

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/235754963>

Insights into Secondary Organic Aerosol Formation Mechanisms from Measured Gas/Particle Partitioning of Specific Organic Tracer Compounds

ARTICLE in ENVIRONMENTAL SCIENCE & TECHNOLOGY · FEBRUARY 2013

Impact Factor: 5.33 · DOI: 10.1021/es304587x · Source: PubMed

CITATIONS

17

READS

54

13 AUTHORS, INCLUDING:



David Robert Worton

National Physical Laboratory

86 PUBLICATIONS 910 CITATIONS

SEE PROFILE



Shang Liu

University of California, San Diego

40 PUBLICATIONS 1,143 CITATIONS

SEE PROFILE



Jennifer G Murphy

University of Toronto

83 PUBLICATIONS 1,045 CITATIONS

SEE PROFILE

Insights into Secondary Organic Aerosol Formation Mechanisms from Measured Gas/Particle Partitioning of Specific Organic Tracer Compounds

Yunliang Zhao,[†] Nathan M. Kreisberg,[‡] David R. Worton,^{†,‡} Gabriel Isaacman,[†] Robin J. Weber,[†] Shang Liu,[§] Douglas A. Day,^{§,¶} Lynn M. Russell,[§] Milos Z. Markovic,[#] Trevor C. VandenBoer,[#] Jennifer G. Murphy,[#] Susanne V. Hering,[‡] and Allen H. Goldstein^{*,†}

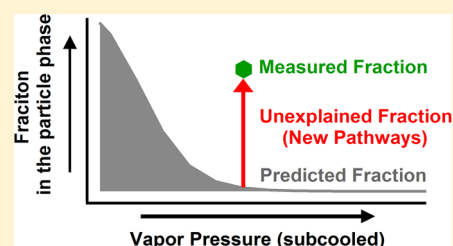
[†]Department of Environmental Science, Policy and Management, University of California, Berkeley, California

[‡]Aerosol Dynamics Inc., Berkeley, California

[§]Scripps Institution of Oceanography, University of California, San Diego, California

[#]Department of Chemistry, University of Toronto, Toronto, Canada

ABSTRACT: In situ measurements of organic compounds in both gas and particle phases were made with a thermal desorption aerosol gas chromatography (TAG) instrument. The gas/particle partitioning of phthalic acid, pinonaldehyde, and 6,10,14-trimethyl-2-pentadecanone is discussed in detail to explore secondary organic aerosol (SOA) formation mechanisms. Measured fractions in the particle phase (f_{part}) of 6,10,14-trimethyl-2-pentadecanone were similar to those expected from the absorptive gas/particle partitioning theory, suggesting that its partitioning is dominated by absorption processes. However, f_{part} of phthalic acid and pinonaldehyde were substantially higher than predicted. The formation of low-volatility products from reactions of phthalic acid with ammonia is proposed as one possible mechanism to explain the high f_{part} of phthalic acid. The observations of particle-phase pinonaldehyde when inorganic acids were fully neutralized indicate that inorganic acids are not required for the occurrence of reactive uptake of pinonaldehyde on particles. The observed relationship between f_{part} of pinonaldehyde and relative humidity suggests that the aerosol water plays a significant role in the formation of particle-phase pinonaldehyde. Our results clearly show it is necessary to include multiple gas/particle partitioning pathways in models to predict SOA and multiple SOA tracers in source apportionment models to reconstruct SOA.



INTRODUCTION

Secondary organic aerosol (SOA) accounts for the majority of organic aerosol (OA) on a global scale^{1,2} and more than 80% in the afternoon during summer in urban areas.³ Understanding the formation and distribution of SOA is important because SOA plays a significant role in affecting climate change on both global and regional scales.^{4,5} However, predictions of SOA by traditional models based on laboratory measurements of SOA yields from volatile organic compounds and absorptive partitioning theory have been shown to substantially underestimate ambient SOA loadings in polluted regions.^{6–9} The discrepancies between measurements and models could in part be attributed to poor understanding of formation pathways of SOA in the ambient atmosphere.

Laboratory studies have shown that, in addition to absorptive gas/particle partitioning following the formation of low-volatility oxygenated compounds through gas-phase oxidation,^{10,11} other SOA formation pathways such as reactive uptake of gaseous species onto particles^{12,13} and gas-phase nonoxidative reactions¹⁴ could be important. However, these pathways remain poorly understood. For example, laboratory studies have shown that reactive uptake of oxygenated organic compounds onto acidic particles can significantly increase SOA yields, but there is no agreement on the extent of enhancement

of SOA yields.^{12,15,16} Additionally, laboratory studies of reactive uptake of oxygenated compounds have focused primarily on small carbonyl compounds and found that not all of them significantly contribute to SOA when their concentrations used in the laboratory studies are scaled to atmospheric levels.^{12,13} As a result, the contribution of individual compounds to SOA cannot be generalized solely on the basis of their functional groups. Ambient measurements are crucial to examining the importance of laboratory proposed SOA mechanisms.

Ambient measurements with an Aerodyne quadrupole aerosol mass spectrometer (Q-AMS) have been made to examine the effects of aerosol acidity on SOA formation, and the results showed that no significant enhancement in SOA formation was observed during acidic periods identified on the basis of the inorganic ion charge balance.¹⁷ However, the importance of acid-catalyzed reactions in SOA formation might not be evident using the inorganic ion charge balance as the indicator of aerosol acidity because organic acids could also provide sufficient acidity for the occurrence of these reactions.¹⁸

Received: November 9, 2012

Revised: February 25, 2013

Accepted: February 28, 2013

Published: February 28, 2013

Additionally, the variability in the amount of SOA formed through acid-catalyzed reactions could be obscured by SOA formed through other pathways if there is not an analytical method to distinguish them. In comparison with bulk organic analysis, time-resolved speciated measurements of gas- and particle-phase organic compounds are particularly useful to determine concentrations of organic compounds involved in acid-catalyzed reactions and distinguish SOA products formed through acid-catalyzed reactions from other pathways. Moreover, these measurements provide information to examine factors affecting atmospheric SOA formation that have previously been investigated in laboratory studies, such as relative humidity (RH) and acidity, and enable one to discover new SOA formation pathways in the atmosphere.^{10,12,19}

Williams et al.²⁰ demonstrated that a thermal desorption aerosol gas chromatography (TAG) instrument was able to capture the trends of gas/particle partitioning of individual species, wherein a Teflon filter was placed upstream of the collection cell to separate gases from particles. The fraction of organic species in the particles measured with this TAG is overestimated because the collection cell utilized in this TAG is designed for collection of particles and incapable of complete collection of gas-phase organics. Additionally, the gas/particle separation by a filter is subject to sorption of organic vapors on the filter and volatilization of collected organics²¹ and consequently causes difficulty in quantifying the extent of overestimation. In the present study, a denuder is used, representing an improved method to separate gases from particles²¹ and allowing the upper limit of overestimation to be quantified. The investigation of different SOA formation pathways is made by conducting time-resolved, speciated measurements of gas/particle partitioning of oxygenated semivolatile/intermediate-volatility organic compounds (S/IVOCs) in the ambient atmosphere with this modified TAG. The factors affecting these pathways are investigated using temporal variability of measured gas/particle partitioning of organic species in combination with supporting measurements, such as RH. This study improves the understanding of SOA formation in the ambient atmosphere and will likely lead to useful parametrization of SOA formation.

METHODS

Sampling and Analysis. A modified TAG instrument was deployed to measure organic species in both gas and particle phases during the CALifornia at the NEXus of Air Quality and Climate Change (CalNex) campaign from May 31st to June 27th, 2010 at the Bakersfield California Supersite. The modification was made before this field campaign by adding an activated charcoal denuder (30 mm OD, 40 cm length, ~490 channels, Mast carbon, UK) into the sampling inlet as a parallel sampling line to a bypass line made of stainless steel tubing. The denuder was housed inside a homemade aluminum cylindrical tube with a tapered cap in each end connected to the sampling line upstream and downstream.

A detailed description of the TAG can be found elsewhere.^{22,23} Only the sampling and operation relevant to this study are described here. During the sampling, ambient air was sampled at 10 L/min from the center of a larger flow, drawn from approximately 5 m above ground at 200 L/min through a 6-in. (i.d.) rigid duct, and sampled through a sharp cut PM_{2.5} cyclone (10 L/min, BGI Inc., Waltham, MA). Downstream of the cyclone, a flow split was made to discard 10% of air flow. Subsequently, 90% of the ambient flow was sampled through

the denuder line (or bypass line) and delivered into a customized Collection and Thermal Desorption (CTD) cell through a 9 L/min critical orifice for collection of organics. The CTD cell is made of stainless steel and passivated with an Inertium coating.²² Collection of particles is through inertial impaction, and collection of organic gases is through adsorption onto the surface of the CTD cell. The aerodynamic particle diameter corresponding to 50% collection is ~0.07 μm so that the entire accumulation mode mass falls within the instrument's collection range.²² The capability of the CTD cell to capture trends of concentrations of organic gases has been shown in Williams et al.²⁰ Gas/particle separation was achieved by alternating ambient air between the denuder and the bypass line. The samples collected through the denuder ("denuded samples") were expected to be only particle-phase organics while those collected through the bypass line ("undenuded samples") were total organics, the sum of collected gas and particle-phase organics. The sampling duration of each sample was 90 min from May 31st to June 9th (Sampling Period I) and 30 min from June 10th to 27th (Sampling Period II). The CTD cell was maintained at 28 °C during the sampling and was continuously held at the same temperature for 1 min to purge residual air out of the CTD cell with a helium flow of 20 mL/min at the conclusion of ambient sampling. Following the purge, the thermal desorption of collected organics was carried out in a helium flow by heating the CTD cell from 28 to 300 °C at a rate of ~30 °C/min and held at 300 °C for 9 min followed by thermal injection into a gas chromatograph (GC). The chromatographic separation of organic species was achieved by a capillary GC column (Rxi-5Sil MS; 30 m length, 0.25 mm i.d., 0.25 μm film thickness, Restek). The GC oven temperature was held at 45 °C for 18 min for the sample injection from the CTD cell to GC followed, in order, by: (1) a ramp to 150 °C at 15 °C/min; (2) a ramp from 150 to 330 °C at 9 °C/min, and (3) a hold at 330 °C for 4 min. Identification and quantification was achieved using a quadrupole mass spectrometer (Agilent, 5973) calibrated on the basis of responses to authentic standards that were manually injected into the CTD cell at regular time intervals throughout the campaign.²⁴

The gas collection efficiency of the denuder was determined in the beginning, middle, and end of the campaign using the difference of the amount of gas-phase organics collected downstream of the denuder and bypass lines with a Fiberfilm glass fiber filter (Pall Corp.) placed upstream of the cyclone to remove particles. Particle penetration through the denuder was determined using an optical particle spectrometer (model UHSAS, Droplet Measurement Technologies) to measure the number size distributions of ambient particles at the inlet and outlet of the denuder before this campaign.

A broad suite of complementary measurements were concurrently made at this site, including a full range of meteorological, trace gas, and aerosol measurements. The measurements utilized in this study included nonrefractory PM₁ inorganic and organic aerosol components, carboxylic acid group, gas-phase ammonia, and meteorological data. Non-refractory PM₁ aerosol components were measured using a high-resolution time-of-flight aerosol mass spectrometer (HR-TOF-AMS; Aerodyne, Billerica, MA) using the methods described in Liu et al.²⁵ PM₁ was also collected by Teflon filters for measurements of the organic acid group (–COOH) by Fourier transform infrared (FTIR) spectroscopy.²⁵ Gas-

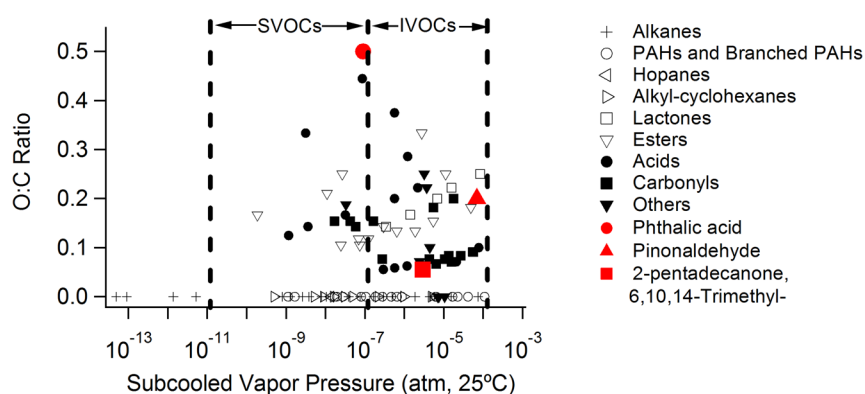


Figure 1. O/C ratios of organic compounds measured by TAG as a function of subcooled vapor pressure at 25 °C. The compounds of interest are colored in red.

phase ammonia was measured using an ambient ion monitor/ion chromatograph (AIM-IC).²⁶

Particle-Phase Fraction Calculations. Because particle-phase and total organics were not collected simultaneously, the measured fraction of a given compound in the particle phase (f_{part}) in sample n was calculated using the particle-phase concentration ($C_{\text{part},n}$) divided by the average of the previous and subsequent total concentrations ($C_{\text{total},n-1}$, $C_{\text{total},n+1}$):

$$f_{\text{part}} = \frac{2C_{\text{part},n}}{C_{\text{total},n-1} + C_{\text{total},n+1}} \quad (1)$$

The gas/particle partitioning coefficient (k_{om}) for absorptive partitioning into organic aerosol was calculated by the equation described by Pankow:¹⁰

$$k_{\text{om}} = \frac{RT}{10^6 P_L^0 \delta \text{MW}} \quad (2)$$

where R is the ideal gas constant ($8.2 \times 10^{-5} \text{ m}^3 \text{ atm mol}^{-1} \text{ K}^{-1}$), T is temperature (K), P_L^0 is the vapor pressure of the pure compound (atm) at the temperature of interest, δ is the activity coefficient of the compound in the absorbing phase, and MW is the average molecular weight (g mol^{-1}) of the absorbing phase.¹⁰ The particle-phase fraction based on partitioning theory ($f_{\text{part},T}$) was calculated from the partitioning coefficient constant (k_{om}) and the mass concentration of organic aerosol in $\mu\text{g m}^{-3}$ (C_{OA}):

$$f_{\text{part},T} = \left(1 + \frac{1}{k_{\text{om}} \times C_{\text{OA}}} \right)^{-1} \quad (3)$$

The data collected by other instruments were averaged according to the TAG sampling duration of 30 or 90 min. Throughout the period of TAG measurements, the average OA concentration (C_{OA}) from HR-TOF-AMS measurements was $3.7 \pm 1.8 \mu\text{g m}^{-3}$ ($0.5\text{--}11.2 \mu\text{g m}^{-3}$), and average temperature was $26 \pm 6 \text{ }^\circ\text{C}$ ($12\text{--}37 \text{ }^\circ\text{C}$). In our study, the theoretical fractions of organic species in the particle phase were calculated using the average temperature and average OA concentration ($T = 26 \text{ }^\circ\text{C}$, $C_{\text{OA}} = 3.7 \mu\text{g m}^{-3}$) and both molecular weight ($\text{MW} = 200 \text{ g mol}^{-1}$) and activity coefficient ($= 0.3$ and 3) from the literature.^{10,11} Subcooled vapor pressures used in this study were from the Estimation Programs Interface (EPI) Suite developed by the US Environmental Protection Agency's Office of Pollution Prevention and Toxics and Syracuse Research Corporation (SRC).²⁷

RESULTS AND DISCUSSIONS

More than 150 compounds were measured by the TAG, covering a broad vapor pressure range and different functional groups (Figure 1). Most identified compounds were present in the vapor pressure range of S/IVOCs defined by Robinson et al.²⁸ (Figure 1). The gas/particle partitioning of three oxygenated compounds, pinonaldehyde, phthalic acid, and 6, 10, 14-trimethyl-2-pentadecanone, is discussed in detail to explore SOA formation in the ambient atmosphere. Pinonaldehyde is a major product of α -pinene ozonolysis with gaseous yields of pinonaldehyde being 0.39–0.69.²⁹ Phthalic acid and 6,10,14-trimethyl-2-pentadecanone have been used as SOA tracers in chemical mass balance and positive matrix factorization model calculations.^{3,30,31}

Although f_{part} of the compounds of interest were overestimated in this study because their gas-phase organics were only partially collected by the collection cell, which was designed for collecting particle-phase organics, the extent of this overestimation can be indicated by f_{part} of n -alkanes. Average collection efficiencies of the denuder for pinonaldehyde, phthalic acid, and 6,10,14-trimethyl-2-pentadecanone were over 98%. Average losses of the particle number inside the denuder were less than 10% for particle sizes spanning the particle spectrometer's range ($0.05\text{--}1 \mu\text{m}$). The efficient separation of organic gases and particles by the denuder limits the source of this overestimation to under collection of gas-phase organics. The gas/particle partitioning of n -alkanes can be well described by the absorptive gas/particle partitioning theory,³² and n -alkanes have the lower or same adsorption coefficient constants on the surface of sampling substrates relative to other compounds with the same vapor pressures.³³ As a result, measured particle-phase fractions of n -alkanes, the sum of absorptive gas/particle partitioning and overestimation caused by incomplete collection of their vapors, are the upper limit of the overestimation of TAG measurements in the vapor pressure range of these n -alkanes.

The reference compounds selected on the basis of the similar subcooled vapor pressure for pinonaldehyde, phthalic acid, and 6, 10, 14-trimethyl-2-pentadecanone are n -tetradecane, n -heptadecane, and n -nonadecane, respectively (Figure 2). If measured particle-phase fractions of these oxygenated organic compounds are far larger than those of their reference compounds, as is the case for phthalic acid and pinonaldehyde, additional SOA formation pathways must occur beyond absorptive gas/particle partitioning and the overestimation due to under collection of gas-phase organics.

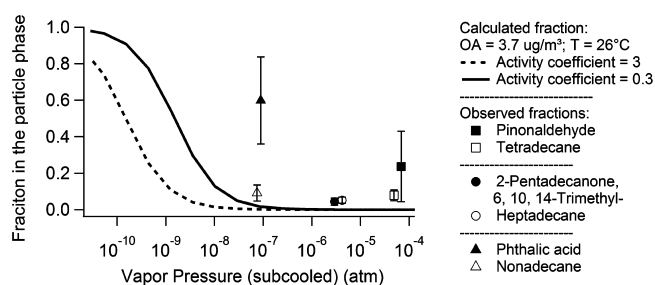


Figure 2. Average measured fractions for selected oxygenated organic compounds (solid markers) and their corresponding reference compounds (empty markers). The vertical bar is one standard deviation of the mean. The solid and dashed lines are the predicted fractions of organic compounds in the particle phase with different vapor pressures using eqs 2 and 3.

Pinonaldehyde. The mean f_{part} of pinonaldehyde was $20 \pm 20\%$, which was much higher than that of its reference compound, *n*-tetradecane (Figure 2). The fraction of pinonaldehyde in particles was observed to increase as RH increased (Figure 3a), but the contribution to the fraction of

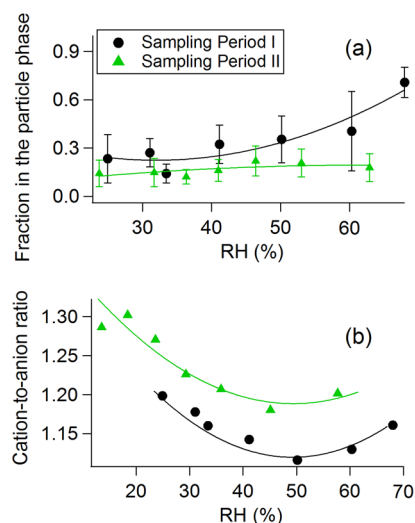


Figure 3. (a) Measured fraction of pinonaldehyde in the particle phase as a function of RH (average 5 or 6 points in each bin in Sampling Period I; 12 points in each bin in Sampling Period II). The error bar is one standard deviation of the mean. The x -axis value is the average value of RH in each bin. Fractions greater than 3 standard deviations outside of the mean in each sampling period are considered outliers and excluded in this plot. (b) Average cation-to-anion ratio of inorganic species (sulfate, nitrate, and ammonium) as a function of RH (average 7 points in each bin in Sampling Period I; 27 points in each bin in Sampling Period II).

pinonaldehyde in particles estimated using the amount of pinonaldehyde partitioning into aerosol water is negligible even if a ratio of the aerosol water to the dry aerosol mass equal to one was assumed and all of the aerosol water was available to take up pinonaldehyde. Moreover, this assumed ratio of the aerosol water to the dry aerosol mass is inconsistent with the average RH of 34% observed during TAG measurements because a ratio of generally less than 0.3 is expected at this average RH.^{34–36} The measurements of particle-phase pinonaldehyde reported here were with negligible sampling artifacts due to adsorption of gas-phase pinonaldehyde to the collection cell because the denuder efficiently removed organic

vapors. Therefore, our observations of particle-phase pinonaldehyde clearly show that gas-phase pinonaldehyde had been converted into forms with the lower vapor pressures prior to the collection.

Low-volatility compounds (e.g., oligomers) formed from monomers with direct involvement of pinonaldehyde have been observed in chamber experiments^{19,29,37} and ambient samples.³⁷ In our study, low-volatility compounds were measured as a pinonaldehyde monomer, consistent with previous TAG measurements in a forest area.²³ The reason may be attributed to the use of the thermal desorption method which could decompose low-volatility compounds into their original monomers.¹² These low-volatility compounds were not directly measured in our study, but the variability in concentrations of pinonaldehyde can still be used to investigate factors affecting the formation of low-volatility compounds. In the following discussion, the term of particle-phase pinonaldehyde is taken to include all low-volatility compounds formed with direct involvement of pinonaldehyde. The cation-to-anion ratio, calculated using molar concentrations of ammonium and anions ($=2 \times [\text{sulfate}] + [\text{nitrate}]$) measured by HR-TOF-AMS, is used as an indicator of availability of acids in our study. The presence of excess ammonium is indicated when the cation-to-anion ratio is greater than one.

Particle-phase pinonaldehyde was observed while the cation-to-anion ratio, calculated using ammonium, sulfate, and nitrate, was greater than one, indicating that the presence of inorganic acids is not required for the formation of particle-phase pinonaldehyde (Figure 4). The excess ammonium observed in

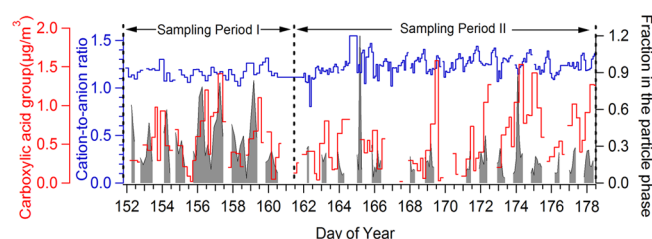


Figure 4. Temporal change of the cation-to-anion ratio of measured inorganic ions, carboxylic acid group, and the fraction of pinonaldehyde in the particle phase. Pinonaldehyde was predominantly observed during the night when the wind blew from vegetated areas located to the east and southeast of the field site. During the day, pinonaldehyde was rarely observed as the wind switched away from the vegetated areas. Site description was provided in Liu et al.²⁵ Additionally, particle-phase pinonaldehyde was not detected when the total concentration of pinonaldehyde was low.

particles is attributed to particle-phase organic acids. Since FTIR measures carboxylic acids as an acid group ($-\text{COOH}$),³⁸ excess organic acids, unneutralized by ammonium, were obviously present in particles (Figure 4). Our observations of particle-phase pinonaldehyde and availability of acids are consistent with the results of chamber experiments of α -pinene ozonolysis that oligomers are formed on the neutralized ammonium sulfate particles^{18,37} and organic acids produced from gas-phase hydrocarbon oxidation are sufficient to catalyze these heterogeneous reactions.¹⁸

Laboratory studies have shown that high aerosol acidity leads to the high yield of oligomers from pinonaldehyde and oxidation products of α -pinene.^{18,29,37} However, the laboratory observed trend is not displayed by the relationship between f_{part} of pinonaldehyde and the organic acid group measured by

FTIR (Figure 4). The reason could be that the contribution of organic acids to the aerosol acidity cannot be directly indicated by their concentration because different organic acids have different dissociation constants and organic acids and their conjugate base can serve as a buffer solution. The cation-to-anion ratio of inorganic ions showed a general trend that the high cation-to-anion ratio was along with the low f_{part} of pinonaldehyde (Figure 4), but the acidity estimated on the basis of the cation-to-anion ratio would have large uncertainties when the cation-to-anion ratio is near one.³⁹ Moreover, this trend was not found when other factors affecting the relationship between aerosol acidity and f_{part} of pinonaldehyde were considered, such as RH (Figure 3b) which can change the composition and mass of SOA⁴⁰ and the aerosol acidity.²⁹ As shown in Figure 3a, f_{part} of pinonaldehyde displayed a positive dependence on RH in Sampling Period I, consistent with previous TAG measurements in a forested area.²³ However, the cation-to-anion ratio calculated from inorganic ions did not consistently decrease as RH increased (Figure 3b). As a result, the effect of the aerosol acidity on f_{part} of pinonaldehyde is not shown by the relationship between the cation-to-anion ratio and the f_{part} of pinonaldehyde observed in our study.

In comparison with Sampling Period I, f_{part} of pinonaldehyde was generally lower in Sampling Period II and showed a different dependence on RH (Figure 3a, Figure 4) while this pattern was not observed for its reference compound, *n*-tetradecane. In addition, the difference in the relationship between f_{part} and RH in the two sampling periods is supported by independent measurements of the cation-to-anion ratio which showed a different relationship to RH in two sampling periods (Figure 3b, Figure 4). Therefore, the observed difference between f_{part} of pinonaldehyde and RH in the two sampling periods would represent their real relationship in the atmosphere. The high f_{part} of pinonaldehyde was not observed at the elevated RH in Sampling Period II, although the particle-phase concentration of pinonaldehyde was observed to increase as RH increased. The relationships between RH and f_{part} of pinonaldehyde suggest that RH favors the formation of particle-phase pinonaldehyde in the atmosphere, but it is not the main factor affecting the formation of particle-phase pinonaldehyde. Further studies are needed to examine the effect of RH on the yield of particle-phase pinonaldehyde in the atmosphere and laboratory.

Phthalic Acid. The mean f_{part} of phthalic acid was $60 \pm 20\%$, substantially higher than that of its reference compound, *n*-nonadecane (Figure 2). To reproduce this mean f_{part} for phthalic acid using gas/particle partitioning theory, a substantially lower activity coefficient ($\sim 5 \times 10^{-3}$) than the estimated range from 0.3 to 3 for SOA in the atmosphere¹¹ would be needed. The partitioning of phthalic acid into aerosol water cannot explain the mean f_{part} for phthalic acid, based on its Henry's law constant of 2.0×10^{-11} atm m³ mole⁻¹ at 25 °C²⁷ and the assumptions that the ratio of aerosol water content to dry aerosol mass is one and all aerosol water is available to take up phthalic acid. The dissociation of phthalic acid in the aerosol water is also considered, but the contribution due to its dissociation to its mean f_{part} is negligible even when pH is estimated on the basis of neutralized inorganic ions without inclusion of other organic acids. Moreover, the aerosol water content is unlikely to be that high at the average RH of 34% in the atmosphere.^{34–36} Therefore, there must be at least an additional partitioning pathway whereby particle-phase phthalic acid is formed.

We infer that a likely pathway for phthalic acid partitioning to particles is through its reaction with gas-phase ammonia. This is supported by the presence of excess ammonium in the particle phase indicated by the cation-to-anion ratio of inorganic species measured by HR-TOF-AMS (Figure 4). Evidence for reactions between organic acids and gas-phase ammonia is provided by Na et al.,¹⁴ whose results showed that ammonia dramatically increased SOA yields by reactions with organic acids in chamber experiments. Furthermore, the strong correlation between gas-phase ammonia and f_{part} of phthalic acid (linear regression $R^2 = 0.8$ between average f_{part} and the ammonia concentration) supports the hypothesis that phthalic acid partitioning to particles is through reactions with gas-phase ammonia (Figure 5).

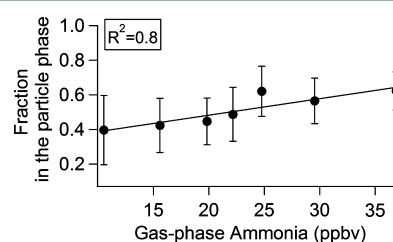


Figure 5. Fraction of phthalic acid in the particle phase as a function of the concentration of gas-phase ammonia. Each bin of seven bins has 18 data points.

Reactions with ammonia can convert phthalic acid into ammonium salts with the low vapor pressures and subsequently favor its partitioning into particles. Subcooled vapor pressures of the formed salts can be more than 100 times lower than that of phthalic acid, even if just the monoammonium salt was formed (the subcooled vapor pressure drop is estimated on the basis of the vapor pressure drop of organic acids after forming ammonium salt from USEPA EPI suite²⁷). Additional support needed for the presence of phthalic acid ammonium salts is that these salts can be measured as phthalic acid by the TAG instrument using a thermal desorption technique to extract collected organics. This support is given in Hajek et al.⁴¹ wherein the investigation of the thermal decomposition of ammonium salt of isophthalic acid shows that simultaneous release of both ammonia and isophthalic acid molecules from diammonium salts occurs without dehydration or amide formation.

6,10,14-Trimethyl-2-pentadecanone. The mean f_{part} of 6,10,14-trimethylpentadecanone was $4 \pm 2\%$, similar to that of its reference compound, *n*-heptadecane, suggesting that there is no reactive uptake of it on particles during the campaign, contrary to the observations of pinonaldehyde. These results are in agreement with previous studies on the gas/particle partitioning of ketones.^{13,42} Esteve and Noziere⁴² suggested that aldol condensation was too slow to contribute significantly to SOA under atmospheric conditions. Kroll et al.¹³ showed that ketones did not produce observable volume growth in the presence of acidic seeds even with concentrations of over 500 ppb. Other measured compounds with a ketone functional group in our study, such as benzophenone and 1-hydroxycyclohexyl-phenyl methanone, were also present primarily in the gas phase.

Implications. In situ measurements of both gas- and particle-phase organic compounds have clearly shown that multiple gas/particle partitioning pathways occur in the

atmosphere and the contribution of oxygenated compounds to SOA can be substantially increased through other gas/particle partitioning pathways relative to absorptive gas/particle partitioning. Our results indicate that the occurrence of reactive uptake of pinonaldehyde into particles does not require the availability of inorganic acids and subsequently imply that this pathway is likely widespread. However, the pathway of formation of condensable salts indicated by our observations of the gas/particle partitioning of phthalic acid could be only significant in ammonia-rich environments. Additionally, no good correlation ($r = 0.2$) was found for f_{part} between pinonaldehyde and phthalic acid. Further in situ, time-resolved measurements of gas/particle partitioning covering more oxygenated organic compounds are needed to investigate SOA formation in various environments and provide parametrization for inclusion of these pathways in SOA models. Since our results show that each of three SOA tracers investigated here has a distinct pathway to partition to particles, multiple tracers are needed in source apportionment models to adequately represent SOA formation. Additionally, these tracers are present in both gas and particle phases. As a result, it raises a concern about the accuracy of the source apportionment models using these SOA tracers without correcting for gas adsorption on the sampling substrates.

AUTHOR INFORMATION

Corresponding Author

*E-mail: ahg@berkeley.edu.

Present Address

[‡]Cooperative Institute for Research in the Environmental Sciences, University of Colorado, Boulder, Colorado.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the California Air Resources Board (CARB) award number 09-316 and the Department of Energy STTR program award number DE-FG02-08ER86335. We thank John Karlik, Ron Cohen, University of California Extension Staff, and Kern County Staff, for logistical support during the Bakersfield CalNex study. We would also like to thank Drew Gentner, Abhinav Guha, and Rachel O'Brien for their assistance in operating the Goldstein Mobile Lab.

REFERENCES

- (1) Kanakidou, M.; Seinfeld, J. H.; Pandis, S. N.; Barnes, I.; Dentener, F. J.; Facchini, M. C.; Van Dingenen, R.; Ervens, B.; Nenes, A.; Nielsen, C. J.; Swietlicki, E.; Putaud, J. P.; Balkanski, Y.; Fuzzi, S.; Horth, J.; Moortgat, G. K.; Winterhalter, R.; Myhre, C. E. L.; Tsigaridis, K.; Vignati, E.; Stephanou, E. G.; Wilson, J. Organic aerosol and global climate modelling: A review. *Atmos. Chem. Phys.* **2005**, *5*, 1053–1123.
- (2) Goldstein, A. H.; Galbally, I. E. Known and unexplored organic constituents in the earth's atmosphere. *Environ. Sci. Technol.* **2007**, *41*, 1514–1521.
- (3) Williams, B. J.; Goldstein, A. H.; Kreisberg, N. M.; Hering, S. V.; Worsnop, D. R.; Ulbrich, I. M.; Docherty, K. S.; Jimenez, J. L. Major components of atmospheric organic aerosol in southern California as determined by hourly measurements of source marker compounds. *Atmos. Chem. Phys.* **2010**, *10*, 11577–11603.
- (4) Hoyle, C. R.; Myhre, G.; Bernsten, T. K.; Isaksen, I. S. A. Anthropogenic influence on SOA and the resulting radiative forcing. *Atmos. Chem. Phys.* **2009**, *9*, 2715–2728.
- (5) Goldstein, A. H.; Koven, C. D.; Heald, C. L.; Fung, I. Y. Biogenic carbon and anthropogenic pollutants combine to form a cooling haze over the southeastern United States. *Proc. Natl. Acad. Sci. U.S.A.* **2009**, *106*, 8835–8840.
- (6) Heald, C. L.; Jacob, D. J.; Park, R. J.; Russell, L. M.; Huebert, B. J.; Seinfeld, J. H.; Liao, H.; Weber, R. J. A large organic aerosol source in the free troposphere missing from current models. *Geophys. Res. Lett.* **2005**, *32*, L18809; doi: 10.1029/2005GL023831.
- (7) Heald, C. L.; Ridley, D. A.; Kreidenweis, S. M.; Drury, E. E. Satellite observations cap the atmospheric organic aerosol budget. *Geophys. Res. Lett.* **2010**, *37*, L24808; doi: 10.1029/2010GL045095.
- (8) Volkamer, R.; Jimenez, J. L.; San Martini, F.; Dzepina, K.; Zhang, Q.; Salcedo, D.; Molina, L. T.; Worsnop, D. R.; Molina, M. J. Secondary organic aerosol formation from anthropogenic air pollution: Rapid and higher than expected. *Geophys. Res. Lett.* **2006**, *33*, L17811; doi: 10.1029/2006GL026899.
- (9) Spracklen, D. V.; Jimenez, J. L.; Carslaw, K. S.; Worsnop, D. R.; Evans, M. J.; Mann, G. W.; Zhang, Q.; Canagaratna, M. R.; Allan, J.; Coe, H.; McFiggans, G.; Rap, A.; Forster, P. Aerosol mass spectrometer constraint on the global secondary organic aerosol budget. *Atmos. Chem. Phys.* **2011**, *11*, 12109–12136.
- (10) Pankow, J. F. An absorption-model of gas-particle partitioning of organic-compounds in the atmosphere. *Atmos. Environ.* **1994**, *28*, 185–188.
- (11) Seinfeld, J. H.; Pankow, J. F. Organic atmospheric particulate material. *Annu. Rev. Phys. Chem.* **2003**, *54*, 121–140.
- (12) Jang, M. S.; Czoschke, N. M.; Lee, S.; Kamens, R. M. Heterogeneous atmospheric aerosol production by acid-catalyzed particle-phase reactions. *Science* **2002**, *298*, 814–817.
- (13) Kroll, J. H.; Ng, N. L.; Murphy, S. M.; Varutbangkul, V.; Flagan, R. C.; Seinfeld, J. H. Chamber studies of secondary organic aerosol growth by reactive uptake of simple carbonyl compounds. *J. Geophys. Res.* **2005**, *110*, D23207; doi: 10.1029/2005JD006004.
- (14) Na, K.; Song, C.; Switzer, C.; Cocker, D. R. Effect of ammonia on secondary organic aerosol formation from alpha-pinene ozonolysis in dry and humid conditions. *Environ. Sci. Technol.* **2007**, *41*, 6096–6102.
- (15) Iinuma, Y.; Boge, O.; Miao, Y.; Sierau, B.; Gnauk, T.; Herrmann, H. Laboratory studies on secondary organic aerosol formation from terpenes. *Faraday Discuss.* **2005**, *130*, 279–294.
- (16) Kroll, J. H.; Seinfeld, J. H. Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere. *Atmos. Environ.* **2008**, *42*, 3593–3624.
- (17) Zhang, Q.; Jimenez, J. L.; Worsnop, D. R.; Canagaratna, M. A case study of urban particle acidity and its influence on secondary organic aerosol. *Environ. Sci. Technol.* **2007**, *41*, 3213–3219.
- (18) Gao, S.; Ng, N. L.; Keywood, M.; Varutbangkul, V.; Bahreini, R.; Nenes, A.; He, J. W.; Yoo, K. Y.; Beauchamp, J. L.; Hodyss, R. P.; Flagan, R. C.; Seinfeld, J. H. Particle phase acidity and oligomer formation in secondary organic aerosol. *Environ. Sci. Technol.* **2004**, *38*, 6582–6589.
- (19) Tillmann, R.; Hallquist, M.; Jonsson, A. M.; Kiendler-Scharr, A.; Saathoff, H.; Iinuma, Y.; Mentel, T. F. Influence of relative humidity and temperature on the production of pinonaldehyde and OH radicals from the ozonolysis of alpha-pinene. *Atmos. Chem. Phys.* **2010**, *10*, 7057–7072.
- (20) Williams, B. J.; Goldstein, A. H.; Kreisberg, N. M.; Hering, S. V. In situ measurements of gas/particle-phase transitions for atmospheric semivolatile organic compounds. *Proc. Natl. Acad. Sci. U.S.A.* **2010**, *107*, 6676–6681.
- (21) Turpin, B. J.; Saxena, P.; Andrews, E. Measuring and simulating particulate organics in the atmosphere: problems and prospects. *Atmos. Environ.* **2000**, *34*, 2983–3013.
- (22) Williams, B. J.; Goldstein, A. H.; Kreisberg, N. M.; Hering, S. V. An in-situ instrument for speciated organic composition of atmospheric aerosols: Thermal Desorption Aerosol GC/MS-FID (TAG). *Aerosol Sci. Technol.* **2006**, *40*, 627–638.
- (23) Worton, D. R.; Goldstein, A. H.; Farmer, D. K.; Docherty, K. S.; Jimenez, J. L.; Gilman, J. B.; Kuster, W. C.; de Gouw, J.; Williams, B. J.

Kreisberg, N. M.; Hering, S. V.; Bench, G.; McKay, M.; Kristensen, K.; Glasius, M.; Surratt, J. D.; Seinfeld, J. H. Origins and composition of fine atmospheric carbonaceous aerosol in the Sierra Nevada Mountains, California. *Atmos. Chem. Phys.* **2011**, *11*, 10219–10241.

(24) Kreisberg, N. M.; Hering, S. V.; Williams, B. J.; Worton, D. R.; Goldstein, A. H. Quantification of hourly speciated organic compounds in atmospheric aerosols, measured by an in-situ thermal desorption aerosol gas chromatograph (TAG). *Aerosol Sci. Technol.* **2009**, *43*, 38–52.

(25) Liu, S.; et al. Secondary organic aerosol formation from fossil fuel sources contribute majority of summertime organic mass at Bakersfield. *J. Geophys. Res.* **2012**, DOI: 10.1029/2012JD018170.

(26) Markovic, M. Z.; VandenBoer, T. C.; Murphy, J. G. Characterization and optimization of an online system for the simultaneous measurement of atmospheric water-soluble constituents in the gas and particle phases. *J. Environ. Monit.* **2012**, *14*, 1872–1884.

(27) US EPA; Estimation Program Interface (EPI) Suite. Version v4.10. <http://www.epa.gov/oppt/exposure/pubs/episuite.html>.

(28) Robinson, A. L.; Donahue, N. M.; Shrivastava, M. K.; Weitkamp, E. A.; Sage, A. M.; Grieshop, A. P.; Lane, T. E.; Pierce, J. R.; Pandis, S. N. Rethinking organic aerosols: Semivolatile emissions and photochemical aging. *Science* **2007**, *315*, 1259–1262.

(29) Liggio, J.; Li, S. M. Reactive uptake of pinonaldehyde on acidic aerosols. *J. Geophys. Res.* **2006**, *111*, D24303; doi: 10.1029/2005JD006978.

(30) Zheng, M.; Cass, G. R.; Schauer, J. J.; Edgerton, E. S. Source apportionment of PM_{2.5} in the southeastern United States using solvent-extractable organic compounds as tracers. *Environ. Sci. Technol.* **2002**, *36*, 2361–2371.

(31) Shrivastava, M. K.; Subramanian, R.; Rogge, W. F.; Robinson, A. L. Sources of organic aerosol: Positive matrix factorization of molecular marker data and comparison of results from different source apportionment models. *Atmos. Environ.* **2007**, *41*, 9353–9369.

(32) Fraser, M. P.; Cass, G. R.; Simoneit, B. R. T.; Rasmussen, R. A. Air quality model evaluation data for organics 0.4. C-2-C-36 non-aromatic hydrocarbons. *Environ. Sci. Technol.* **1997**, *31*, 2356–2367.

(33) Goss, K. U.; Schwarzenbach, R. P. Gas/solid and gas/liquid partitioning of organic compounds: Critical evaluation of the interpretation of equilibrium constants. *Environ. Sci. Technol.* **1998**, *32*, 2025–2032.

(34) Khlystov, A.; Stanier, C. O.; Takahama, S.; Pandis, S. N. Water content of ambient aerosol during the Pittsburgh air quality study. *J. Geophys. Res.* **2005**, *110*, D07S10; doi: 10.1029/2004JD004651.

(35) Schuster, G. L.; Lin, B.; Dubovik, O. Remote sensing of aerosol water uptake. *Geophys. Res. Lett.* **2009**, *36*, 103814; doi: 10.1029/2008GL036576.

(36) Engelhart, G. J.; Hildebrandt, L.; Kostenidou, E.; Mihalopoulos, N.; Donahue, N. M.; Pandis, S. N. Water content of aged aerosol. *Atmos. Chem. Phys.* **2011**, *11*, 911–920.

(37) Tolocka, M. P.; Jang, M.; Ginter, J. M.; Cox, F. J.; Kamens, R. M.; Johnston, M. V. Formation of oligomers in secondary organic aerosol. *Environ. Sci. Technol.* **2004**, *38*, 1428–1434.

(38) Russell, L. M.; Bahadur, R.; Hawkins, L. N.; Allan, J.; Baumgardner, D.; Quinn, P. K.; Bates, T. S. Organic aerosol characterization by complementary measurements of chemical bonds and molecular fragments. *Atmos. Environ.* **2009**, *43*, 6100–6105.

(39) Xue, J.; Lau, A. K. H.; Yu, J. Z. A study of acidity on PM_{2.5} in Hong Kong using online ionic chemical composition measurements. *Atmos. Environ.* **2011**, *45*, 7081–7088.

(40) Nguyen, T. B.; Roach, P. J.; Laskin, J.; Laskin, A.; Nizkorodov, S. A. Effect of humidity on the composition of isoprene photooxidation secondary organic aerosol. *Atmos. Chem. Phys.* **2011**, *11*, 6931–6944.

(41) Hajek, M.; Malek, J.; Bazant, V. Kinetics of thermal decomposition of ammonium salts of terephthalic and isophthalic acids. *Collect. Czech. Chem. Commun.* **1971**, *36*, 84–91.

(42) Esteve, W.; Noziere, B. Uptake and reaction kinetics of acetone, 2-butanone, 2,4-pentanedione, and acetaldehyde in sulfuric acid solutions. *J. Phys. Chem. A* **2005**, *109*, 10920–10928.