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Organic Aerosol Formation: Laboratory Studies to Guide the Development of Comprehensive Formation Mechanisms and Representation in Global Aerosol Models

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John H. Seinfeld, Principal Investigator

California Institute of Technology

EXECUTIVE SUMMARY

This project addressed the following research need in the Atmospheric System Research (ASR) Science and Program Plan: "Measurements downwind of urban sources of aerosol particles and precursor gases have shown that the mass concentration of *secondary organic aerosol* (SOA) can be several-fold greater than can be explained on the basis of current model calculations using observed precursor concentrations. ASR will continue conducting laboratory experiments on both gas-phase and aqueous-phase SOA formation to characterize the particle formation and the organic gases that react to form new organic aerosol material on aerosol seeds. ASR will use these experiments to guide the development of comprehensive chemical mechanisms... to guide the development of parameterizations that are simple enough to be applied to aerosol life cycle models."

The overall objective of the proposed research was to perform research to close the gap between observed and model-predicted levels of atmospheric organic aerosols by: (1) identifying and quantifying important atmospheric SOA sources; and (2) developing and applying representations of SOA formation. The technical approaches comprised: (1) laboratory chamber studies of SOA formation; and (2) model development and implementation. The experimental portion of the proposed research included two major thrusts: (1) study of the detailed molecular routes to SOA formation and SOA yields for important VOC precursors; and (2) development and implementation of experimental strategies to perform chamber experiments that can simulate multi-generation multi-day oxidation relevant to the complete life cycle of organic aerosols.

VOC precursors studied were: glyoxal, *m*-xylene, C_{12} alkanes, α-pinene, naphthalene, phenol and methoxyphenols (biomass burning intermediates), and isoprene. We applied the Statistical Oxidation Model (SOM) of Cappa et al. (2013) and developed a new SOA model, the Functional Group Oxidation Model (FGOM) to represent aging of SOA to form low volatility products. We developed a laboratory chamber procedure to evaluate the effect of mixing of organic aerosol components on particle volatility. We showed how the dynamics of SOA size distribution evolution can be used to infer the presence of particle-phase chemistry. With respect to the difference between ambient observed organic aerosol levels and those generated in laboratory chambers (on which all atmospheric models of SOA are based), we made a major breakthrough in showing that chamber wall deposition of low-volatility VOC oxidation products leads to measured SOA yields that can be low by a factor of ~ 3. We are continuing to study this, but every indication is that vapor wall loss in chambers is the "smoking gun" of low SOA yields vs. ambient observations.

This project has resulted in 22 peer-reviewed publications.

1. Galloway, M.M., C.L. Loza, P.S. Chhabra, A.W.H. Chan, L.D. Yee, J.H. Seinfeld and F.N. Keutsch, Analysis of photochemical and dark glyoxal uptake: Implications for SOA formation, *Geophys. Res. Lett.* **38**, L17811, doi: 10.1029/2011GL048514 (2011).

The dependence of glyoxal uptake onto deliquesced ammonium sulfate seed aerosol was studied under photochemical (light + hydroxyl radical (OH)) and dark conditions. In this study, the chemical composition of aerosol formed from glyoxal is identical in the presence or absence of OH. In addition, there was no observed OH dependence on either glyoxal uptake or glyoxal driven aerosol growth for this study. These findings demonstrate that, for the system used here, glyoxal uptake is not affected by the presence of OH. In combination with previous studies, this shows that the exact nature of the type of seed aerosol, in particular the presence of a coating, has a large influence on fast photochemical uptake of glyoxal. Due to the challenge of relating this seed aerosol dependence to ambient conditions, this work highlights the resulting difficulty in quantitatively including SOA formation from glyoxal in models.

2. Loza, C.L., P.S. Chhabra, L.D. Yee, J.S. Craven, R.C. Flagan, and J.H. Seinfeld, Chemical aging of *m*-xylene secondary organic aerosol: Laboratory chamber study, *Atmos. Chem. Phys.* **12**, 151–167 (2012).

Secondary organic aerosol (SOA) can reside in the atmosphere for a week or more. While its initial formation from the gas-phase oxidation of volatile organic compounds tends to take place in the first few hours after emission, SOA can continue to evolve chemically over its atmospheric lifetime. Simulating this chemical aging over an extended time in the laboratory has proven to be challenging. We present here a procedure for studying SOA aging in laboratory chambers that is applied to achieve 36 h of oxidation. The formation and evolution of SOA from the photooxidation of *m*-xylene under low-NO_x conditions and in the presence of either neutral or acidic seed particles is studied. In SOA aging, increasing molecular functionalization leads to less volatile products and an increase in SOA mass, whereas gas- or particle-phase fragmentation chemistry results in more volatile products and a loss of SOA. The challenge is to discern from measured chamber variables the extent to which these processes are important for a given SOA system. In the experiments conducted, *m*-xylene SOA mass, calculated under the assumption of size-invariant particle composition, increased over the initial 12–13 h of photooxidation and decreased beyond that time, suggesting the existence of fragmentation chemistry. The oxidation of the SOA, as manifested in the O:C elemental ratio and fraction of organic ion detected at *m/z* 44 measured by the Aerodyne aerosol mass spectrometer, increased continuously starting after 5 h of irradiation until the 36 h termination. This behavior is consistent with an initial period in which, as the mass of SOA increases, products of higher volatility partition to the aerosol phase, followed by an aging period in which gas- and particle-phase reaction products become increasingly more oxidized. When irradiation is stopped 12.4 h into one experiment, and OH generation ceases, minimal loss of SOA is observed, indicating that the loss of SOA is either light- or OH induced. Chemical ionization mass spectrometry measurements of low-volatility *m*-xylene oxidation products exhibit behavior indicative of continuous photooxidation chemistry. A condensed chemical mechanism of *m*-xylene oxidation under low-NO_x conditions is capable of reproducing the general behavior of gas-phase evolution observed here. Moreover, order of magnitude analysis of the mechanism suggests that gas-phase OH reaction of low volatility SOA precursors is the dominant pathway of aging the *m*-xylene system although OH reaction with particle surfaces cannot be ruled out. Finally, the effect of size-dependent particle composition and size-dependent particle wall loss rates on different particle wall loss correction methods is discussed.

3. Yee, L.D., J.S. Craven, C.L. Loza, K.A. Schilling, N.L. Ng, M.R. Canagaratna, P.J. Ziemann, R.C. Flagan, and J.H. Seinfeld, Secondary organic aerosol formation from low-

NO_x photooxidation of dodecane: Evolution of multigeneration gas-phase chemistry and aerosol composition, *J. Phys. Chem. A* **116**, 6211–6230 (2012).

The extended photooxidation of and secondary organic aerosol (SOA) formation from dodecane ($C_{12}H_{26}$) under low-NO_x conditions, such that $RO_2 + HO_2$ chemistry dominates the fate of the peroxy radicals, is studied in the Caltech Environmental Chamber based on simultaneous gas and particle-phase measurements. A mechanism simulation indicates that greater than 67% of the initial carbon ends up as fourth and higher generation products after 10 h of reaction, and simulated trends for seven species are supported by gas-phase measurements. A characteristic set of hydroperoxide gas-phase products are formed under these low-NO_x conditions. Production of semivolatile hydroperoxide species within three generations of chemistry is consistent with observed initial aerosol growth. Continued gas-phase oxidation of these semivolatile species produces multifunctional low volatility compounds. This study elucidates the complex evolution of the gas-phase photooxidation chemistry and subsequent SOA formation through a novel approach comparing molecular level information from a chemical ionization mass spectrometer (CIMS) and high *m/z* ion fragments from a Aerodyne high-resolution time-of-flight aerosol mass spectrometer (HR-ToF-AMS). Combination of these techniques reveals that particle-phase chemistry leading to peroxyhemiacetal formation is the likely mechanism by which these species are incorporated in the particle phase. The current findings are relevant toward understanding atmospheric SOR formation and aging from the "unresolved complex mixture," comprising, in part, long-chain alkanes.

4. Eddingsaas, N.C., C.L. Loza, L.D. Yee, J.H. Seinfeld, and P.O. Wennberg, α-pinene photooxidation under controlled chemical conditions – Part 1: Gas-phase composition in low- and high-NO_x environments, *Atmos. Chem. Phys.* **12**, 6489–6504 (2012).

The OH oxidation of α-pinene under both low and high-NO_x environments was studied in the Caltech atmospheric chambers. Ozone was kept low to ensure OH was the oxidant. The initial α-pinene concentration was 20–50 ppb to ensure that the dominant peroxy radical pathway under low-NO_x conditions is reaction with HO_2, produced from reaction of OH with H_2O_2, and under high-NO_x conditions, reactions with NO. Here we present the gas-phase results observed. Under low-NO_x conditions the main first generation oxidation products are a number of α-pinene hydroxy hydroperoxides and pinonaldehyde, accounting for over 40% of the yield. In all, 65–75% of the carbon can be accounted for in the gas phase; this excludes first-generation products that enter the particle phase. We suggest the pinonaldehyde forms from $RO_2 + HO_2$ through an alkoxy radical channel that regenerates OH, a mechanism typically associated with acyl peroxy radicals, not alkyl peroxy radicals. The OH oxidation and photolysis of α-pinene hydroxy hydroperoxides leads to further production of pinonaldehyde, resulting in total pinonaldehyde yield from low-NO_x OH oxidation of ~33%. The low-NO_x OH oxidation of pinonaldehyde produces a number of carboxylic acids and peroxyacids known to be important secondary organic aerosol components. Under high-NO_x OH conditions, pinonaldehyde was also found to be the major first-generation OH oxidation product. The high-NO_x OH oxidation of pinonaldehyde did not produce carboxylic acids and peroxyacids. A number of organonitrates and peroxyacyl nitrates are observed and identified from α-pinene and pinonaldehyde.

5. Eddingsaas, N.C., C.L. Loza, L.D. Yee, M.N. Chan, K.A. Schilling, P.S. Chhabra, J.H. Seinfeld, and P.O. Wennberg, α-pinene photooxidation under controlled chemical conditions – Part 2: SOA Yield and composition in low- and high-NO_x environments, *Atmos. Chem. Phys.* **12**, 7413–7427 (2012).

The gas-phase oxidation of α-pinene produces a large amount of secondary organic aerosol (SOA) in the atmosphere. A number of carboxylic acids, organosulfates and nitrooxy organosulfates associated with α-pinene have been found in field samples and some are used as tracers of α-pinene oxidation. α-pinene reacts readily with OH and O_3 in the atmosphere followed by reactions with both HO_2 and NO. Due to the large number of potential reaction pathways, it can be difficult to determine what conditions lead to SOA. To better understand the SOA yield and chemical composition from low- and high-NO_x OH oxidation of α-pinene, studies were conducted in the Caltech atmospheric chamber under controlled chemical conditions. Experiments used low O_3 concentrations to ensure that OH was the main oxidant and low α-pinene concentrations such that the peroxy radical (RO_2) reacted primarily with either HO_2 under low-NO_x conditions or NO under high-NO_x conditions. SOA yield was suppressed under conditions of high-NO_x. SOA yield under high-NO_x conditions was greater when ammonium sulfate/sulfuric acid seed particles (highly acidic) were present prior to the onset of growth than when ammonium sulfate seed particles (mildly acidic) were present; this dependence was not observed under low-NO_x conditions. When aerosol seed particles were introduced after OH oxidation, allowing for later generation species to be exposed to fresh inorganic seed particles, a number of low-NO_x products partitioned to the highly acidic aerosol. This indicates that the effect of seed acidity and SOA yield might be under-estimated in traditional experiments where aerosol seed particles are introduced prior to oxidation. We also identify the presence of a number of carboxylic acids that are used as tracer compounds of α-pinene oxidation in the field as well as the formation of organosulfates and nitrooxy organosulfates. A number of the carboxylic acids were observed under all conditions, however, pinic and pinonic acid were only observed under low-NO_x conditions. Evidence is provided for particle-phase sulfate esterification of multi-functional alcohols.

6. Metcalf, A.R., C.L. Loza, M.M. Coggon, J.S. Craven, H.H. Jonsson, R.C. Flagan, and J.H. Seinfeld, Secondary organic aerosol coating formation and evaporation: Chamber studies using black carbon seed aerosol and the single-particle soot photometer, *Aerosol Sci. Technol.* **47**, 326–347 (2013).

We report a protocol for using black carbon (BC) aerosol as the seed for secondary organic aerosol (SOA) formation in an environmental chamber. We employ a single-particle soot photometer (SP2) to probe single-particle SOA coating growth dynamics and find that SOA growth on nonspherical BC aerosol is diffusion-limited. Aerosol composition measurements with an Aerodyne high resolution time-of-flight aerosol mass spectrometer (AMS) confirm that the presence of BC seed does not alter the composition of SOA as compared to self-nucleated SOA or condensed SOA on ammonium sulfate seed. We employ a 3-wavelength photoacoustic soot spectrometer (PASS-3) to measure optical properties of the systems studied, including fullerene soot as the surrogate BC seed, nucleated naphthalene SOA from high-NO_x photooxidation, and nucleated α-pinene SOA from low-NO_x photooxidation. A core-and-shell Mie scattering model of the light absorption enhancement is in good agreement with measured enhancements for both the low- and high-NO_x α-pinene photooxidation systems, reinforcing the assumption of a core-shell morphology for coated BC particles. A discrepancy between measured and modeled absorption enhancement factors in the naphthalene photooxidation system is attributed to the wavelength-dependence of refractive index of the naphthalene SOA. The coating of high-NO_x α-pinene SOA decreases after reaching a peak thickness during irradiation, reflecting a volatility change in the aerosol, as confirmed by the relative magnitudes of f_{43} and f_{44} in the AMS spectra. The protocol described here provides a framework by which future studies of SOA optical properties and single-particle growth dynamics may be explored in environmental chambers.

7. Craven, J.S., L.D. Yee, N.L. Ng, M.R. Canagaratna, C.L. Loza, K.A. Schilling, R.L.N. Yavatelli, J.A. Thornton, P.J. Ziemann, R.C. Flagan, and J.H. Seinfeld, Analysis of secondary organic aerosol formation and aging using positive matrix factorization of high-resolution aerosol mass spectra: Application to the dodecane low NO_x system, *Atmos. Chem. Phys.* **12**, 11795–11817 (2012).

Positive matrix factorization (PMF) of high-resolution laboratory chamber aerosol mass spectra is applied for the first time, the results of which are consistent with molecular level MOVI-HRToF-CIMS aerosol-phase and CIMS gas-phase measurements. Secondary organic aerosol was generated by photooxidation of dodecane under low-NO_x conditions in the Caltech environmental chamber. The PMF results exhibit three factors representing a combination of gas-particle partitioning, chemical conversion in the aerosol, and wall deposition. The slope of the measured high-resolution aerosol mass spectrometer (HR-ToF-AMS) composition data on a Van Krevelen diagram is consistent with that of other low-NO_x alkane systems in the same O:C range. Elemental analysis of the PMF factor mass spectral profiles elucidates the combinations of functionality that contribute to the slope on the Van Krevelen diagram.

8. Cappa, C.D., X. Zhang, C.L. Loza, J.S. Craven, L.D. Yee, and J.H. Seinfeld, Application of the Statistical Oxidation Model (SOM) to secondary organic aerosol formation from photooxidation of C_{12} alkanes, *Atmos. Chem. Phys.* **13**, 1591–1606 (2013).

Laboratory chamber experiments are the main source of data on the mechanism of oxidation and the secondary organic aerosol (SOA) forming potential of volatile organic compounds. Traditional methods of representing the SOA formation potential of an organic do not fully capture the dynamic, multi-generational nature of the SOA formation process. We apply the Statistical Oxidation Model (SOM) of Cappa and Wilson (2012) to model the formation of SOA from the formation of the four C_{12} alkanes, dodecane, 2-methyl undecane, cyclododecane and hexylcyclohexane, under both high- and low-NO_x conditions, based upon data from the Caltech chambers. In the SOM, the evolution of reaction products is defined by the number of carbon (N_C) and oxygen (N_O) atoms, and the model parameters are (1) the number of oxygen atoms added per reaction, (2) the decrease in volatility upon addition of an oxygen atom and (3) the probability that a given reaction leads to fragmentation of the molecules. Optimal fitting of the model to chamber data is carried out using the measured SOA mass concentration and the aerosol O:C atomic ratio. The use of the kinetic, multi-generational SOM is shown to provide insights into the SOA formation process and to offer promise for application to the extensive library of existing SOA chamber experiments that is available.

9. Zhang, X., and J.H. Seinfeld, A functional group oxidation model (FGOM) for SOA formation and aging, *Atmos. Chem. Phys.* **13**, 5907–5926 (2013).

Secondary organic aerosol (SOA) formation from a volatile organic compound (VOC) involves multiple generations of oxidation that include functionalization and fragmentation of the parent carbon backbone and likely particle-phase oxidation and/or accretion reactions. Despite the typical complexity of the detailed molecular mechanism of SOA formation and aging, a relatively small number of functional groups characterize the oxidized molecules that constitute SOA. Given the carbon number and set of functional groups, the volatility of the molecule can be estimated. We present here a functional group oxidation model (FGOM) that represents the process of SOA formation and aging. The FGOM contains a set of parameters that are to be determined by fitting of the model to laboratory chamber data: total organic aerosol concentration, and O:C and H:C atomic ratios. The sensitivity of the model prediction to variation of the adjustable parameters allows one to assess the relative importance of various pathways involved in SOA formation. An analysis of SOA formation from the high- and low-NO_x photooxidation of four C_{12} alkanes (n-dodecane, 2-methylundecane, hexylcyclohexane, and cyclododecane) using the FGOM is presented, and comparison with the statistical oxidation model (SOM) of Cappa et al. (2013) is discussed.

10. Yee, L.D., K.E. Kautzman, C.L. Loza, K.A. Schilling, M.M. Coggon, P.S. Chhabra, M.N. Chan, S.P. Hersey, J.D. Crounse, P.O. Wennberg, R.C. Flagan, and J.H. Seinfeld, Secondary organic aerosol formation from biomass burning intermediates: Phenol and Methoxyphenols, *Atmos. Chem. Phys.* **13**, 8019–8043 (2013).

The formation of secondary organic aerosol from oxidation of phenol, guaiacol (2-methoxyphenol), and syringol (2,6-dimethoxyphenol), major components of biomass burning, is described. Photooxidation experiments were conducted in the Caltech laboratory chambers under low-NO_x (< 10 ppb) conditions using H_2O_2 as the OH source. Secondary organic aerosol (SOA) yields (ratio of mass of SOA formed to mass of primary organic reacted) greater than 25% are observed. Aerosol growth is rapid and linear with the primary organic conversion, consistent with the formation of essentially non-volatile products. Gas- and aerosol-phase oxidation products from the guaiacol system provide insight into the chemical mechanisms responsible for SOA formation. Syringol SOA yields are lower than those of phenol and guaiacol, likely due to novel methoxy group chemistry that leads to early fragmentation in the gas-phase photooxidation. Atomic oxygen to carbon (O:C) ratios calculated from high-resolution-time-of-flight Aerodyne Aerosol Mass Spectrometer (HR-ToF-AMS) measurements of the SOA in all three systems are ~ 0.9, which represent among the highest such ratios achieved in laboratory chamber experiments and are similar to that of aged atmospheric organic aerosol. The global contribution of SOA from intermediate volatility and semivolatile organic compounds has been shown to be substantial (Pye and Seinfeld, 2010). An approach to representing SOA formation from biomass burning emissions in atmospheric models could involve one or more surrogate species for which aerosol formation under well-controlled conditions has been quantified. The present work provides data for such an approach.

11. Loza, C.L., M.M. Coggon, T.B. Nguyen, A. Zuend, R.C. Flagan, and J.H. Seinfeld, On the mixing and evaporation of secondary organic aerosol components, *Environ. Sci. Technol.* **47**, 6173–6180 (2013).

The physical state and chemical composition of an organic aerosol affect its degree of mixing and its interactions with condensing species. We present here a laboratory chamber procedure for studying the effect of the mixing of organic aerosol components on particle evaporation. The procedure is applied to the formation of secondary organic aerosol (SOA) from α-pinene and toluene photooxidation. SOA evaporation is induced by heating the chamber aerosol from room temperature (25°C) to 42°C over 7 h and detected by a shift in the peak diameter of the SOA size distribution. With this protocol, α-pinene SOA is found to be more volatile than toluene SOA. When SOA is formed from the two precursors sequentially, the evaporation behavior of the SOA most closely resembles that of SOA from the second parent hydrocarbon, suggesting that the structure of the mixed SOA resembles a core of SOA from the initial precursor coated by a layer of SOA from the second precursor. Such a core-and-shell configuration of the organic aerosol phases implies limited mixing of the SOA from the two precursors on the time scale of the experiments, consistent with a high viscosity of at least one of the phases.

12. Yee, L.D., J.S. Craven, C.L. Loza, K.A. Schilling, N.L. Ng, M.R. Canagaratna, P.J. Ziemann, R.C. Flagan, and J.H. Seinfeld, Effect of chemical structure on secondary organic aerosol formation from C_{12} alkanes, *Atmos. Chem. Phys.* **13**, 11121–11140 (2013).

The secondary organic aerosol (SOA) formation from four C_{12} alkanes (*n*-dodecane, 2-methylundecane, hexylcyclohexane, and cyclododecane) is studied in the Caltech Environmental Chamber under low-NO_x conditions, in which the principal fate of the peroxy radical formed in the initial OH reaction is reaction with HO_2. Simultaneous gas- and particle-phase measurements elucidate the effect of alkane structure on the chemical mechanisms underlying SOA growth. Reaction of branched structures leads to fragmentation and more volatile products, while cyclic structures are subject to faster oxidation and lead to less volatile products. Product identifications reveal that particle-phase reactions involving peroxyhemiacetal formation from several multifunctional hydroperoxide species are key components of initial SOA growth in all four systems. The continued chemical evolution of the particle-phase is structure-dependent, with 2-methylundecane SOA formation exhibiting the least extent of chemical processing and cyclododecane SOA achieving sustained growth with the greatest variety of chemical pathways. The extent of chemical development is not necessarily reflected in the oxygen to carbon (O:C) ratio of the aerosol as cyclododecane achieves the lowest O:C, just above 0.2, by the end of the experiment and hexylcyclohexane the highest, approaching 0.35.

13. Shiraiwa, M., L.D. Yee, K.A. Schilling, C.L. Loza, J.S. Craven, A. Zuend, P.J. Ziemann, and J.H. Seinfeld, Size distribution dynamics reveal particle-phase chemistry in organic aerosol formation, *Proc. Natl. Acad. Sci. USA* **110**, 11746–11750 (2013).

Organic aerosols are ubiquitous in the atmosphere and play a central role in climate, air quality, and public health. The aerosol size distribution is key in determining its optical properties and cloud condensation nucleus activity. The dominant portion of organic aerosol is formed through gas-phase oxidation of volatile organic compounds, so-called secondary organic aerosols (SOAs). Typical experimental measurements of SOA formation include total SOA mass and atomic oxygen-to-carbon ratio. These measurements, alone, are generally insufficient to reveal the extent to which condensed-phase reactions occur in conjunction with the multigeneration gas-phase photooxidation. Combining laboratory chamber experiments and kinetic gas-particle modeling for the dodecane SOA system, here we show that the presence of particle-phase chemistry is reflected in the evolution of the SOA size distribution as well as its mass concentration. Particle-phase reactions are predicted to occur mainly at the particle surface, and the reaction products contribute more than half of the SOA mass. Chamber photooxidation with a midexperiment aldehyde injection confirms that heterogeneous reaction of aldehydes with organic hydroperoxides forming peroxyhemiacetals can lead to a large increase in SOA mass. Although experiments need to be conducted with other SOA precursor hydrocarbons, current results demonstrate coupling between particle-phase chemistry and size distribution dynamics in the formation of SOAs, thereby opening up an avenue for analysis of the SOA formation process.

14. Loza, C.L., J.S. Craven, L.D. Yee, M.M. Coggon, R.H. Schwantes, M. Shiraiwa, X. Zhang, K.A. Schilling, N.L. Ng, M.R. Canagaratna, P.J. Ziemann, R.C. Flagan, and J.H. Seinfeld, Secondary organic aerosol yields of 12-carbon alkanes, *Atmos. Chem. Phys.* **14**, 1423–1439 (2014).

Secondary organic aerosol (SOA) yields were measured for cyclododecane, hexylcyclohexane, *n*-dodecane, and 2-methylundecane under high-NO_x conditions, in which alkyl peroxy radicals (RO_2) react primarily with NO, and under low-NO_x conditions, in which RO_2 reacts primarily with HO_2. Experiments were run until 95–100% of the initial alkane had reacted. Particle wall loss was evaluated as two limiting cases using a new approach that requires only suspended particle number-size distribution data and accounts for size-dependent particle wall losses and condensation. SOA yield differed by a factor of 2 between the two limiting cases, but the same trends among alkane precursors were observed for both limiting cases. Vapor-phase wall losses were addressed through a modeling study and increased SOA yield uncertainty by approximately 30%. SOA yields were highest from cyclododecane under both NO_x conditions. SOA yields ranged from 3.3% (dodecane, low-NO_x conditions) to 160% (cyclododecane, high-NO_x conditions). Under high-NO_x conditions, SOA yields increased from 2-methylundecane < dodecane ~ hexylcyclohexane < cyclododecane, consistent with previous studies. Under low-NO_x conditions, SOA yields increased from 2-methylundecane ~ dodecane < hexylcyclohexane < cyclododecane. The presence of cyclization in the parent alkane structure increased SOA yields, whereas the presence of branch points decreased SOA yields due to increased vapor-phase fragmentation. Vapor-phase fragmentation was found to be more prevalent under high-NO_x conditions than under low-NO_x conditions. For different initial mixing ratios of the same alkane and same NO_x conditions, SOA yield did not correlate with SOA mass throughout SOA growth, suggesting kinetically limited SOA growth for these systems.

15. Zaveri, R., R.C. Easter, J.E. Shilling, and J.H. Seinfeld, Modeling kinetic partitioning of secondary organic aerosol and size distribution dynamics: Representing effects of volatility, phase state, and particle-phase reaction, *Atmos. Chem. Phys.* **14**, 5153–5181 (2014).

This paper describes and evaluates a new framework for modeling kinetic gas-particle partitioning of secondary organic aerosol (SOA) that takes into account diffusion and chemical reaction within the particle phase. The framework uses a combination of (a) an analytical quasi-steady-state treatment for the diffusion–reaction process within the particle phase for fast-reacting organic solutes, and (b) a two-film theory approach for slow- and nonreacting solutes. The framework is amenable for use in regional and global atmospheric models, although it currently awaits specification of the various gas- and particle-phase chemistries and the related physicochemical properties that are important for SOA formation. Here, the new framework is implemented in the computationally efficient Model for Simulating Aerosol Interactions and Chemistry (MOSAIC) to investigate the competitive growth dynamics of the Aitken and accumulation mode particles. Results show that the timescale of SOA partitioning and the associated size distribution dynamics depend on the complex interplay between organic solute volatility, particle-phase bulk diffusivity, and particle-phase reactivity (as exemplified by a pseudo-first-order reaction rate constant), each of which can vary over several orders of magnitude. In general, the timescale of SOA partitioning increases with increase in volatility and decrease in bulk diffusivity and rate constant. At the same time, the shape of the aerosol size distribution displays appreciable narrowing with decrease in volatility and bulk diffusivity and increase in rate constant. A proper representation of these physicochemical processes and parameters is needed in the next generation models to reliably predict not only the total SOA mass, but also its composition- and number-diameter distributions, all of which together determine the overall optical and cloud-nucleating properties.

16. Zhang, X., C.D. Cappa, S. Jathar, R.C. McVay, J.J. Ensberg, M.J. Kleeman, and J.H. Seinfeld, Influence of vapor wall loss in laboratory chambers on yields of secondary organic aerosol, *Proc. Natl. Acad. Sci. USA* **111**, 5802–5807 (2014).

Secondary organic aerosol (SOA) constitutes a major fraction of submicrometer atmospheric particulate matter. Quantitative simulation of SOA within air-quality and climate models—and its resulting impacts—depends on the translation of SOA formation observed in laboratory chambers into robust parameterizations. Worldwide data have been accumulating indicating that model predictions of SOA are substantially lower than ambient observations. Although possible explanations for this mismatch have been advanced, none has addressed the laboratory chamber data themselves. Losses of particles to the walls of chambers are routinely accounted for, but there has been little evaluation of the effects on SOA formation of losses of semivolatile vapors to chamber walls. Here, we experimentally demonstrate that such vapor losses can lead to substantially underestimated SOA formation, by factors as much as 4. Accounting for such losses has the clear potential to bring model predictions and observations of organic aerosol levels into much closer agreement.

17. Napier, W.J., J.J. Ensberg, and J.H. Seinfeld, Insight into the numerical challenges of implementing 2-dimensional SOA models in atmospheric chemical transport models, *Atmos. Environ.* **96**, 331–344 (2014).

The new generation of secondary organic aerosol (SOA) models that represent gas- and particle-phase chemistry and thermodynamic partitioning using discrete two-dimensional grids (e.g. SOM, 2D-VBS) cannot be efficiently implemented into three-dimensional atmospheric chemical transport models (CTMs) due to the large number of bins (tracers) required. In this study, we introduce a novel mathematical framework, termed the Oxidation State/Volatility Moment Method, that is designed to address these computational burdens so as to allow the new generation of SOA models to be implemented into CTMs. This is accomplished by mapping the two-dimensional grids onto probability distributions that conserve carbon and oxygen mass. Assessment of the Moment Method strengths (speed, carbon and oxygen conservation) and weaknesses (numerical drift) provide valuable insight that can guide future development of SOA modules for atmospheric CTMs.

18. Schilling Fahnestock, K.A., L.D. Yee, C.L. Loza, M.M. Coggon, R. Schwantes, X. Zhang, N.F. Dalleska, and J.H. Seinfeld, Secondary organic aerosol composition from C_{12} alkanes, *J. Phys. Chem. A* **119**, 4281–4297 (2014).

The effects of structure, NO_x conditions, relative humidity, and aerosol acidity on the chemical composition of secondary organic aerosol (SOA) are reported for the photooxidation of three C_{12} alkanes: *n*-dodecane, cyclododecane, and hexylcyclohexane. Acidity was modified through seed particle composition: NaCl, $(NH_4)_2SO_4$, and $(NH_4)_2SO$ + H_2SO_4. Off-line analysis of SOA was carried out by solvent extraction and gas chromatography−mass spectrometry (GC/MS) and direct analysis in real-time mass spectrometry. We report here 750 individual masses of SOA products identified from these three alkane systems and 324 isomers resolved by GC/MS analysis. The chemical compositions for each alkane system provide compelling evidence of particle-phase chemistry, including reactions leading to oligomer formation. Major oligomeric species for alkane SOA are peroxyhemiacetals, hemiacetals, esters, and aldol condensation products. Furans, dihydrofurans, hydroxycarbonyls, and their corresponding imine analogues are important participants in these oligomer-producing reactions. Imines are formed in the particle phase from the reaction of the ammonium sulfate seed aerosol with carbonyl-bearing compounds present in all the SOA systems. Under high-NO conditions, organonitrate products can lead to an increase of aerosol volume concentration by up to a factor of 5 over that in low-NO conditions. Structure was found to play a key role in determining the degree of functionalization and fragmentation of the parent alkane, influencing the mean molecular weight of the SOA produced and the mean atomic O:C ratio.

19. McVay, R.C., C.D. Cappa, and J.H. Seinfeld, Vapor-wall deposition in chambers: Theoretical considerations, *Environ. Sci. Technol.* **48**, 10251–10258 (2014).

In order to constrain the effects of vapor-wall deposition on measured secondary organic aerosol (SOA) yields in laboratory chambers, researchers recently varied the seed aerosol surface area in toluene oxidation and observed a clear increase in the SOA yield with increasing seed surface area (Zhang, X.; et al. *Proc. Natl. Acad. Sci. USA* **2014**, *111*, 5802). Using a coupled vapor-particle dynamics model, we examine the extent to which this increase is the result of vapor-wall deposition versus kinetic limitations arising from imperfect accommodation of organic species into the particle phase. We show that a seed surface area dependence of the SOA yield is present only when condensation of vapors onto particles is kinetically limited. The existence of kinetic limitation can be predicted by comparing the characteristic time scales of gas-phase reaction, vapor-wall deposition, and gas-particle equilibration. The gas-particle equilibration time scale depends on the gas-particle accommodation coefficient α_p. Regardless of the extent of kinetic limitation, vapor-wall deposition depresses the SOA yield from that in its absence since vapor molecules that might otherwise condense on particles deposit on the walls. To accurately extrapolate chamber-derived yields to atmospheric conditions, both vapor-wall deposition and kinetic limitations must be taken into account.

20. Nguyen, T.B., J.D. Crounse, R.H. Schwantes, A.P. Teng, K.H. Bates, X. Zhang, J.M. St. Clair, W.H. Brune, G.S. Tyndall, F.N. Keutsch, J.H. Seinfeld, and P.O. Wennberg, Overview of the Focused Isoprene eXperiment at the California Institute of Technology (FIXCIT): Mechanistic chamber studies on the oxidation of biogenic compounds, *Atmos. Chem. Phys.* **14**, 13531–13549 (2014).

The Focused Isoprene eXperiment at the California Institute of Technology (FIXCIT) was a collaborative atmospheric chamber campaign that occurred during January 2014. FIXCIT is the laboratory component of a synergistic field and laboratory effort aimed toward (1) better understanding the chemical details behind ambient observations relevant to the southeastern United States, (2) advancing the knowledge of atmospheric oxidation mechanisms of important biogenic hydrocarbons, and (3) characterizing the behavior of field instrumentation using authentic standards. Approximately 20 principal scientists from 14 academic and government institutions performed parallel measurements at a forested site in Alabama and at the atmospheric chambers at Caltech. During the 4 week campaign period, a series of chamber experiments was conducted to investigate the dark- and photo-induced oxidation of isoprene, α-pinene, methacrolein, pinonaldehyde, acylperoxy nitrates, isoprene hydroxy nitrates (ISOPN), isoprene hydroxy hydroperoxides (ISOPOOH), and isoprene epoxydiols (IEPOX) in a highly controlled and atmospherically relevant manner. Pinonaldehyde and isomer-specific standards of ISOPN, ISOPOOH, and IEPOX were synthesized and contributed by campaign participants, which enabled explicit exploration into the oxidation mechanisms and instrument responses for these important atmospheric compounds. The present overview describes the goals, experimental design, instrumental techniques, and preliminary observations from the campaign. This work provides context for forthcoming publications affiliated with the FIXCIT campaign. Insights from FIXCIT are anticipated to aid significantly in interpretation of field data and the revision of mechanisms currently implemented in regional and global atmospheric models.

21. Nguyen, T.B., K.H. Bates, J.D. Crounse, R.H. Schwantes, X. Zhang, H.G. Kjaergaard, J.D. Surratt, P. Lin, A. Laskin, J.H. Seinfeld, and P.O. Wennberg, Mechanism of the

hydroxyl radical oxidation of methacryloyl peroxynitrate (MPAN) and its pathway toward secondary organic aerosol formation in the atmosphere, *Phys. Chem. Chem. Phys.* **17**, 17914–17926 (2015).

Methacryloyl peroxynitrate (MPAN), the acyl peroxynitrate of methacrolein, has been suggested to be an important secondary organic aerosol (SOA) precursor from isoprene oxidation. Yet, the mechanism by which MPAN produces SOA through reaction with the hydroxyl radical (OH) is unclear. We systematically evaluate three proposed mechanisms in controlled chamber experiments and provide the first experimental support for the theoretically-predicted lactone formation pathway from the MPAN + OH reaction, producing hydroxymethyl-methyl-α-lactone (HMML). The decomposition of the MPAN–OH adduct yields HMML + NO_3 (~ 75%) and hydroxyacetone + CO + NO_3 (~ 25%), out-competing its reaction with atmospheric oxygen. The production of other proposed SOA precursors, *e.g.*, methacrylic acid epoxide (MAE), from MPAN and methacrolein are negligible (< 2%). Furthermore, we show that the beta-alkenyl moiety of MPAN is critical for lactone formation. Alkyl radicals formed cold *via* H-abstraction by OH do not decompose to HMML, even if they are structurally identical to the MPAN–OH adduct. The SOA formation from HMML, from polyaddition of the lactone to organic compounds at the particle interface or in the condensed phase, is close to unity under dry conditions. However, the SOA yield is sensitive to particle liquid water and solvated ions. In hydrated inorganic particles, HMML reacts primarily with H_2O to produce the monomeric 2-methylglyceric acid (2MGA) or with aqueous sulfate and nitrate to produce the associated organosulfate and organonitrate, respectively. 2MGA, a tracer for isoprene SOA, is semivolatile and its accommodation in aerosol water decreases with decreasing pH. Conditions that enhance the production of neutral 2MGA suppress SOA mass from the HMML channel. Considering the liquid water content and pH ranges of ambient particles, 2MGA will exist largely as a gaseous compound in some parts of the atmosphere.

22. Mai, H., M. Shiraiwa, R.C. Flagan, and J.H. Seinfeld, The equilibration time scale of gas-particle partitioning for secondary organic aerosol, *Environ. Sci. Technol.*, submitted for publication.

Compelling experimental evidence indicates that secondary organic aerosol can exhibit the properties of viscous, semi-solid particles, calling into question the traditional assumption of gas-particle equilibrium partitioning. Here we evaluate the time scale to achieve gas-particle partitioning equilibrium from both the analytical solution of an idealized gas-particle transport problem and a full numerical simulation. Conditions under which the time scale for gas-particle equilibrium partitioning is controlled by gas-phase diffusion, interfacial transport, and particle-phase diffusion are shown. The numerical simulations demonstrate the effects on the equilibration time scale of particle size change owing to growth and depletion of vapor by growing particles.