

Field observation on secondary organic aerosols during Asian dust storm periods: Formation mechanism of oxalic acid and related compounds on dust surface

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HIGHLIGHTS

- High concentration of oxalic acid observed during the dust events.
- Oxalic acid, glyoxal and methylglyoxal dominated in coarse particles.
- Aqueous-phase formation of oxalic acid on dust surface.

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ABSTRACT

Chemical evolution of East Asian dust during transpacific transport has been given much attention for inorganic species such as sulfate, nitrate and ammonium. However, the role of organic species during the transport has almost entirely been ignored. To understand the formation mechanism of secondary organic aerosols (SOA) on dust surfaces, this study investigated the concentrations and compositions of dicarboxylic acids, keto-carboxylic acids, α -dicarbonyls and inorganic ions in size-segregated aerosols (9-stages) collected in Xi'an, central China during the two dust storm episodes in the springs of 2009 and 2011 and compared with those in nondust storm periods. During the events the ambient particulate dicarboxylic acids were 932–2240 ng m⁻³, which are comparable and even higher than those in nondust periods. Molecular compositions of the above SOA are similar to those in nondust periods with oxalic acid being the leading species. In the presence of the dust storms, all the above mentioned SOA species in Xi'an were predominantly enriched on the coarse particles (>2.1 μ m), and oxalic acid well correlated with NO₃⁻ ($R^2 = 0.72$, $p < 0.001$) rather than SO₄²⁻. This phenomenon differs greatly from the SOA in any other nondust period that is usually characterized by an enrichment of oxalic acid in fine mode and a strong correlation of oxalic acid with SO₄²⁻. We propose a formation pathway to explain these observations, in which nitric acid and/or nitrogen oxides react with dust to produce Ca(NO₃)₂ and form a liquid phase on the surface of dust aerosols via water vapor-absorption of Ca(NO₃)₂, followed by a partitioning of the gas-phase water-soluble organic precursors (e.g. glyoxal and methylglyoxal) into the aqueous-phase and a subsequent oxidation into oxalic acid. To the best of our knowledge, we found for the first time the enrichment of glyoxal and methylglyoxal on dust surface. Our data suggest an important role of nitrate in the heterogeneous formation process of SOA on the surface of dust.

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1. Introduction

Dicarboxylic acids are a major class of secondary organic aerosol (SOA) species in the atmosphere and ubiquitously found from the ground surface to the free troposphere (Fu et al., 2008;

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Myriokefalitakis et al., 2011; Wang et al., 2006). A pervasive layer of dicarboxylic acids have been observed as residual particles from evaporated droplets above cumulus clouds over the Gulf of Mexico and Houston, Texas regions (Sorooshian et al., 2007), indicating that dicarboxylic acids are important cloud condensation nuclei (CCN). Oxalic acid is a leading species of dicarboxylic acids. Global tropospheric loading of oxalic acid is 0.2–0.3 Tg, contributing to 5–9% of the atmospheric water-soluble organic carbon burden (Myriokefalitakis et al., 2011). Dicarboxylic acids from primary emission sources such as biomass burning (Meng et al., 2013) and vehicle exhausts (Huang and Yu, 2007) are relatively low, while those in the atmosphere originate largely from photochemical oxidation (Meng et al., 2014; Plath, 2009; Wang et al., 2002, 2010). Dicarboxylic acids can be produced via gas-phase oxidation of volatile organic compounds (VOC) such as aromatics and cyclic alkenes (Hallquist et al., 2009; Kawamura et al., 1996, 2003), but other studies have reported that aqueous-phase chemistry is the predominant formation mechanism for oxalic acid (Carlton et al., 2007; Myriokefalitakis et al., 2011; Warneck, 2003; Yu et al., 2005). For example, Myriokefalitakis et al. (2011) used a 3-D model embedded with an aqueous-phase chemical scheme to simulate global distribution of oxalic acid and concluded that most oxalic acid is formed in-cloud. However, on the ground surface oxalic acid is largely formed in aerosol aqueous-phase (Hallquist et al., 2009). Under this condition water-soluble precursors such as glyoxal and methylglyoxal partition into the aqueous-phase and subsequently oxidize into oxalic acid (Ervens and Volkamer, 2010; Ervens et al., 2011). In addition, larger molecular weight dicarboxylic acids (e.g., malonic and succinic acids) and other compounds in the aqueous-phase can also be photochemically oxidized into oxalic acid (Agarwal et al., 2010; Carlton et al., 2007; Miyazaki et al., 2009; Mochida et al., 2003, 2007; Wang et al., 2012).

Taklimakan and Gobi deserts are the major sources of dust storms in East Asia (McNaughton et al., 2009; Peltier et al., 2008; Uno et al., 2009). Surface dust in these regions can be lofted into the troposphere during spring and early summer by cold front systems and the Mongolia cyclic depression and are transported eastward into the North Pacific (Fairlie et al., 2010; Formenti et al., 2011; Leaitch et al., 2009). During the long-range transport, mineral dust can internally mix with sulfate, nitrate, ammonium, amine and other organic compounds via heterogeneous reaction and/or adsorption (Bahadur et al., 2012; Hanisch and Crowley, 2001a,b; Leaitch et al., 2009; McNaughton et al., 2009; Seinfeld et al., 2004; Wang et al., 2014; Zamora et al., 2011, 2013). Sullivan and Prather (2007) reported a diurnal cycle of oxalic acid in mineral dust in East Asian outflow regions and proposed that the mixing state of oxalic acid was resulted from photochemical oxidation of volatile organic compounds (VOCs), followed by partitioning of the diacids and precursors to the Asian dust with subsequent heterogeneous and aqueous oxidation. Here we present new evidence on the heterogeneous formation of SOA on dust surfaces by investigating dicarboxylic acids (C_2 – C_{11}) and their precursors (i.e., keto-carboxylic acids and α -dicarbonyls) in size-segregated particles collected in Xi'an, China during three dust storm events. We first investigate molecular compositions of the diacids and the precursors, as well as inorganic ions, in the samples. Then we identify the changes in their size distributions in the presence of dust via a comparison with those previously observed in nondust periods. Finally, we propose a new mechanism on how the heterogeneous formations of oxalic acid and other related SOA proceed on the dust surface based on the results above and verify the mechanism through the correlation analysis of the species in the dust samples.

2. Experimental section

2.1. Sample collection

Three sets of size-resolved particles were collected using a 9-stage air sampler equipped with pre-combusted quartz fiber filters at an airflow rate of 28.3 L min^{-2} . The cutoff points of particles are 0.43, 0.65, 1.1, 2.1, 3.3, 4.7, 5.8, and $9.0 \mu\text{m}$, respectively. The air sampler was set on the rooftop of a three-story building (about 12 m above ground) in the urban center of Xi'an, China (Fig. 1). Two massive dust storm episodes occurred in Xi'an on April 24th, 2009 (named DSI) and on March 29th–30th, 2011 (named DSII). One set of the size-resolved samples was collected during the DSI event for 10 h (8:00–18:00), and the other two sets of the samples were collected during the DSII periods each lasting for 12 h (18:00–6:00 named DSII-1 and 7:00–19:00 named DSII-2). Two sets of field blank samples were collected after the sampling and treated similarly as the dust samples. The mass of particles on each filter was determined by weighing the filter mass before and after sampling using a Sartorius MC5 electronic microbalance (Sartorius, Göttingen, Germany) with $\pm 1 \mu\text{g}$ sensitivity after 48 h equilibration in a glass chamber ($25 \pm 0.5 \text{ }^\circ\text{C}$, $35 \pm 2\% \text{ RH}$). All the sample filters were sealed individually in an aluminum foil bag and stored at $-20 \text{ }^\circ\text{C}$ prior to analysis. Meteorological parameters were measured hourly (Table 1). Based on the 72h-backward trajectories of air masses arriving in Xi'an at the mid-time point of the three sampling periods (Fig. 1) (Calculated by the US NOAA Hysplit Model), we found that air masses during the DSI event originated from the eastern part of the Gobi desert and traveled across the North China Plain (NCP), while air masses during the DSII-1 and DSII-2 periods originated from the Taklimakan desert and the western part of the Gobi desert, respectively, and moved eastward.

2.2. Sample analysis

2.2.1. Inorganic ions, water-soluble organic carbon (WSOC) and water-soluble inorganic carbon (WSIC)

Analytical methods for inorganic ions, WSOC and WSIC were reported elsewhere (Wang et al., 2010, 2011). Briefly, one forth of each filter was cut into pieces and extracted with Milli-Q pure water for three times each in 15 min under ultrasonication. Then the combined extracts were determined for inorganic ions using an ion chromatograph (Dionex-600) and for WSOC and WSIC using a Shimadzu TOC/N-5000 analyzer.

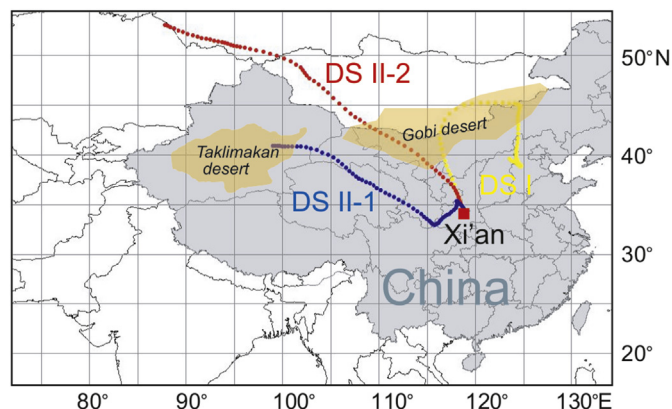


Fig. 1. A map description of the location of Xi'an, central China and 72h-backward trajectories of air masses arriving in Xi'an during the dust events.

Table 1

Meteorological parameters during the three dust storm periods.

	Time	T ^a , °C	RH ^b , %	V ^c , km
DSI	2009/04/24 (8:00–18:00)	17 ± 3.1	39 ± 15	5.7 ± 1.9
DSII-1	2011/04/29 (18:00–6:00)	25 ± 4.1	29 ± 7	3.9 ± 2.5
DSII-2	2011/04/30 (7:00–19:00)	24 ± 3.6	19 ± 13	5.3 ± 1.9

^a T: temperature.^b RH, relative humidity.^c V: visibility.

2.2.2. Dicarboxylic acids, keto-carboxylic acids and α -dicarbonyls

Dicarboxylic acids, keto-carboxylic acids and α -dicarbonyls in the size-resolved samples were quantified using a method developed by Kawamura and Watanabe (2004). Briefly, one fourth of the filter was cut in pieces and extracted with Mill-Q pure water for three times each lasting for 15 min. Then the combined extracts were concentrated by drying, followed by a reaction with 14% BF₃/butanol at 100 °C for one hour. Afterward, the derivatives were dissolved in hexane and washed with Mill-Q pure water for three times. The hexane layer was further concentrated and analyzed using a gas chromatograph (GC) equipped with a FID detector. Compounds in the samples were also verified using gas chromatography-mass spectrometry (GC/MS). The GC oven temperature was programmed from 50 °C (2 min) to 120 °C at 15 °C min⁻¹ and then to 300 °C at 5 °C min⁻¹ with a final isothermal hold at 300 °C for 16 min.

To determine the recoveries of the target compounds in the samples, a few micrograms of pure oxalic acid and related compounds, which are comparable to the abundances of those in the real samples, were spiked onto a blank filter and treated in the same manner as the real samples. The recoveries were 82 ± 2.0% for oxalic acid and 90 ± 8.0% for other organic compounds (Cheng et al., 2013). Oxalic acid and related compounds in the field blank samples are less than 5% of those in the real samples, indicating no significant contamination for the samples. Data reported here were corrected by the field blanks but not corrected by the recoveries.

3. Results and discussion

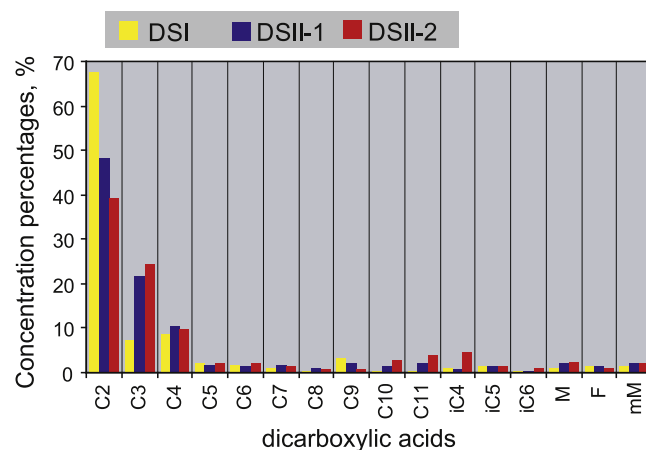
3.1. Molecular composition

A series of dicarboxylic acids (C₂–C₁₁), ketocarboxylic acids (C₂–C₄) and α -dicarbonyls were detected in the 9-stage samples. The sums of individual compounds on the nine stages are shown in Table 2. Their relative abundances are plotted as percentages and shown in Fig. 2. Oxalic acid (C₂) was the dominant species with concentrations being 1511, 539 and 365 ng m⁻³ during the dust events of DSI, DSII-1 and DSII-2, respectively (Table 2). The second highest dicarboxylic acid in DSI was succinic acid (C₄), followed by malonic acid (C₃). In contrast, in DSII-1 and DSII-2 periods C₃ is the second highest diacid, followed by C₄. As shown in Fig. 2, C₂ is the dominant species and accounts for 67%, 48% and 39% of the total diacids in the DSI, DSII-1 and DSII-2 events, respectively. Such a molecular composition is similar to that in nondust period (Wang et al., 2012). Maleic acid (M) is the stereoisomer of fumaric acid (F) and can be transformed into F during aerosol ageing process (Miyazaki et al., 2009; Mochida et al., 2003). During the DSI, DSII-1 and DSII-2 events M/F ratio was 0.87, 1.5 and 2.5, respectively. Such higher percentage of C₂ and lower ratio of M/F may indicate that particles in the DSI episode were more aged compared to those in the DSII-1 and DSII-2 periods.

Keto-carboxylic acids in the DSI event amounted to 706 ng m⁻³ with pyruvic acid (Pyr) being the dominant species, followed by glyoxylic acid (ω C₂) (Table 2). On the contrary, keto-carboxylic acids

Table 2Ambient concentrations^a of dicarboxylic acids, keto-carboxylic acids, α -dicarbonyls, and other species during dust storm events in Xi'an, Central China.

	DSI	DSII-1	DSII-2
I. Dicarboxylic acids, ng m⁻³			
Oxalic (C ₂)	1511	539	365
Malonic (C ₃)	163	241	230
Succinic (C ₄)	200	117	93
Glutaric (C ₅)	50	19	19
Adipic (C ₆)	39	16	21
Pimelic (C ₇)	20	21	14
Suberic (C ₈)	8	11	5.0
Azelaic (C ₉)	73	23	8.0
Sebalic (C ₁₀)	12	16	25
Undecanedioic (C ₁₁)	10	22	37
Methylmalonic (iC ₄)	26	6.8	43
Methylsuccinic (iC ₅)	29	15	12
Methylglutaric (iC ₆)	8.5	3.4	10
Maleic (M)	26	25	23
Fumaric (F)	30	17	9.3
Methylmaleic (mM)	35	25	19
Subtotal	2240	1118	932
II. Keto-carboxylic acids, ng m⁻³			
Pyruvic (Pyr)	435	62	39
Glyoxylic (ω C ₂)	210	102	86
3-Oxopropanoic (ω C ₃)	30	20	18
4-Oxobutanoic (ω C ₄)	31	44	36
Subtotal	706	228	178
III. α-Dicarbonyls, ng m⁻³			
Glyoxal (Gly)	147	148	126
Methylglyoxal (mGly)	196	33	30
Subtotal	343	181	156
IV. Inorganic ions, μg m⁻³			
F ⁻	0.1	1	1
Cl ⁻	19	6	2
NO ₃ ⁻	22	9	4
SO ₄ ²⁻	32	28	17
NH ₄ ⁺	2	1	1
Na ⁺	6	26	32
K ⁺	3	1	1
Mg ²⁺	2	2	1
Ca ²⁺	11	27	9
Subtotal	97	100	67
V. Other species, μg m⁻³			
WSOC ^b	38	46	38
WSIC ^b	27	28	13
Particle mass (PM)	682	1144	2406

^a Concentration is the sum of the measured species on all the stages.^b WSOC and WSIC are water-soluble organic and inorganic carbon, respectively.**Fig. 2.** Molecular composition of dicarboxylic acids in total suspended particles (TSP) during the dust storm events in Xi'an city, central China.

in the DSII-1 and DSII-2 events were much lower and ω_{C_2} was the highest in this compound class with pyruvic acid being the second one. Moreover, 3-oxopropanoic acid (ω_{C_3}) concentration was comparable to that of 4-oxobutanoic acid (ω_{C_4}) in DSI but only about 50% of ω_{C_4} during the DSII-1 and DSII-2 periods. These molecular compositions may indicate the differences in chemical composition of SOA precursors in the eastern and northwestern regions of China. Glyoxal (Gly) presented a similar level in the three periods, but methylglyoxal (mGly) showed a much lower concentration in DSII-1 and DSII-2 events in comparison with that in DSI (Table 2).

Air mass during the DSI event was transported from North China Plain (NCP) (Fig. 1), where nitrogen oxides and gaseous HNO_3 are higher than in central and northwestern China (Akimoto and Narita, 1994; Wang et al., 2013). Thus, a high level (22 g m^{-3} , Table 2) of NO_3^- was observed, which was about 2–5 times higher than that in DSII-1 and DSII-2 periods. Our previous study found that fine particles ($<2.1 \mu\text{m}$) in Xi'an during the DSI period became more acidic, compared to those in nondust events, because of an enhanced heterogeneous formation of nitrate on the dust surface (Wang et al., 2013). By comparison with the simultaneous measurement of physicochemical properties (e.g., composition, concentration, size distribution, diurnal variation and acidity) of aerosols over the mountaintop (2060 m above sea level) of Mt. Hua, which is near the city, the study (Wang et al., 2013) further found that in the DSI event a major fraction of particulate nitrate ($\sim 60\%$ of the mass) resulted from the heterogeneous reaction of gaseous nitric acid and nitrogen oxides from local sources with dust. In contrast, only a minor fraction of sulfate ($\sim 10\%$ of the mass) originated from oxidation of local emitted SO_2 , while the major fraction ($\sim 90\%$ of the mass) was derived from desert soil dust. Air masses in the DSII-1 and DSII-2 events were transported from northwestern China, where nitrogen oxides and SO_2 are lower; thus compared to that ($22 \mu\text{g m}^{-3}$, Table 2) in DSI, much lower levels of nitrate in TSP were observed in the DSII-1 and DSII-2 events (9 and $4 \mu\text{g m}^{-3}$, respectively, Table 2). CO_3^{2-} and HCO_3^- are the two forms of water-soluble inorganic carbon (WSIC) in atmospheric aerosols. During the DSII-1 and DSII-2 events SO_4^{2-} in the size-resolved particles strongly linearly correlated with WSIC ($R^2 \geq 0.85$, $p < 0.001$) (Fig. 3). Since carbonates (i.e. CO_3^{2-} and HCO_3^-) are the common components in Asian dust, such correlations suggest that sulfate in DSII-1 and DSII-2 was most likely derived from soil rather than from secondary oxidation. Such a phenomenon is consistent with the result reported by Wu et al. (2012), which shows that TSP collected during dust storm periods in Taklimakan desert contains $4.7 \pm 1.8\%$ of

sulfate with a negligible amount of NO_3^- ($0.2 \pm 0.04\%$). Gaseous HNO_3 in the atmosphere is mostly formed via homogeneous reaction of NO_2 with OH radical (Rodhe et al., 1981). The formed HNO_3 may quickly react with dust to form hygroscopic $\text{Ca}(\text{NO}_3)_2$, which can deliquesce under a low relative humidity (RH) and form a liquid film on the particle surface (Sullivan et al., 2009a, b), further promoting reaction and absorption of nitrogen oxides and other water-soluble species onto dust.

3.2. Size distribution

To further explore the formation mechanisms of SOA during the dust storm episodes in Xi'an, we plotted the detailed size distributions of major species. As shown in Fig. 4a, C_2 showed a monomodal pattern with a dominance in the coarse mode ($>2.1 \mu\text{m}$), in contrast to C_3 and C_4 , both dicarboxylic acids presented a bimodal pattern with a major peak in the coarse mode ($>2.1 \mu\text{m}$) and a minor peak in the fine mode ($<2.1 \mu\text{m}$) (Fig. 4b and c). Such size distributions are different from those in nondust storm periods, in which diacids C_2 , C_3 and C_4 are dominant in the fine mode (Wang et al., 2012). For example, we measured the three compounds in Xi'an during the nondust storm periods and found that C_2 , C_3 and C_4 showed a bimodal pattern in summer and winter with a major peak in the fine mode ($<2.1 \mu\text{m}$) and a minor peak in the coarse mode ($>2.1 \mu\text{m}$) (Wang et al., 2012). Many other studies have also found that C_2 in the atmosphere is mostly formed in aqueous phase and enriched in fine particles (Mochida et al., 2003; Yu et al., 2005; Wang et al., 2002, 2012). Therefore, the fact that C_2 , C_3 and C_4 dominated in coarse particles ($>2.1 \mu\text{m}$) in Xi'an during the three dust storm periods suggests a different formation mechanism when dust is present, which will be discussed later.

As shown in Fig. 4d–i, keto-carboxylic acids and α -dicarbonyls also exhibited a bimodal size distribution pattern with a dominant peak in the coarse mode and a small peak in fine mode. In our previous study we found these diacid precursors were enriched in the fine mode with a small peak in the coarse range in the absence of dust (Wang et al., 2012). When dust was present nitrate and sulfate shifted into larger particles with a large peak in the coarse mode (Fig. 4j–k). Such a shift was also observed for ammonium during the DSII-1 and DS II-2 events, which are characterized by two equivalent peaks in the fine and coarse modes (Fig. 4l). Currently we can not clearly explain the occurrence of the coarse mode of ammonium, one possible explanation is the reaction of gas-phase ammonia with non-neutralized nitric acid in the aqueous phase of dust surface.

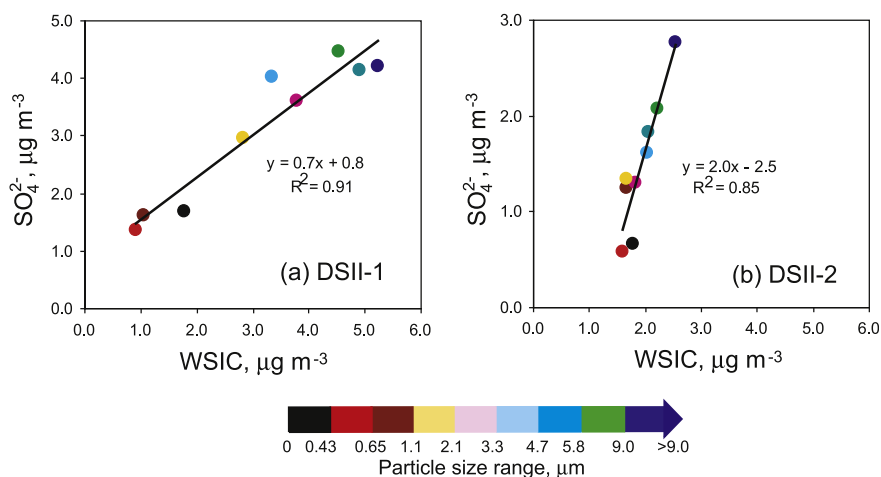


Fig. 3. Correlation between sulfate and WSIC (water-soluble inorganic carbon) in size-segregated particles during the DSII-1 and DSII-2 events.

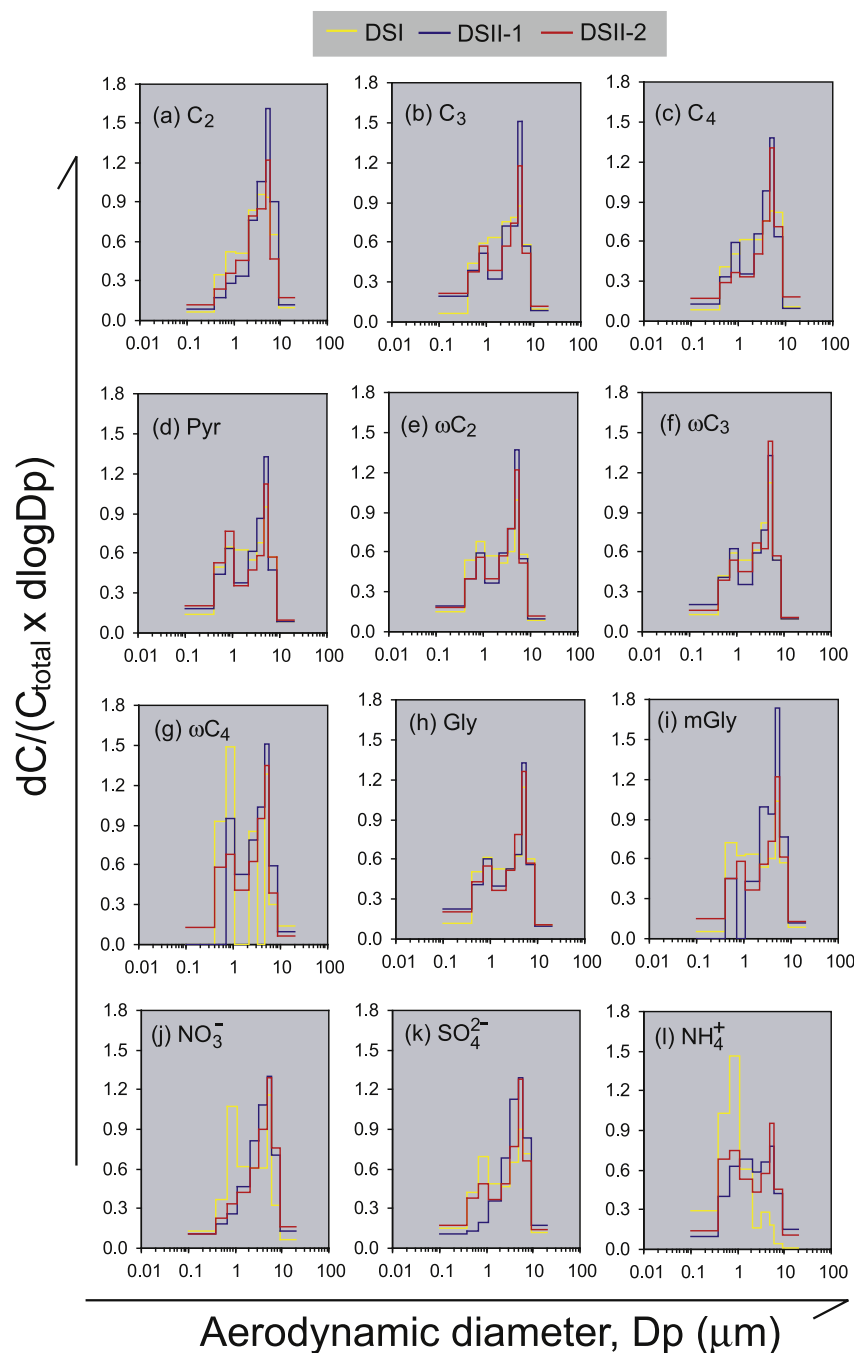


Fig. 4. Size distributions of dicarboxylic acids, keto-carboxylic acids, α -dicarbonyls and inorganic ions during the dust storm events in Xi'an city, China.

3.3. Formation mechanisms of oxalic acid and related SOA on dust surfaces

Our previous study on stable carbon isotopic compositions of diacids and the related compounds in size-resolved particles suggested that both Gly and mGly are produced in gas phase and partition into aerosol aqueous-phase, followed by oxidation by OH radical and other oxidants to form ωC_2 that is further oxidized into C_2 (Wang et al., 2012). Thus, a linear correlation between ωC_2 and C_2 was observed for the dust samples ($R^2 = 0.66$, Fig. 5a). Gaseous HNO_3 in Xi'an is 0.1–4.3 ppbv (unpublished data). Under these urban conditions, calcium nitrate can be formed within a few minutes via a reaction of the acid gas with dust and deliquesce at

$RH > 8\%$, forming a liquid film on dust surface (Sullivan et al., 2009a, b; Tobo et al., 2010). Based on the above comparison on size distributions of the diacids and related compounds during the dust storm and nondust storm periods, we propose a three-step heterogeneous formation pathway for SOA on the dust surface during the events as follows (Fig. 6). First, in the presence of dust storm calcium nitrate is formed on the surface of dust particles via heterogeneous reactions of gaseous HNO_3 and nitrogen oxides with dust and absorbs water vapor to create a liquid phase on the particle surface. Then gaseous water-soluble organics such as Gly and mGly partition into the aqueous phase and subsequently oxidize into keto-carboxylic acids (e.g., ωC_2 and ωC_3) and/or polymerize into large multifunctional compounds (e.g., oligomers). The keto-

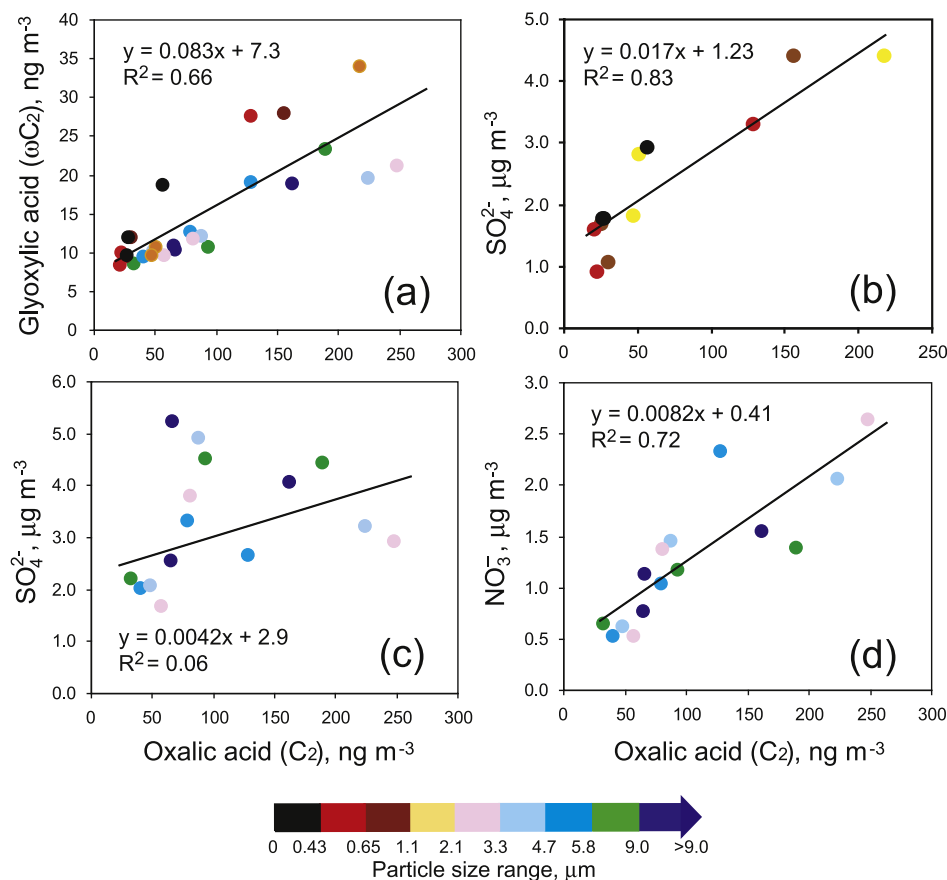


Fig. 5. Linear fit regression for oxalic acid (C_2) with (a) glyoxylic acid (ωC_2) in particles with different sizes, (b) sulfate in fine particles ($<2.1 \mu\text{m}$), (c) sulfate in coarse particles ($>2.1 \mu\text{m}$) and (d) nitrate in coarse particles ($>2.1 \mu\text{m}$).

acids and the high molecular weight compounds further oxidize into the low molecular weight diacids such as C_2 and C_3 .

To confirm the above proposed mechanism, correlations of the target compounds in different size ranges were investigated. From Fig. 5b we can see a robust linear correlation between C_2 and sulfate in the fine mode ($<2.1 \mu\text{m}$) ($R^2 = 0.83$, $p < 0.001$), which is consistent with those in nondust aerosols (Wang et al., 2012; Yu et al., 2005). However, there was no such a correlation between the coarse modes of C_2 and sulfate (Fig. 5c). As discussed above the coarse mode of sulfate originated from desert regions, whereas the fine modes of sulfate resulted from secondary oxidation. Fine modes of C_2 and sulfate share a common formation pathway such as aqueous phase oxidation; thus both well correlated even in the presence of dust storm. On the contrary, a strong linear correlation ($R^2 = 0.72$, $p < 0.001$) was observed between NO_3^- and C_2 in particles larger than $2.1 \mu\text{m}$ (Fig. 5d), which is found for the first time.

NO_3^- largely stayed in the coarse mode (Fig. 4j). Thus the significant correlation between the coarse modes of NO_3^- and C_2 can be explained by the formation pathways we proposed for the SOA on the dust surface. $\text{Ca}(\text{NO}_3)_2$ is much more hygroscopic than CaSO_4 (Sullivan et al., 2009a, b). Our results suggest that compared to sulfate nitrate takes a more important role in the heterogeneous formation process of oxalic acid on the dust surface.

Atmospheric oxalic acid is predominantly enriched in aerosol phase as it is a low-volatility compound with a vapor pressure lower than 0.1 mm Hg . Indeed, Limbeck et al. (2001) found that after cloud droplet evaporation 90% of oxalic acid remains in the particle phase, which suggests that condensation of gaseous oxalic acid onto pre-existing particles is not a major formation pathway of oxalic acid in aerosol phase. The coarse mode of oxalic acid observed in the dust events in Xi'an was not likely formed by in-cloud process, because once enter a cloud dust particles can

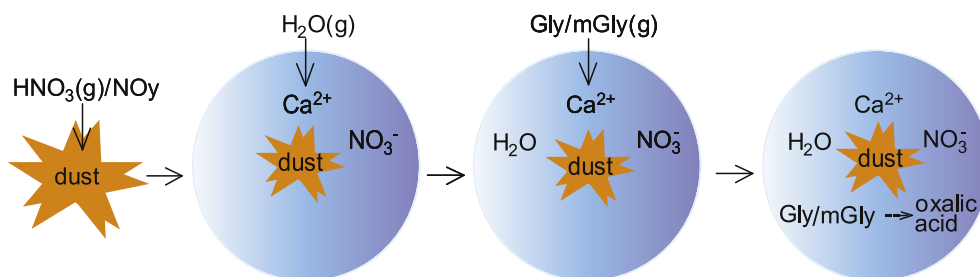


Fig. 6. A diagram illustrating the three-step formation pathway of secondary organic aerosols (e.g., oxalic acid (C_2)) on the dust surface.

activate as cloud condensation nuclei (CCN) and settle at a significant speed (Andreae and Rosenfeld, 2008). A few studies have pointed out that organic acids including oxalic acid in soil are metabolism products of fungi and plant roots (Gadd, 1999; Jones, 1998). However, because there was no significant correlation ($R^2 = 0.02$, $p < 0.001$) found for oxalic acid and Ca^{2+} in the size-segregated samples, we assumed the soil derived oxalic acid might not be important in the current study. Instead, the aqueous phase oxidation occurring on the surface of dust particles is the most likely formation pathway, as we proposed above.

As seen in Fig. 7, $\text{C}_2/\omega\text{C}_2$ mass ratio was higher in the coarse particles than in the fine particles during the dust events, probably indicating that oxidation of ωC_2 into C_2 is more efficient in the coarse particles. The reaction rate constant ($3.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) of glyoxylic acid with OH radical to produce C_2 is lower than that ($2.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) of its anion, glyoxylate (Tan et al., 2009). Thus, coarse particles, which are basic in most cases especially in dust storm periods, are favorable for the transformation of ωC_2 into C_2 .

4. Summary and conclusions

Three sets of size-segregated aerosols (9-stages) were collected in Xi'an during the two dust storm events occurring in the springs of 2009 and 2011 and measured for dicarboxylic acids ($\text{C}_2\text{--C}_{11}$), keto-carboxylic acids ($\text{C}_2\text{--C}_4$), α -dicarbonyls and inorganic ions. Concentrations of oxalic acid in the three sets of samples are 1151, 539 and 365 ng m^{-3} , respectively, which are comparable and even higher than those in nondust periods. Oxalic acid is the dominant species, accounting for over 40% of the total diacids; such a molecular composition is similar to that in nondust period. Oxalic acid and related compounds were enriched in the coarse particles ($>2.1 \mu\text{m}$) during the events, in contrast to a fine mode ($<2.1 \mu\text{m}$) enrichment that typically occurs in nondust period. Linear fit regression analysis showed that during the dust events the coarse mode of oxalic acid strongly correlated with nitrate ($R^2 = 0.72$, $p < 0.001$) but not correlated with sulfate. Such a phenomenon is different from the cases in nondust periods, which often shows a strong correlation between oxalic acid and sulfate. We propose a three-step formation pathway to explain the observations as follows. First, $\text{Ca}(\text{NO}_3)_2$ is produced by heterogeneous reactions of gaseous nitric acid and/or nitrogen oxides with dust and forms a liquid phase on the dust surface by absorbing water vapor as $\text{Ca}(\text{NO}_3)_2$ is highly hygroscopic. Then, the gas-phase glyoxal and methylglyoxal partitioning into the liquid phase, and subsequently oxidize into glyoxylic acid and/or polymerize into large molecular weight compounds (e.g., oligomers). Finally, the keto-acid and polymers further oxidize into oxalic acid. It should be noted that the dust-associated oxalic acid, in addition to the heterogeneous formation, might also in part be derived from biosynthesis of fungi in soil and other biota. The significance of oxalic acid from soil relative to the heterogeneous reaction needs a further study, which is

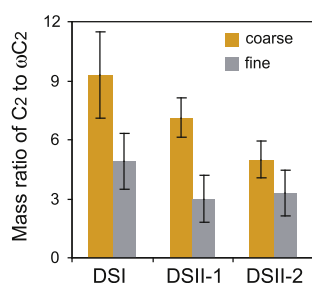


Fig. 7. Concentration ratios of oxalic acid (C_2) to glyoxylic acid (ωC_2) in the coarse ($>2.1 \mu\text{m}$), and fine ($<2.1 \mu\text{m}$) particles during the dust storm periods.

helpful for understanding the impact of Asian dust on the downwind aerosol chemistry.

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