Chemical composition of atmospheric nanoparticles formed from nucleation in Tecamac, Mexico: Evidence for an important role for organic species in nanoparticle growth


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[1] We report Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) measurements of the composition of ambient 10–33 nm diameter particles formed from nucleation on 16 March 2006 in Tecamac, Mexico during the Megacity Initiative: Local and Global Research Observations (MILAGRO) field study. On this day, nucleated particles contained far more organics than sulfates: average ion molar ratios with measurement uncertainties for nitrate, organics and sulfur species were 6 ± 2%, 84 ± 5%, and 10 ± 1%, respectively. The measured organic species include nitrogen-containing organic compounds, organic acids, and hydroxy organic acids. Independent calculations show that sulfuric acid condensation could have accounted for only 10 ± 2% of the growth that was observed on this day, which is consistent with the TDCIMS measurements of composition. It follows that organic compounds play a dominant role in the high growth rates that were observed. Citation: Smith, J. N., M. J. Dunn, T. M. VanReken, K. Iida, M. R. Stolzenburg, P. H. McMurry, and L. G. Huey (2008), Chemical composition of atmospheric nanoparticles formed from nucleation in Tecamac, Mexico: Evidence for an important role for organic species in nanoparticle growth, Geophys. Res. Lett., 35, L04808, doi:10.1029/2007GL032523.

1. Introduction

[2] The effects of aerosols on climate represent the single largest source of uncertainty in our understanding of climate change [Intergovernmental Panel on Climate Change, 2007]. One key challenge is to understand and predict the way in which aerosols perturb climate through the modification of clouds and precipitation. This requires an understanding of the mechanisms by which particles form and grow to sizes that make them potential cloud condensation nuclei. Particle formation from homogeneous nucleation has been observed throughout the troposphere [Kulmala et al., 2004], and models suggest that this mechanism may dominate over primary particle production in many parts of the world [Spracklen et al., 2006]. While significant progress is being made in the prediction of atmospheric new particle formation [e.g., Kuang et al., 2007; McMurry et al., 2005; Merikanto et al., 2007], much less is known about the mechanisms by which these nascent particles grow by condensation and coagulation. One study has modeled the contribution of H$_2$SO$_4$, currently the only species known to contribute to the growth of newly formed particles, to aerosol growth using all observations that were available at that time [Stolzenburg et al., 2005]. That study concluded that in Atlanta during the mornings, observed growth rates were due primarily to H$_2$SO$_4$ condensation. However, in most other locations and later in the day in Atlanta growth rates are typically 2 to 20 times greater than can be explained by H$_2$SO$_4$ condensation. This suggests that other species are contributing to the growth of nanoparticles (defined here as particles with diameters smaller than 50 nm). A number of theoretical [Kerminen et al., 2000; Zhang and Wexler, 2002] and experimental [e.g., Allan et al., 2006; Wehner et al., 2005] studies generally support the notion that organics play a crucial role, yet only one direct measurement of the organic species responsible for nanoparticle growth has been reported [Mäkelä et al., 2001]. That study in a boreal forest found that newly formed particles were enriched with dimethylamine.

[3] The work described below is thus motivated by the need to identify the species responsible for nanoparticle growth so that models can predict the impact of new particle formation on climate. We report measurements of nanoparticle composition during a new particle formation event that took place on 16 March 2006 during the Megacity Initiative: Local and Global Research Observations (MILAGRO) field study. These measurements were made with the Thermal Desorption Chemical Ionization Mass Spectrometer (TDCIMS) [Smith et al., 2004; Voisin et al., 2003]. We then compare the results of TDCIMS measurements to those from models that assess the role of H$_2$SO$_4$ on condensation growth.

2. Methods

[4] The data reported here were obtained at the “T1” field site in Tecamac, Mexico (19.703N latitude, 98.982W longitude, 2273 m altitude), situated about 40 km NE of central Mexico City. Our analysis will focus on a new particle formation event from 16 March 2006, in which intense particle production and growth occurred at a time during which all crucial measurements required for our analysis were performed. Figure 1 shows a contour plot of the particle size distribution function obtained using a...
species thermally desorbed from particles through either mass spectra, in which ions are created from the neutral chemical constituents reported here are from negative ion Canagaratna et al. [2007]. The temperature was selected to ensure desorption of non-volatile components. The desorption temperature was linearly ramped from room temperature to 500 °C over a period of 90 s. The upper temperature was selected to ensure desorption of non-refractory constituents [Canagaratna et al., 2007]. The chemical constituents reported here are from negative ion mass spectra, in which ions are created from the neutral species thermally desorbed from particles through either proton or electron transfer with \( (\text{H}_2\text{O})_n\text{SO}_4 \) reagent ions, with \( n \) ranging from 1 to 4. This effectively ionizes sulfate, nitrate, and organic components; however, the latter class of compounds does decompose into lower molecular weight multifunctional organic ions. Since the measurements reported here we have addressed this fragmentation issue and have recently reported laboratory measurements of carboxylic acid nanoparticles in which the parent ion undergoes minimal fragmentation. For the present study, however, we will interpret the TDCIMS data to infer compound classes for the organics in nanoparticles (e.g., organic acids, hydroxy organic acids, nitrogen-containing organic compounds).

[7] Growth rates for the 16 March event were calculated using a newly developed technique that allows for the estimation of growth rates when it is difficult to follow the peak of the evolving particle size distribution in time [Iida et al., 2008]. This is true of the 16 March event (Figure 1), where concentrations of freshly nucleated 3 to 6 nm particles remain high for most of the event. This method assumes that the dependence of ambient aerosol charged fraction on diameter is controlled by condensational growth and collision with ambient ions. The size-resolved charged fraction was measured using a scanning mobility particle sizing system that alternately sampled neutralized and naturally charged aerosol. Ambient ions were measured using an Inclined Grid Mobility Analyzer [Tammet, 2002]. Gas phase \( \text{H}_2\text{SO}_4 \) concentrations during the 16 March event were measured with a chemical ionization mass spectrometer (CIMS) [Sjostedt et al., 2007]. We estimate the contribution of \( \text{H}_2\text{SO}_4 \) to growth rates using the collision-limited growth rate in the free molecular regime, which is size independent [Friedlander, 2000].

3. Observations

[8] Table 1 shows the major observed peaks in the mass spectra and their identity based on our current understanding of the chemical ionization process in the TDCIMS. The most abundant organic ions are formic and acetic acid (33%). Also important were CN\(^-\) (26 amu, 12%) and a strong and persistent 42 amu ion (28%) that can be assigned to a deprotonated cyanic acid or its isomers (CNO\(^-\)) and/or \( \text{C}_2\text{H}_2\text{N}^- \). While it is not clear as to the mechanism by which these nitrogen-containing organics form in particles, it is worth noting that both the 26 and 42 amu ions are observed in spectra of particulate amines analyzed with ATOFMS [Angelino et al., 2001], which may be relevant if high-energy dissociative pathways lead to the formation of these ions in the TDCIMS. Nitrate has been previously observed in nanoparticles in a variety of locales [Smith et al., 2005; Tolocka et al., 2004]. The three ions \( \text{SO}_3^- \) (10%), \( \text{SO}_4^- \) (0.5%), and \( \text{SO}_3^- \) (0.1%), are clearly related since all three compounds exhibit similar profiles of ion abundance.
vs. temperature, forming at temperatures of around 400–500°C. Laboratory investigations show that particulate sulfate can decompose into these ions; however, the conditions and mechanisms for this are unclear. We attribute these ions to sulfate based on these laboratory studies as well as the elemental composition of highest molecular weight species.

Figure 2 summarizes the TDCIMS measurements of the molecular composition of nanoparticles during the 16 March event. In the figure, we group the sulfur-containing ions as “sulfate,” and group all other compounds except nitrate as “organic.” The data are presented as ion molar ratio, which is the ratio of the average ion abundance for each compound class to the total average ion abundance, after normalizing the ion signal by the collected particulate mass. Organics dominate composition during the entire measurement period, ranging from 63 ± 15% to 98 ± 29%. In general sulfate varies from negligible amounts at 11:30 to 12 ± 5% between 12:25 and 13:40 (all times are presented as local MST). A small decrease in sulfate to 6 ± 2% is observed at 13:48. Nitrate is observed on three separate occasions: first in 16 nm diameter particles at around 11:30, where it peaks at 20 ± 8%, next at 13:00 where it reaches 12 ± 5%, then finally at 14:30 where it reaches its peak molar ratios in 33 nm particles of 28 ± 11%. Average ion molar ratios with 1σ uncertainties for nitrate, organics and sulfate were 6 ± 9%, 84 ± 10%, and 10 ± 5%, respectively.

One measure of our success in consistently analyzing the chemical compounds in the sampled aerosol can be obtained by analyzing the variability in the mass normalized average ion current for each sample. During the 16 March event the mass normalized average ion current was 38 Hz pg⁻¹ with a standard deviation of 12 Hz pg⁻¹. This value is similar in magnitude to the instrument response to laboratory generated carboxylic acid aerosol. Most importantly, the relative standard deviation of the mass normalized ion current is 31%, which is less than the measurement uncertainty of the TDCIMS. The constancy of total ion current, combined with the fact that we apply sufficiently high desorption temperatures as to evaporate non-refractory aerosol constituents, are necessary, although not sufficient, requirements for equating ion molar ratios to the actual molar ratios of aerosol constituents. Other factors, including species decomposition and ionization efficiencies, are the foci of our ongoing laboratory characterization of the TDCIMS.

The CIMS measurements of gaseous H₂SO₄ are shown in Figure 3a. Sulfuric acid reached a peak of 8 × 10⁷ molecules cm⁻³ at 11:30 before decreasing to a local minimum of 3 × 10⁷ molecules cm⁻³ at 13:50. This local minimum occurs at the same time as the local minimum in particulate sulfate (Figure 2). A second peak of 6.3 × 10⁷ molecules cm⁻³ occurred later at 14:30, and then following this sulfuric acid steadily decreased due to reduced photochemistry in the late afternoon. Figure 3b shows the model results of the growth rates during the event. During the period of the reported TDCIMS measurements (11:00–16:00), the growth rate was quite constant with an average of 24 nm h⁻¹ and a standard deviation of only 5 nm h⁻¹. The modeled contribution of H₂SO₄ to the aerosol growth is also plotted in Figure 3b and averages 2.2 ± 0.6 nm h⁻¹. This modeled growth rate due to sulfuric acid is 10 ± 2% of the total estimated growth rate.

### 4. Discussion

The average TDCIMS-derived ion molar ratio of sulfate in particles, reported above, was 10 ± 5%. During
the event the sulfate ratio did not vary significantly beyond the measurement uncertainty, which ranged from 35 to 41% of the declared values. This measurement of sulfate concentration agrees with the model results for the fraction of the observed growth rate that can be attributed to sulfuric acid, in which we predict that 10 ± 2% of the growth rate can be explained by sulfuric acid condensation. This agreement is remarkable considering that these are independent analyses of nanoparticle composition: the TDCIMS being a measure of the non-refractory constituents that are ionized by our proton- and electron-transfer techniques whereas the growth rate analysis is based upon sulfuric acid and particle size distribution measurements. This contrasts to our last reported measurements of nanoparticle composition using the TDCIMS in Atlanta during the ANARChE campaign, where we concluded that nanoparticles formed from nucleation were almost entirely composed of ammonium sulfate [Smith et al., 2005]. During that study modeled growth rates agreed with this observation during the periods in which these measurements were reported [Stolzenburg et al., 2005]. As stated above, there were periods during that study in which organics were presumed to play an important role based on the modeled growth rates, however TDCIMS measurements were not available in the size range for which these growth rates were observed.

[14] Based on the measurements and analysis presented above, we conclude that oxygenated organics and nitrogen-containing organics can play a dominant role in the growth of nanoparticles from a size of 10 to 30 nm. These compounds must possess extremely low volatility in order to overcome the Kelvin effect, leading one to question their exact identity. Our measurements, in which we detect ions that indicate the presence of inorganic and organic acids as well as organic bases (amines), are consistent with the mechanism of aerosol growth through the formation of stable organic salts [e.g., Angelino et al., 2001]. Additional studies are underway to determine whether organic salt formation is pertinent to nanoparticle growth. Finally, since most models for the growth of freshly nucleated particles only consider sulfuric acid condensation [e.g., Spracklen et al., 2006], the growth rates of newly formed particles can be underestimated by as much as an order of magnitude. The probability that a freshly nucleated particle grows to a larger size before it is lost by coagulation with preexisting particles depends exponentially on the inverse of growth rates [Lehtinen et al., 2007; McMurry, 1983; McMurry et al., 2005]. This underestimates in growth rates will lead to substantial underestimates in the calculated concentrations of cloud condensation nuclei that arise from new particle formation by as much as several orders of magnitude.

Figure 3. (a) Gas phase sulfuric acid concentration (molec. cm$^{-3}$) during event. (b) Estimated growth rate from charged fraction analysis. Also plotted is the growth rate that can be attributed to H$_2$SO$_4$, and the ratio of these two growth rates.

McMurry, P. H. (1983), New particle formation in the presence of an aerosol: Rates, time scales and sub-0.01 μm size distributions, J. Colloid Interface Sci., 95(1), 72–80.


