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Mechanisms of Formation of Secondary Organic Aerosols and Implications for Global Radiative Forcing

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Introduction

Organic material constitutes about 50% of global atmospheric aerosol mass, and the dominant source of organic aerosol is the oxidation of volatile hydrocarbons, to produce secondary organic aerosol (SOA). Understanding the formation of SOA is crucial to predicting present and future climate effects of atmospheric aerosols.

The goal of this program is to significantly increase our understanding of secondary organic aerosol (SOA) formation in the atmosphere. Ambient measurements indicate that the amount of SOA in the atmosphere exceeds that predicted in current models based on existing laboratory chamber data. This would suggest that either the SOA yields measured in laboratory chambers are understated or that all major organic precursors have not been identified. In this research program we are systematically exploring these possibilities.

A list of each of the research projects completed during 2008 - 2011 under support of **DE-FG02-05ER63983** follows:

1. Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere (Kroll et al., 2008)

Secondary organic aerosol (SOA), particulate matter composed of compounds formed from the atmospheric transformation of organic species, accounts for a substantial fraction of tropospheric aerosol. The formation of low volatility (semivolatile and possibly nonvolatile) compounds that make up SOA is governed by a complex series of reactions of a large number of organic species, so the experimental characterization and theoretical description of SOA formation presents a substantial challenge. In this review we outline what is known about the chemistry of formation and continuing transformation of low-volatility species in the atmosphere. The primary focus is chemical processes that can change the volatility of organic compounds: (1) oxidation reactions in the gas phase, (2) reactions in the particle phase, and (3) continuing chemistry (in either phase) over several generations. Gas-phase oxidation reactions can reduce volatility by the addition of polar functional groups or increase it by the cleavage of carbon-carbon bonds; key branch points that control volatility are the initial attack of the oxidant, reactions of alkylperoxy (RO_2) radicals, and reactions of alkoxy (RO) radicals. Reactions in the particle phase include oxidation reactions as well as accretion reactions, non-oxidative processes leading to the formation of high-molecular-weight species. Organic carbon in the atmosphere is continually subject to reactions in the gas and particle phases throughout its atmospheric lifetime (until lost by physical deposition or oxidized to CO or CO_2), implying continual changes in volatility over the timescales of several days. The volatility changes arising from these chemical reactions must be parameterized and included in models in order to gain a quantitative and predictive understanding of SOA formation.

2. Secondary organic aerosol (SOA) formation from reaction of isoprene with nitrate radicals (NO_3) (Ng et al., 2008)

Secondary organic aerosol (SOA) formation from the reaction of isoprene with nitrate radicals

(NO_3) is investigated in the Caltech indoor chambers. Experiments are performed in the dark and under dry conditions (RH<10%) using N_2O_5 as a source of NO_3 radicals. For an initial isoprene concentration of 18.4 to 101.6 ppb, the SOA yield (defined as the ratio of the mass of organic aerosol formed to the mass of parent hydrocarbon reacted) ranges from 4.3% to 23.8%. By examining the time evolutions of gas-phase intermediate products and aerosol volume in real time, we are able to constrain the chemistry that leads to the formation of low-volatility products. Although the formation of ROOR from the reaction of two peroxy radicals (RO_2) has generally been considered as a minor channel, based on the gas-phase and aerosol-phase data it appears that RO_2+RO_2 reaction (self reaction or cross-reaction) in the gas phase yielding ROOR products is a dominant SOA formation pathway. A wide array of organic nitrates and peroxides are identified in the aerosol formed and mechanisms for SOA formation are proposed. Using a uniform SOA yield of 10% (corresponding to $M_o \cong 10 \mu g\ m^{-3}$), it is estimated that ~2 to 3 Tg yr^{-1} of SOA results from isoprene+NO_3. The extent to which the results from this study can be applied to conditions in the atmosphere depends on the fate of peroxy radicals in the nighttime troposphere.

3. Organosulfate Formation in Biogenic Secondary Organic Aerosol (Surratt et al., 2008)

Organosulfates of isoprene, α-pinene, and *β*-pinene have recently been identified in both laboratory-generated and ambient secondary organic aerosol (SOA). In this study, the mechanism and ubiquity of organosulfate formation in biogenic SOA is investigated by a comprehensive series of laboratory photooxidation (i.e., OH-initiated oxidation) and nighttime oxidation (i.e., NO_3-initiated oxidation under dark conditions) experiments using nine monoterpenes (α-pinene, *β*-pinene, *d*-limonene, *l*-limonene, α-terpinene, *γ*-terpinene, terpinolene, Δ^3-carene, and *β*-phellandrene) and three monoterpenes (α-pinene, *d*-limonene, and *l*-limonene), respectively. Organosulfates were characterized using liquid chromatographic techniques coupled to electrospray ionization combined with both linear ion trap and high-resolution time-of-flight mass spectrometry. Organosulfates are formed only when monoterpenes are oxidized in the presence of acidified sulfate seed aerosol, a result consistent with prior work. Archived laboratory-generated isoprene SOA and ambient filter samples collected from the southeastern U.S. were reexamined for organosulfates. By comparing the tandem mass spectrometric and accurate mass measurements collected for both the laboratory-generated and ambient aerosol, previously uncharacterized ambient organic aerosol components are found to be organosulfates of isoprene, α-pinene, *β*-pinene, and limonene-like monoterpenes (e.g., myrcene), demonstrating the ubiquity of organosulfate formation in ambient SOA. Several of the organosulfates of isoprene and of the monoterpenes characterized in this study are ambient tracer compounds for the occurrence of biogenic SOA formation under acidic conditions. Furthermore, the nighttime oxidation experiments conducted under highly acidic conditions reveal a viable mechanism for the formation of previously identified nitrooxy organosulfates found in ambient nighttime aerosol samples. We estimate that the organosulfate contribution to the total organic mass fraction of ambient aerosol collected from K-puszta, Hungary, a field site with a similar organosulfate composition as that found in the present study for the southeastern U.S., can be as high as 30%.

4. New Insights into the Production of Acids and Organic Nitrates (Paulot, et al, 2009)

We describe a nearly explicit chemical mechanism for isoprene photooxidation guided by chamber studies that include time-resolved observation of an extensive suite of volatile compounds. We provide new constraints on the chemistry of the poorly-understood isoprene δ-hydroxy channels, which account for more than one third of the total isoprene carbon flux and a larger fraction of the nitrate yields. We show that the *cis* branch dominates the chemistry of the δ-hydroxy channel with less than 5% of the carbon following the *trans* branch. The modelled yield of isoprene nitrates is 12±3% with a large difference between the δ and β branches. The oxidation of these nitrates releases about 50% of the NO_x. Methacrolein nitrates (modeled yield ≃ 15±3% from methacrolein) and methylvinylketone nitrates (modelled yield ≃ 11±3% yield from methylvinylketone) are also observed. Propanone nitrate, produced with a yield of 1% from isoprene, appears to be the longest-lived nitrate formed in the total oxidation of isoprene. We find a large molar yield of formic acid and suggest a novel mechanism leading to its formation from the organic nitrates. Finally, the most important features of this mechanism are summarized in a condensed scheme appropriate for use in global chemical transport models.

5. Photooxidation of 2-Methyl-3-Buten-2-ol (MBO) as a Potential Source of Secondary Organic Aerosol (Chan et al., 2009)

2-Methyl-3-buten-2-ol (MBO) is an important biogenic hydrocarbon emitted in large quantities by pine forests. Atmospheric photooxidation of MBO is known to lead to oxygenated compounds, such as glycolaldehyde, which is the precursor to glyoxal. Recent studies have shown that the reactive uptake of glyoxal onto aqueous particles can lead to formation of secondary organic aerosol (SOA). In this work, MBO photooxidation under high- and low-NO_x conditions was performed in dual laboratory chambers to quantify the yield of glyoxal and investigate the potential for SOA formation. The yields of glycolaldehyde and 2-hydroxy-2-methylpropanal (HMPR), fragmentation products of MBO photooxidation, were observed to be lower at lower NO_x concentrations. Overall, the glyoxal yield from MBO photooxidation was 25% under high-NO_x and 4% under low-NO_x conditions. In the presence of wet ammonium sulfate seed and under high-NO_x conditions, glyoxal uptake and SOA formation were not observed conclusively, due to relatively low (<30 ppb) glyoxal concentrations. Slight aerosol formation was observed under low-NO_x and dry conditions, with aerosol mass yields on the order of 0.1%. The small amount of SOA was not related to glyoxal uptake, but is likely a result of reactions similar to those that generate isoprene SOA under low-NO_x conditions. The difference in aerosol yields between MBO and isoprene photooxidation under low-NO_x conditions is consistent with the difference in vapor pressures between triols (from MBO) and tetrols (from isoprene). Despite its structural similarity to isoprene, photooxidation of MBO is not expected to make a significant contribution to SOA formation.

6. Glyoxal uptake on ammonium sulphate seed aerosol: reaction products and reversibility of uptake under dark and irradiated conditions (Galloway et al., 2009)

Chamber studies of glyoxal uptake onto ammonium sulphate aerosol were performed under dark and irradiated conditions to gain further insight into processes controlling glyoxal uptake onto ambient aerosol. Organic fragments from glyoxal dimers and trimers were observed within the aerosol under dark and irradiated conditions. Glyoxal monomers and oligomers were the dominant organic compounds formed under the conditions of this study; glyoxal oligomer formation and overall organic growth were found to be reversible under dark conditions. Analysis of high resolutiontime-of-flight aerosol mass spectra provides evidence for irreversible formation of carbon-nitrogen (C-N) compounds in the aerosol. We have identified 1H-imidazole-2-carboxaldehyde as one C-N product. To the authors' knowledge, this is the first time C-N compounds resulting from condensed phase reactions with ammonium sulphate seed have been detected in aerosol. Organosulphates were not detected under dark conditions. However, active photochemistry was found to occur within aerosol during irradiated experiments. Carboxylic acids and organic esters were identified within the aerosol. An organosulphate, which had been previously assigned as glyoxal sulphate in ambient samples and chamber studies of isoprene oxidation, was observed only in the irradiated experiments. Comparison with a laboratory synthesized standard and chemical considerations strongly suggest that this organosulphate is glycolic acid sulphate, an isomer of the previously proposed glyoxal sulphate.

7. Secondary organic aerosol formation from photooxidation of naphthalene and alkylnaphthalenes: Implications for oxidation of intermediate volatility organic compounds (IVOCs) (Chan et al., 2009)

Current atmospheric models do not include secondary organic aerosol (SOA) production from gas-phase reactions of polycyclic aromatic hydrocarbons (PAHs). Recent studies have shown that primary emissions undergo oxidation in the gas phase, leading to SOA formation. This opens the possibility that low-volatility gas-phase precursors are a potentially large source of SOA. In this work, SOA formation from gas-phase photooxidation of naphthalene, 1-methylnaphthalene (1-MN), 2-methylnaphthalene (2-MN), and 1,2-dimethylnaphthalene (1,2-DMN) is studied in the Caltech dual 28-m^3 chambers. Under high-NO_x conditions and aerosol mass loadings between 10 and 40 $\mu g\ m^{-3}$, the SOA yields (mass of SOA per mass of hydrocarbon reacted) ranged from 0.19 to 0.30 for naphthalene, 0.19 to 0.39 for 1-MN, 0.26 to 0.45 for 2-MN, and constant at 0.31 for 1,2-DMN. Under low-NO_x conditions, the SOA yields were measured to be 0.73, 0.68, and 0.58, for naphthalene, 1-MN, and 2-MN, respectively. The SOA was observed to be semivolatile under high-NO_x conditions and essentially nonvolatile under low-NO_x conditions, owing to the higher fraction of ring-retaining products formed under low-NO_x conditions. When applying these measured yields to estimate SOA formation from primary emissions of diesel engines and wood burning, PAHs are estimated to yield 3-5 times more SOA than light aromatic compounds over photooxidation timescales of less than 12 h. PAHs can also account for up to 54% of the total SOA from oxidation of diesel emissions, representing a potentially large source of urban SOA.

8. Terpenylic Acid and Related Compounds from the Oxidation of α-Pinene:

Implications for New Particle Formation and Growth above Forests (Claeys, et al., 2009)

Novel secondary organic aerosol (SOA) products from the monoterpene R-pinene with unique dimer-forming properties have been identified as lactone-containing terpenoic acids, i.e., terpenylic and 2-hydroxyterpenylic acid, and diaterpenylic acid acetate. The structural characterizations were based on the synthesis of referencecompoundsand detailed interpretation of mass spectral data. Terpenylic acid and diaterpenylic acid acetate are early oxidation products generated upon both photooxidation and ozonolysis, while 2-hydroxyterpenylic acid is an abundant SOA tracer in ambient fine aerosol that can be explained by further oxidation of terpenylic acid. Quantum chemical calculations support that noncovalent dimer formation involving double hydrogen bonding interactions between carboxyl groups of the monomers is energetically favorable.

9. The formation, properties and impact of secondary organic aerosol: current and emerging issues (Hallquist, et al., 2009)

Secondary organic aerosol (SOA) accounts for a significant fraction of ambient tropospheric aerosol and a detailed knowledge of the formation, properties and transformation of SOA is therefore required to evaluate its impact on atmospheric processes, climate and human health. The chemical and physical processes associated with SOA formation are complex and varied, and, despite considerable progress in recent years, a quantitative and predictive understanding of SOA formation does not exist and therefore represents a major research challenge in atmospheric science. This review begins with an update on the current state of knowledge on the global SOA budget and is followed by an overview of the atmospheric degradation mechanisms for SOA precursors, gas-particle partitioning theory and the analytical techniques used to determine the chemical composition of SOA. A survey of recent laboratory, field and modeling studies is also presented. The following topical and emerging issues are highlighted and discussed in detail: molecular characterization of biogenic SOA constituents, condensed phase reactions and oligomerization, the interaction of atmospheric organic components with sulfuric acid, the chemical and photochemical processing of organics in the atmospheric aqueous phase, aerosol formation from real plant emissions, interaction of atmospheric organic components with water, thermodynamics and mixtures in atmospheric models. Finally, the major challenges ahead in laboratory, field and modeling studies of SOA are discussed and recommendations for future research directions are proposed.

10. Modeling of secondary organic aerosol yields from laboratory chamber data (Chan, et al., 2009)

Laboratory chamber data serve as the basis for constraining models of secondary organic aerosol (SOA) formation. Current models fall into three categories: empirical two-product (Odum), product-specific, and volatility basis set. The product-specific and volatility basis set models are applied here to represent laboratory data on the ozonolysis of α-pinene under dry, dark, and low-NO_x conditions in the presence of ammonium sulfate seed aerosol. Using five major identified products, the model is fit to the chamber data. From the optimal fitting, SOA oxygen-to carbon (O/C) and hydrogen-to-carbon (H/C) ratios are modeled. The discrepancy between measured H/C ratios and those based on the oxidation products used in the model fitting suggests the potential importance of particle-phase reactions. Data fitting is also carried out using the volatility basis set, wherein oxidation products are parsed into volatility bins. The product-specific model is most likely hindered by lack of explicit inclusion of particle-phase accretion compounds. While prospects for identification of the majority of SOA products for major volatile organic compounds (VOCs) classes remain promising, for the near future empirical product or volatility basis set models remain the approaches of choice.

11. Unexpected Epoxide Formation in the Gas-Phase Photooxidation of Isoprene (Paulot, et al., 2009)

Emissions of nonmethane hydrocarbon compounds to the atmosphere from the biosphere exceed those from anthropogenic activity. Isoprene, a five-carbon diene, contributes more than 40% of these emissions. Once emitted to the atmosphere, isoprene is rapidly oxidized by the hydroxyl radical OH. We report here that under pristine conditions isoprene is oxidized primarily to hydroxyhydroperoxides. Further oxidation of these hydroxyhydroperoxides by OH leads efficiently to the formation of dihydroxyepoxides and OH reformation. Global simulations show an enormous flux-nearly 100 teragrams of carbon per year-of these epoxides to the atmosphere. The discovery of these highly soluble epoxides provides a missing link tying the gas-phase degradation of isoprene to the observed formation of organic aerosols.

12. Chemical Composition of Gas- and Aerosol-Phase Products from the Photooxidation of Naphthalene (Kautzman, et al., 2010)

The current work focuses on the detailed evolution of the chemical composition of both the gas- and aerosolphase constituents produced from the OH-initiated photooxidation of naphthalene under low- and high-NO_x conditions. Under high-NO_x conditions ring-opening products are the primary gas-phase products, suggesting that the mechanism involves dissociation of alkoxy radicals (RO) formed through an RO_2 + NO pathway, or a bicyclic peroxy mechanism. In contrast to the high-NO_x chemistry, ring-retaining compounds appear to dominate the low-NO_x gas-phase products owing to the RO_2 + HO_2 pathway. We are able to chemically characterize 53-68% of the secondary organic aerosol (SOA) mass. Atomic oxygen-to-carbon (O/C), hydrogento-carbon (H/C), and nitrogen-to-carbon (N/C) ratios measured in bulk samples by high-resolution electrospray ionization time-of-flight mass spectrometry (HR-ESI-TOFMS) are the same as the ratios observed with online high-resolution time-of-flight aerosol mass spectrometry (HR-ToF-AMS), suggesting that the chemical compositions and oxidation levels found in the chemically-characterized fraction of the particle phase are representative of the bulk aerosol. Oligomers, organosulfates (R-OSO_3), and other high-molecular-weight (MW) products are not observed in either the low- or high-NO_x SOA; however, in the presence of neutral ammonium sulfate seed aerosol, an organic sulfonic acid (R-SO_3), characterized as hydroxybenzene sulfonic acid, is observed in naphthalene SOA produced under both high- and low-NO_x conditions. Acidic compounds and organic peroxides are found to account for a large fraction of the chemically characterized high- and low-NO_x SOA. We propose that the major gas- and aerosol-phase products observed are generated through the formation and further reaction of 2-formylcinnamaldehyde or a bicyclic peroxy intermediate. The chemical similarity between the laboratory SOA and ambient aerosol collected from Birmingham, Alabama (AL) and Pasadena, California (CA) confirm the importance of PAH oxidation in the formation of aerosol within the urban atmosphere.

13. Reactive intermediates revealed in secondary organic aerosol formation from isoprene (Surratt, et al., 2010)

Isoprene is a significant source of atmospheric organic aerosol; however, the oxidation pathways that lead to secondary organic aerosol (SOA) have remained elusive. Here, we identify the role of two key reactive intermediates, epoxydiols of isoprene (IEPOX = β-IEPOX + δ-IEPOX) and methacryloylperoxynitrate (MPAN), which are formed during isoprene oxidation under low- and high-NO_x conditions, respectively. Isoprene low-NO_x SOA is enhanced in the presence of acidified sulfate seed aerosol (mass yield 28.6%) over that in the presence of neutral aerosol (mass yield 1.3%). Increased uptake of IEPOX by acid-catalyzed particle-phase reactions is shown to explain this enhancement. Under high-NO_x conditions, isoprene SOA formation occurs through oxidation of its secondgeneration product, MPAN. The similarity of the composition of SOA formed from the photooxidation of MPAN to that formed from isoprene and methacrolein demonstrates the role of MPAN in the formation of isoprene high-NO_x SOA. Reactions of IEPOX and MPAN in the presence of anthropogenic pollutants (i.e., acidic aerosol produced from the oxidation of SO_2 and NO_2, respectively) could be a substantial source of “missing urban SOA” not included in current atmospheric models.

14. Elemental analysis of chamber organic aerosol using an aerodyne high-resolution aerosol mass spectrometer (Chhabra, et al., 2009)

The elemental composition of laboratory chamber secondary organic aerosol (SOA) from glyoxal uptake, α-pinene ozonolysis, isoprene photooxidation, single-ring aromatic photooxidation, and naphthalene photooxidation is evaluated using Aerodyne high-resolution time-of-flight mass spectrometer data. SOA O/C ratios ranged from 1.13 for glyoxal to 0.30-0.43 for α-pinene ozonolysis. The elemental composition of α-pinene and naphthalene SOA was also confirmed by offline mass spectrometry. The fraction of organic signal at *m/z* 44 is generally a good measure of SOA oxygenation for all systems except for glyoxal uptake, in which *m/z* 44 substantially underpredicts O/C. Although chamber SOA has generally been considered less oxygenated than ambient SOA, single-ring aromatic- and naphthalene-derived SOA can reach O/C ratios upward of 0.7, well within the range of OOA, though still not as high as some ambient measurements. The spectra of aromatic- and isoprene-high-NO_x SOA resemble that of OOA, but the spectrum of glyoxal uptake does not resemble that of any PMF component.

15. A global perspective on aerosol from low-volatility organic compounds (Pye, and

Seinfeld, 2010)

Organic aerosol from primary semivolatile and intermediate volatility compounds is estimated using a global chemical transport model. Semivolatile organic compound (SVOC, saturation concentrations between about 0.1 and 10^4 μg/m^3) oxidation is predicted to be a much larger global source of net aerosol production than oxidation of traditional parent hydrocarbons (terpenes, isoprene, and aromatics). Using a prescribed rate constant and reduction in volatility, the yield of aerosol (defined as the net mass of aerosol formed divided by the total mass of the parent hydrocarbon emitted) from SVOCs is predicted to be about 75% on a global, annually averaged basis. Intermediate volatility compound (IVOC, saturation concentrations between about 10^4 and 10^6 μg/m^3) emissions and oxidation are highly uncertain since they are not typically measured. The use of a naphthalene-like surrogate with different high-NO_x and low-NO_x parameterizations produces an aerosol yield of about 30% or roughly 5 Tg/yr of aerosol from IVOC oxidation on a global basis. Estimates of the total global organic aerosol source presented here range between 60 and 100 Tg/yr. This range reflects uncertainty in the parameters for SVOC volatility, SVOC oxidation, SVOC emissions, and IVOC emissions, as well as wet deposition. The highest estimates result if SVOC emissions are significantly underestimated (by more than a factor of 2) or if wet deposition of the gas-phase semivolatile species is less effective than previous estimates. Compared to a traditional non-volatile primary organic aerosol model without IVOCs, the global estimate of organic aerosol production is at most roughly 10% higher than previous studies. Additional information is needed to constrain the emissions and treatment of SVOCs and IVOCs, which have traditionally not been included in models. Comparisons to winter organic carbon observations over the US indicate that SVOC emissions are significantly underestimated by the traditional POA inventories. The degree to which IVOC emissions or other parameters are uncertain is unknown.

16. Characterization of Vapor Wall Loss in Laboratory Chambers (Loza, et al., 2010)

Laboratory chambers used to study atmospheric chemistry and aerosol formation are subject to wall loss of vapors and particles that must be accounted for in calculating aerosol yields. While particle wall loss in chambers is relatively well-understood and routinely accounted for, that of vapor is less so. Here we address experimental measurement and modeling of vapor losses in environmental chambers. We identify two compounds that exhibit wall loss: 2,3-epoxy-1,4-butanediol (BEPOX), an analog of an important isoprene oxidation product; and glyoxal, a common volatile organic compound oxidation product. Dilution experiments show that BEPOX wall loss is irreversible and glyoxal wall loss is reversible. BEPOX exhibits minimal uptake onto clean chamber walls under dry conditions, with increasing rates of uptake over the life of an in-use chamber. By performing periodic BEPOX wall loss experiments, it is possible to assess quantitatively the aging of chamber walls.

17. Role of aldehyde chemistry and NO_x concentrations in secondary organic aerosol formation (Chan, et al., 2010)

Aldehydes are an important class of products from atmospheric oxidation of hydrocarbons. Isoprene (2-methyl-1,3-butadiene), the most abundantly emitted atmospheric non-methane hydrocarbon, produces a significant amount of secondary organic aerosol (SOA) via methacrolein (a C_4-unsaturated aldehyde) under urban high-NO_x conditions. Previously, we have identified peroxy methacryloyl nitrate (MPAN) as the important intermediate to isoprene and methacrolein SOA in this NO_x regime. Here we show that as a result of this chemistry, NO_2 enhances SOA formation from methacrolein and two other α,β-unsaturated aldehydes, specifically acrolein and crotonaldehyde, a NO_x effect on SOA formation previously unrecognized. Oligoesters of dihydroxycarboxylic acids and hydroxynitrooxycarboxylic acids are observed to increase with increasing NO_2/NO ratio, and previous characterizations are confirmed by both online and offline high-resolution mass spectrometry techniques. Molecular structure also determines the amount of SOA formation, as the SOA mass yields are the highest for aldehydes that are α,β-unsaturated and contain an additional methyl group on the α-carbon. Aerosol formation from 2-methyl-3-buten-2-ol (MBO232) is insignificant, even under high-NO_2 conditions, as PAN (peroxy acyl nitrate, RC(O)OONO2) formation is structurally unfavorable. At atmospherically relevant NO_2/NO ratios (3-8), the SOA yields from isoprene high-NO_x photooxidation are 3 times greater than previously measured at lower NO_2/NO ratios. At sufficiently high NO_2 concentrations, in systems of α,β-unsaturated aldehydes, SOA formation from subsequent oxidation of products from acyl peroxyl radicals+NO_2 can exceed that from RO_2+HO_2 reactions under the same inorganic seed conditions, making RO_2+NO_2 an important channel for SOA formation.

18. Computation of liquid-liquid equilibria and phase stabilities: implications for RH-dependent as/particle partitioning of organic-inorganic aerosols (Zuend, A., et al., 2010)

Semivolatile organic and inorganic aerosol species partition between the gas and aerosol particle phases to maintain thermodynamic equilibrium. Liquid-liquid phase separation into an organic-rich and an aqueous electrolyte phase can occur in the aerosol as a result of the saltingout effect. Such liquid-liquid equilibria (LLE) affect the gas/particle partitioning of the different semivolatile compounds and might significantly alter both particle mass and composition as compared to a one-phase particle. We present a new liquid-liquid equilibrium and gas/particle partitioning model, using as a basis the group-contribution model AIOMFAC (Zuend et al., 2008). This model allows the reliable computation of the liquid-liquid coexistence curve (binodal), corresponding tie-lines, the limit of stability/metastability (spinodal), and further thermodynamic properties of multicomponent systems. Calculations for ternary and multicomponent alcohol/polyol-water-salt mixtures suggest that LLE are a prevalent feature of organic-inorganic aerosol systems. A six-component polyol-water-ammonium sulphate system is used to simulate effects of relative humidity (RH) and the presence of liquid-liquid phase separation on the gas/particle partitioning. RH, salt concentration, and hydrophilicity (water-solubility) are identified as key features in defining the region of a miscibility gap and govern the extent to which compound partitioning is affected by changes in RH. The model predicts that liquid-liquid phase separation can lead to either an increase or decrease in total particulate mass, depending on the overall composition of a system and the particle water content, which is related to the hydrophilicity of the different organic and inorganic compounds. Neglecting non-ideality and liquid-liquid phase separations by assuming an ideal mixture leads to an overestimation of the total particulate mass by up to 30% for the composition and RH range considered in the six-component system simulation. For simplified partitioning parametrizations, we suggest a modified definition of the effective saturation concentration, C^*_j, by including water and other inorganics in the absorbing phase. Such a C^*_j definition reduces the RH dependency of the gas/particle partitioning of semivolatile organics in organic-inorganic aerosols by an order of magnitude as compared to the currently accepted definition, which considers the organic species only.

19. Global modeling of organic aerosol: the importance of reactive nitrogen (Pye, et al., 2010)

Reactive nitrogen compounds, specifically NO_x and NO_3, likely influence global organic aerosol levels. To assess these interactions, GEOS-Chem, a chemical transport model, is updated to include improved biogenic emissions (following MEGAN v2.1/2.04), a new organic aerosol tracer lumping scheme, aerosol from nitrate radical (NO_3) oxidation of isoprene, and NO_x-dependent terpene aerosol yields. As a result of significant nighttime terpene emissions, fast reaction of monoterpenes with the nitrate radical, and relatively high aerosol yields from NO_3 oxidation, biogenic hydrocarbon-NO_3 reactions are expected to be a major contributor to surface level aerosol concentrations in anthropogenically influenced areas such as the United States. By including aerosol from nitrate radical oxidation in GEOS-Chem, terpene aerosol approximately doubles and isoprene aerosol is enhanced by 30 to 40% in the Southeast United States. In terms of the global budget of organic aerosol, however, aerosol from nitrate radical oxidation is somewhat minor (slightly more than 3 Tg/yr) due to the relatively high volatility of organic-NO_3 oxidation products. Globally, 69 to 88 Tg/yr of organic aerosol is predicted to be produced annually, of which 14-15 Tg/yr is from oxidation of monoterpenes and sesquiterpenes and 8-9 Tg/yr from isoprene.

20. Elemental composition and oxidation of chamber organic aerosol (Chhabra , et al., 2011)

Recently, graphical representations of aerosol mass spectrometer (AMS) spectra and elemental composition have been developed to explain the oxidative and aging processes of secondary organic aerosol (SOA). It has been shown previously that oxygenated organic aerosol (OOA) components from ambient and laboratory data fall within a triangular region in the f_{44} vs. f_{43} space, where f_{44} and f_{43} are the ratios of the organic signal at *m/z* 44 and 43 to the total organic signal in AMS spectra, respectively; we refer to this graphical representation as the “triangle plot.” Alternatively, the Van Krevelen diagram has been used to describe the evolution of functional groups in SOA. In this study we investigate the variability of SOA formed in chamber experiments from twelve different precursors in both “triangle plot” and Van Krevelen domains. Spectral and elemental data from the high-resolution Aerodyne aerosol mass spectrometer are compared to offline species identification analysis and FTIR filter analysis to better understand the changes in functional and elemental composition inherent in SOA formation and aging. We find that SOA formed under high- and low-NO_x conditions occupy similar areas in the “triangle plot” and Van Krevelen diagram and that SOA generated from already oxidized precursors

allows for the exploration of areas higher on the “triangle plot” not easily accessible with non-oxidized precursors. As SOA ages, it migrates toward the top of the triangle along a path largely dependent on the precursor identity, which suggests increasing organic acid content and decreasing mass spectral variability. The most oxidized SOA come from the photooxidation of methoxyphenol precursors which yielded SOA O/C ratios near unity. α-pinene ozonolysis
and naphthalene photooxidation SOA systems have had the highest degree of mass closure in previous chemical char acterization studies and also show the best agreement between
AMS elemental composition measurements and elemental composition of identified species within the uncertainty of the AMS elemental analysis. In general, compared to their respective unsaturated SOA precursors, the elemental composition of chamber SOA follows a slope shallower than −1 on the Van Krevelen diagram, which is indicative of oxidation of the precursor without substantial losss of hydrogen, likely due to the unsaturated nature of the precursors. From the spectra of SOA studied here, we are able to reproduce the triangular region originally constructed with ambient OOA compents with chamber aerosol showing that SOA becomes
more chemically similar as it ages. Ambient data in the middle of the triangle represent the ensemble average of many different SOA precursors, ages, and oxidative processes.

21. Analysis of photochemical and dark glyoxal uptake: Implications for SOA formation (M. M. Galloway, et al., 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 lyoxaldriven 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.

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