic behavior of mixed calcite/oxalic acid anhydrous particles

Externally mixed particles were prepared by grinding different components together and then were placed in a flow reactor. After purged with dry N\(_2\), these mixed particles were exposed to vapor at various relative humidity. Fig. 3 shows the case of equal molar ratio of HOx and calcite. For the mixed particles after purged with dry N\(_2\), several peaks at 120, 158, 185, 286, 486, 541, 715, 847, 1088, 1481, and 1707 cm\(^{-1}\) were observed (Fig. 3A). The bands at 715 and 1088 cm\(^{-1}\) are assigned to the asymmetric and symmetric stretching mode of CO\(_3^2\) while the band at 286 cm\(^{-1}\) is attributed to lattice mode in calcite. All other peaks are attributed to anhydrous oxalic acid. When these particles were exposed to vapor, intensity decrease and position shift of above bands were observed. At 31.4% RH, an intense peak at 111 cm\(^{-1}\) due to the hydrogen-bond between H\(_2\)O and HOOCCOOH is observed indicating water absorption in anhydrous HOx (Mohacek-Grosev et al., 2009). It is also supported by the appearance of peaks at 1636 cm\(^{-1}\) assigned to the bending mode (\(\delta\)H\(_2\)O) of water. As RH rise to above 31.4% RH, peak positions shift were observed from 847 cm\(^{-1}\) to 860 cm\(^{-1}\), 1481 cm\(^{-1}\) to 1494 cm\(^{-1}\), and 1707 cm\(^{-1}\) to 1742 cm\(^{-1}\), respectively. These results are similar to that of water adsorbed on pure anhydrous HOx, in which dihydrate of
oxalic acid was formed in water adsorption/absorption process and no deliquescence was observed. However, no peak due to calcium oxalate appears implying no reaction between HOx and calcite occurred even at high relative humidity (~99% RH). More supportive evidence is seen in Fig. 3B. The spectrum of mixed particles subject to a humidifying-dehumidifying cycle was very similar to that of initial mixed particles. These results indicate that only conversion of anhydrous oxalic acid to dihydrate occurred and no reaction between HOx and calcite happened in the humidifying-dehumidifying cycle.

In the presence of 10 wt% Ca(NO₃)₂, the mixed HOx/calcite showed totally different behavior during the humidifying process from that of particles without third component. As seen in Fig. 4A, the spectrum of dry mixed particles was similar to that of mixed HOx/calcite in Fig. 3B except an additional peak at 1065 cm⁻¹ due to anhydrous calcium nitrate (Tang and Fung, 1997). When the RH increased to 20.4% RH, the peak at 111 cm⁻¹ was clearly seen indicating the conversion of anhydrous HOx to dihydrate. The peak at 1065 cm⁻¹ shifted to 1051 cm⁻¹ is due to the deliquescence of Ca(NO₃)₂, which is consistent with the deliquescence point of anhydrous Ca(NO₃)₂ at 18% RH (Tang and Fung, 1997). Moreover, as RH increase to 60.0% RH, peaks at 158, 200, 1468, 1490, and 1637 cm⁻¹ increased as the exposure time increased. It implies that conversion of H₂C₂O₄ and Ca(NO₃)₂ to Ca(C₂O₄)₂-H₂O take place during the water absorption process. It implied that substitution of nitric acid by oxalic acid occurred in this reaction.

Although the acidity of nitric acid is stronger than oxalic acid, it should be noted that the product (calcium oxalate) is less soluble. The water content of the droplet depended on the mass fraction of soluble compounds, like both calcium nitrate and oxalic acid. When both these two compounds were consumed and converted to insoluble calcium oxalate, the water content of the whole droplet would be reduced. The residual nitric acid in the droplet would either react with calcite if it is present, or partition to gas phase due to its low solubility if no calcium carbonate is present.

3.5. Water adsorption isotherms measured by vapor sorption analyzer

Fig. 6 shows the water adsorption isotherms of anhydrous HOx, HOx/CaCO₃ mixture and 10 wt% Ca(NO₃)₂—HOx/CaCO₃ particles at
that the reaction between HOx and CaCO₃ which was catalyzed by process was not continued because the equilibrium time for another study by aerosol the deliquescence of Ca(NO₃)₂ (Al-Abadleh et al., 2003). As RH in the release of CO₂ since the water amount was calculated by the RH above 35%RH. This is due to the decomposition of CaCO₃ resulting interested to note that the water absorbed amount decrease as the change of pressure in the tube (Ma et al., 2010). The adsorption process was not continued because the equilibrium time for achieving the next point was too long. Nevertheless, it supported that the reaction between HOx and CaCO₃ which was catalyzed by the presence of Ca(NO₃)₂ under humid condition.

4. Discussion

Hygroscopic behaviors of calcite, calcium nitrate or HOx have been studied widely. For HOx, hygroscopic growth was measured by various researchers. By using an electrolytic balance (EDB), Peng et al. (2001) determined that oxalic acid does not deliquesce in the range of 10%–90% RH with little growth of particle size. In another study by aerosol flow tube-FTIR, Braban et al. (2003) reported the conversion of anhydrous oxalic acid to dihydrate at 12% RH and a deliquescence point at ~98% RH for oxalic acid particles at 293 K. However, no deliquescence was observed for both HOx and mixed HOx/calcite particles even the recorded RH was 99% RH in this study. It may be due to the true RH in our system did not reach 98% RH since the accuracy of moisture meter is about 2% RH. Nevertheless, it is well known that typical ambient relative humidity is in the range of 20–90% which means deliquescence of dihydrate HOx hardly happen in the atmosphere. Therefore, reaction between HOx and calcite in the atmosphere is limited. In the case of calcite, water adsorption isotherm exhibits a multilayer adsorption type curve without deliquescence (Al-Hosney and Grassian, 2005; Gustafsson et al., 2005), indicating its weak hygroscopic property. It was demonstrated that heterogeneous reaction with HNO₃ alters significantly the hygroscopic property of calcite. The growth factors at 85% RH for CaO₂ and Ca(NO₃)₂ are 1.01 and 1.77, respectively (Gibson et al., 2006). Calcite particles with thin film nitrate coating shows a DRH at ~11% RH (Al-Abadleh et al., 2003). Therefore, the presence of Ca(NO₃)₂ could enhance the water adsorption/absorption capacity of calcite particles, which makes the mixed particles in the solution state in the atmosphere (Al-Abadleh et al., 2003; Liu et al., 2008). In the present study, when Ca(NO₃)₂ was mixed with HOx/calcite mixture, it enhanced the water absorption on these mixed particles under humid condition. It then led to the dissolution of both Ca(NO₃)₂ and HOx, namely Ca²⁺, NO₃⁻, H⁺ and C₂O₄²⁻ in solution. It resulted in the formation of CaC₂O₄ due to its low solubility. Consequent decomposition of calcite by H⁺ in the aqueous phase yield Ca²⁺ and CO₂. In the end, calcite was converted to CaC₂O₄·H₂O which was mixed with Ca(NO₃)₂. Nitrate species, which was involved in the reaction between HOx and calcite, was not lost or produced but had a catalytic effect on this reaction. Therefore, nitrate could be considered as a catalyst to promote this reaction when calcite was present. Based on these results, we deduce a reaction mechanism for Ca(NO₃)₂/CaCO₃/H₂C₂O₄ mixture in humidifying process.

\[
\begin{align*}
\text{H}_2\text{C}_2\text{O}_4 + \text{Ca(NO}_3)_2 + \text{H}_2\text{O} & \rightarrow \text{CaC}_2\text{O}_4 + \text{H}_2\text{O} + 2\text{HNO}_3 \\
2\text{HNO}_3 + \text{CaCO}_3 & \rightarrow \text{Ca(NO}_3)_2 + \text{CO}_2 + \text{H}_2\text{O} \\
\text{H}_2\text{C}_2\text{O}_4 + \text{CaCO}_3 & \rightarrow \text{CaC}_2\text{O}_4 + \text{H}_2\text{O} + \text{CO}_2
\end{align*}
\]

The net reaction between HOx and CaCO₃ in this mixture system can be written as follow:

\[
\text{H}_2\text{C}_2\text{O}_4 + \text{CaCO}_3 \rightarrow \text{CaC}_2\text{O}_4 + \text{H}_2\text{O} + \text{CO}_2
\]

Oxalic acid is considered as a relatively strong acid with pK₁=1.38 and pK₂=4.28 in solution at room temperature. Dihydrate is the stable form of HOx particles under ambient relative humidity (20–90% RH). Therefore, direct reaction between mixed oxalic acid and calcite hardly happen in the atmosphere. However, the presence of coexisting hygroscopic nitrate species could facilitate this reaction greatly. It suggests that the presence of another hygroscopic component can also enhance the reaction between HOx and calcite under humid condition. For other coexisting hygroscopic component (e.g. NH₄NO₃) without soluble Ca²⁺ after deliquescence, reactions (1) and (2) are not existing and only reaction (3) take place after the mixed particles immersing in an aqueous circumstance. Since both the mixtures, HOx/calcite and Ca(NO₃)₂/CaCO₃ are frequently observed in the atmosphere (Laskin et al., 2005; Sullivan et al., 2007; Sullivan and Prather, 2007; Yang et al., 2009; Yang and Yu, 2008), this study has a great significance in understanding the complex processes in the atmosphere.

Firstly, reaction with calcite should be considered as an important sink for HOx. Although direct reaction between HOx and calcite does not readily take place under ambient humid condition, it is very likely to occur in the presence of Ca(NO₃)₂. Calcium oxalate is a preferential trap for both Ca²⁺ and C₂O₄²⁻ as a result of its relatively low solubility. Thus it also brings measurement discrepancy in analyzing atmospheric HOx species in mineral aerosol since HOx was always considered in the form of molecular state or soluble oxalate ion (Sullivan and Prather, 2007; Yang et al., 2009; Yao et al., 2002; Yu et al., 2005). Insoluble oxalate species, such as calcium oxalate, may be neglected.

![Fig. 6. Water adsorption isotherms of HOx (empty square), HOx/CaCO₃ (solid triangle) and 10 wt% Ca(NO₃)₂–HOx/CaCO₃ (solid square) at 278 K. The molar ratio of HOx and CaCO₃ are unity in all experiments.](image-url)
Secondly, the mixing state of aerosol particles always affects their atmospheric vitre and physicochemical properties, especially hygroscopic effect. A common traditional assumption is that mineral dust particles become more hygroscopic and CCN-active after atmospheric processing. However, it is not true in the case of mixed oxalic acid and calcite since the CCN active of CaC2O4 is similar to calcite and less than oxalic acid (Sullivan et al., 2009). Moreover, the hygroscopicity of Ca(NO3)2 will also be lowered by mixing with oxalic acid. On the other hand, it is possible that oxalic acid in the aerosols cannot contribute to the increase of the CCN activity in the atmosphere since it can be converted to insoluble oxalate complex. These results indicate that any other DCA, such as malonic and succinic acids, can also form metal complexes in aerosols because of their high stability (Furukawa and Takahashi, 2011). It may lead to over-estimation of the CCN activity of aerosol particles by treating oxalic acid and other DCAs as hygroscopic. It is suggested that a reevaluation of the climate impacts originated from DCA in aerosols is required.

Thirdly, this study revealed that synergistic process in the atmosphere has a significant effect on the transformation of constitutions in mixed aerosol particles. Although calcite has a neutralization effect on atmospheric acidic gases, such as HNO3, NO2, and SO2 (Dentener et al., 1996), the reactions between calcite and these gaseous pollutants are different. The reactions between calcite with SO2 or oxalic acid are mainly limited on the surface of calcite since calcium sulfate or oxalate are both less-hygroscopic (Sullivan et al., 2009). In contrast, the bulk of calcite can be involved in the reactions with HNO3 or NO2. Because the product Ca(NO3)2 is very hygroscopic which enhanced absorption of water and consequently enhanced further uptake of HNO3 or NO2 (Al-Abadieh et al., 2003; Liu et al., 2008). The presence of Ca(NO3)2 can also promote the reactions between calcite and other acidic gases by providing an aqueous circumstance under humid condition (Prince et al., 2008). When insoluble calcium salts (e.g. CaSO4 2H2O or CaC2O4·H2O) formed in these systems, further decomposition of calcite occurred according to equation (2). These mechanisms can probably interpret the formation of mixed nitrate, sulfate, oxalate and carbonate in atmospheric aerosol particles. Further investigation of these processes will promote our understanding about the transportation of aerosol particles in the atmosphere.

5. Conclusion

In this study, we demonstrated that synergistic effect plays an important role on the humidifying process of calcite, calcium nitrate and oxalic acid mixtures. The coexisting hygroscopic nitrate can make the reaction between calcite and oxalic acid happen under atmospheric ambient humid condition. Substitution of nitrate by oxalate takes place during the humidifying process of calcium nitrate and oxalic acid. The formation of calcium oxalate decreased the hydrophilic property of the mixed particles and resulted in the release of nitric acid.

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References


