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14. ABSTRACT

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RPPR Final Report
as of 14-Dec-2021

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Major Goals: The overall goal of this project was to elucidate the role of the surface in airborne particle systems during uptake of organic gases as well as to understand the 3-D composition in these systems in terms of differences between surface and bulk composition. Specific goals were:

- To develop and apply mass spectrometry techniques for differentiating molecular surface composition from that of the bulk for model laboratory systems, and apply these to more complex systems to understand surface and bulk composition during oxidation reactions.
- To understand gas-surface interactions in complex, multiphase systems in order to explain mechanisms of particle growth that lead to nonuniformities in composition between the surface and the bulk.

Accomplishments: The following has been accomplished:

I. Mass Spectrometry Techniques.

- EASI is an ambient ionization method in which a solvent that passes through a nebulizer capillary is surrounded by a high velocity sheath gas flow. Several model organic particles were generated in core-shell configurations for EASI analysis. In the last report, we described surface and bulk analysis using this technique for glutaric acid particles coated with malonic acid. We showed that EASI could probe the top ~ 4 nm of the particles in the surface-selective mode and accurately interrogated the bulk in that mode. Similar results were obtained for succinic acid core particles coated with malonic acid and pimelic acid core particles coated with malonic acid with coating/core ratios of 25-40 for coatings of 0-30 nm.

A particle system that was difficult to coat was that of succinic acid core particles with oxalic acid as a coating compound. This C2 dicarboxylic acid was too volatile to appreciably condense onto succinic acid particles. Oxalic acid coatings were not detected by SMPS, from which a coating thickness was estimated to be <2 nm based on the SMPS detection limit. This coating measurement was consistent with EASI measurements in orthogonal mode that resulted in coating/core ratios of <0.02, i.e. detection of the predominantly succinic acid core, thus reinforcing the surface-sensitivity of the EASI-MS orthogonal analysis method. We estimate that as the coating thickness increased to approximately 4 nm, the orthogonal mode no longer detected the core of the particles

Further applications of EASI for other particle systems are underway in our laboratory, including heterogeneous ozonolysis of particles composed of solid or liquid unsaturated compounds. Detection of ozonolysis products at the surface and in the bulk with the same analytical technique would lend significant insight into heterogeneous chemistry under conditions of low and high viscosity.

- Matrix Assisted Laser Desorption Ionization (MALDI) mass spectrometry is currently being investigated as a potential surface sensitive method. A thin coating of a MALDI matrix compound is proposed to allow energy absorption from the MALDI laser to the particles followed by transfer to the immediately adjacent region in the particle subsurface and provide a surface sensitive measurement.

Core-shell particles are generated from organic compounds as described above, with the addition of a second coating using a common MALDI matrix compound, 2,5-dihydroxybenzoic acid (DHB). These doubly coated particles have been generated for a few different systems, such as tartaric acid (TA, a diol dicarboxylic acid) coated with adipic acid (C6 diacid) or TA coated with pinonic acid (a product of α-pinene ozonolysis), followed by a second coating with DHB. MALDI measurements of DHB directly coated on core particles (i.e., single coating) indicate that these small molecules are readily detected as sodium and potassium adducts, despite MALDI's typical use as a large molecule method. A core-shell particle system with a second coating of DHB will allow us to evaluate the MALDI probe distance into the particles. An undergraduate student has been trained using the coating system and carrying out SMPS and MALDI measurements.

- The compound N-methyl-2-pyrrolidone (NMP) was found to be released from PALL HEPA filters and, unexpectedly, provided a sensitive method for detection and measurement of amines and especially ammonia which is notoriously difficult to detect at ppb concentrations. NMP efficiently forms adducts with ammonia or alkylamines, [M+NMP+H]+ at atmospheric pressure. The proton affinity of the amine of interest controlled the extent of NMP adduct formation and hence a major advantage of this approach is increased sensitivity to ammonia and amines.

II. Probing Gas-Surface Interactions.

- Evidence for a new mechanism for particle growth was developed during experiments on SOA formation in a large volume, slow flow reactor. Highly viscous, semi-solid SOA was generated in the flow reactor from α-pinene ozonolysis and gas-phase 2EHN, HPN, or HHN was introduced to the SOA throughout its initial particle formation and growth. In a second set of experiments, the SOA was generated in the absence of any organic nitrates, and these fully-grown particles were impacted on an ATR crystal and exposed to the same organic nitrates for uptake measurements. A comparison of the two sets of experiments showed that the fraction of each organic nitrate gas taken up into the growing particles was larger than that taken up in the fully-grown particles at equilibrium.

A partition coefficient that is larger than expected based on equilibrium suggests an enhanced uptake in which gases become trapped during particle formation and growth. This evidence for a "burying" mechanism was published in Environ. Sci. Processes Impacts and has important implications for how particle growth and partitioning are represented in air quality models, especially for highly viscous particles. Ambient particles are highly viscous under many environmental conditions, thus an assumption of equilibrium partitioning, which only holds for low viscosity liquid particles, falls short of accurately describing how gases interact with semi-solid particles. Additionally, the trapping of gases in particles is expected to lengthen the chemical or photochemical lifetimes of the gas. Potential release of these trapped components downwind may affect their regional and global distributions as particles undergo long-range transport.

- The mechanism of gases becoming trapped inside particles as they form and grow was further examined under a variety of SOA precursor concentrations to understand the role of particle mass concentration and composition. A range of <40 µg m-3 to ~800 µg m-3 mass loading was studied as this was expected to cover a wide range of molecular burying candidates. The measured partition coefficients of all three organic nitrates were again found to be larger than their equilibrium partitioning values over all conditions. The results showed no dependence of the enhanced partitioning on precursor α-pinene concentration or particle mass loading. The distribution of gas phase ozonolysis products was examined using a kinetic model, the Master Chemical Mechanism, which indicated that the type and polarity of potential burying candidates do not change significantly over a wide range of conditions, while the total number concentration changes significantly. The results suggest that the number concentration of burying species is more important than their molecular weight or oxygen content. Effective uptake coefficients of the organic nitrates, γON, increased with increasing α-pinene concentration and particle mass concentration. One exception was the alkyl nitrate, 2EHN, which was not detected in the particles formed at the lowest α-pinene concentration. This less polar organic nitrate likely has less affinity for the surface of the particles formed at the lower concentrations. Particle composition measurements showed that the particles formed under the lowest α-pinene concentrations are smaller and more oxygenated than those formed at the other conditions.

Training Opportunities: One undergraduate student (Joey Cheng), one graduate student (Allison Vander Wall), one postdoctoral researcher (Mica Smith), and three researchers (Lisa Wingen, Veronique Pérraud, and Michael Ezell) have contributed to this research as well as a former post-doctoral student (Yue Zhao) who is now a professor of chemistry at Shanghai Jiao Tong University. Five of the seven people carrying out this research are from underrepresented groups in STEM.

RPPR Final Report
as of 14-Dec-2021

Results Dissemination: A total of 12 papers have been published in peer-reviewed journals. The results of this research have been incorporated into presentations given at universities and national meetings.
1. “Introductory Lecture: Atmospheric Chemistry in the Anthropocene”, B. J. Finlayson-Pitts, Faraday Discussions, ¬200 11 (2017).

2. "New Mechanism of Extractive Electrospray Ionization Mass Spectrometry for Heterogeneous Solid Particles", S. Kumbhani, T. Longin, L. M. Wingen, C. Kidd, V. Perraud, and B. J. Finlayson-Pitts, Anal. Chem. 90 2055 (2018). doi: 10.1021/acs.analchem.7b04164

3. “A Cautionary Note on the Effects of Laboratory Air Contaminants on Ambient Ionization Mass Spectrometry Measurements,” S. Kumbhani, L. M. Wingen, V. Perraud and B. J. Finlayson-Pitts, Rapid Communications in Mass Spectrometry, 31 1659 (2017) doi: 10.1002/rcm.7951

4. “Knudsen Cell Studies of the Uptake of Gaseous Ammonia and Amines onto C3 – C7 Solid Dicarboxylic Acids,” M. Fairhurst, M. J. Ezell and B. J. Finlayson-Pitts, Phys. Chem. Chem. Phys., 19 26296 (2017) doi: 10.1039 /c7cp05252a.

5. " Probing Surfaces of Organic Particles by EASI-MS", L. M. Wingen and B. J. Finlayson-Pitts, Chem. Sci., 2019, 10, 884-897. DOI: 10.1039/c8sc03851a.

6. “Understanding Interactions of Organic Nitrates with the Surface and Bulk of Organic Films: Implications for Particle Growth in the Atmosphere", A. C. Vander Wall, P. Lakey, E. Rossich-Molina, V. Perraud, L. M. Wingen, J. Xu, D. Soulsby, R. B. Gerber, M. Shiraiwa, and B. J. Finlayson-Pitts, Environ. Sci.-Processes and Impacts, 2018, 20, 1593-1610. DOI: 10.1039/c8em00348c.

7. "Role of Gas Phase Halogen Bonding in Ambient Chemical Ionization Mass Spectrometry Utilizing Iodine", J. A. Ganske, L. M. Wingen, V. Perraud and B. J. Finlayson-Pitts, ACS Earth & Space Chem., 2019, 3, 1315?1328.DOI: 10.1021/acsearthspacechem.9b00030.

8. "Multiphase Chemistry in the Troposphere: It All Starts... and Ends... with Gases" B. J. Finlayson-Pitts, Int. J. Chem. Kinet. 2019, 1-17. DOI: 10.1002/kin.21305.

9. “Novel Ionization Reagent for the Measurement of Gas Phase Ammonia and Amines using a Stand-alone Atmospheric Pressure Gas Chromatography (APGC) Source,” V. Perraud, X. Li, J. N. Smith, and B. J. Finlayson-Pitts, Rapid Communications in Mass Spectrometry, 2020, 34:e8561, DOI: 10.1002/rcm.8561.

10. “Evidence for a Kinetically Controlled Burying Mechanism for Growth of High Viscosity Secondary Organic Aerosol,” A. C. Vander Wall, V. Perraud, L. M. Wingen, and B. J. Finlayson-Pitts, Environmental Science: Processes and Impacts, 2020, 22, 66-83, DOI: 10.1039/C9EM00379G.

11. “Enhanced Gas Uptake during ? Pinene Ozonolysis Points to a Burying Mechanism” A. C. Vander Wall, L. M. Wingen, V. Perraud, Y. Zhao, and B. J. Finlayson-Pitts, ACS Earth Space Chem. 4 1435 (2020) doi 10.1021 /acsearthspacechem.0c00163

12. “Open Questions on the Chemical Composition of Airborne Particles”, B. J. Finlayson-Pitts, L. M. Wingen, V. Perraud and M. J. Ezell, Commun. Chem. 3, Article number: 108 (2020) doi 10.1038/s42004-020-00347-4

Honors and Awards: Francis P. Garvan–John M. Olin Medal of the American Chemical Society, 2017; 2017-2018 Distinguished Faculty Award for Research, University of California Irvine; 2018 Polanyi Medal, Royal Society of Chemistry; 2019 Environment Prize, Royal Society of Chemistry; 2021 Woman of the Year, 74th Assembly District, California

Protocol Activity Status:

Technology Transfer: Nothing to Report

PARTICIPANTS:

Participant Type: Undergraduate Student
Participant: Joey Cheng
Person Months Worked: 2.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Graduate Student (research assistant)
Participant: Allison Vanderwall
Person Months Worked: 3.00 **Funding Support:**
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National Academy Member: N

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Mica Smith
Person Months Worked: 2.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Staff Scientist (doctoral level)
Participant: Lisa Wingen
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Staff Scientist (doctoral level)
Participant: Veronique Perraud
Person Months Worked: 12.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Other Professional
Participant: Michael Ezell
Person Months Worked: 3.00 **Funding Support:**
Project Contribution:
National Academy Member: N

Participant Type: Faculty
Participant: Yue Zhao
Person Months Worked: 1.00 **Funding Support:**
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Participant Type: PD/PI
Participant: Barbara Finlayson-Pitts

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Date Submitted: 7/5/18 12:00AM Date Published: 6/13/17 11:00AM
Publication Location: Cambridge, England
Article Title: Introductory Lecture: Atmospheric Chemistry in the Anthropocene
Authors: B. J. Finlayson-Pitts
Keywords: emissions, reactions, biogeochemical cycling, heterogeneous reactions, pesticides
Abstract: The term “Anthropocene” was coined by Professor Paul Crutzen in 2000 to describe an unprecedented era in which anthropogenic activities are impacting planet Earth on a global scale. Greatly increased emissions into the atmosphere, reflecting the advent of the Industrial Revolution, have caused significant changes in both the lower and upper atmosphere. Atmospheric reactions of the anthropogenic emissions and of those with biogenic compounds have significant impacts on human health, visibility, climate and weather. Two activities that have had particularly large impacts on the troposphere are fossil fuel combustion and agriculture, both associated with a burgeoning population. Emissions are also changing due to alterations in land use. This paper describes some of the tropospheric chemistry associated with the Anthropocene, with emphasis on areas having large uncertainties. These include heterogeneous chemistry such as those of oxides of nitrogen and the neonicotinoid pesticides, rea
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Article Title: A Cautionary Note on the Effects of Laboratory Air Contaminants on Ambient Ionization Mass Spectrometry Measurements
Authors: S. Kumbhani, L. M. Wingen, V. Perraud and B. J. Finlayson-Pitts
Keywords: ambient ionization mass spectrometry, extractive electrospray mass spectrometrym DART-MS
Abstract: RATIONALE: Ambient ionization mass spectrometry methods are convenient, sensitive and require little sample preparation. However, they are susceptible to species present in air surrounding the mass spectrometer. This study identifies some challenges associated with the potential impacts of indoor air contaminants on ionization and analysis involving open air methods. METHODS: Unexpected effects of volatile organic compounds from floor maintenance activities on ambient ionization mass spectrometry were studied using three different ambient ionization techniques. Extractive electrospray ionization (EESI), direct analysis in real time (DART) and ionization by piezoelectric direct discharge (PDD) plasma were demonstrated in this study to be affected by indoor air contaminants. Identification of contaminant vapors was verified by comparison to standards using EESI-MS/MS product ion scans. RESULTS: Emissions of diethylene glycol monoethyl ether and ethylene glycol monobutyl ether are id
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Article Title: Knudsen Cell Studies of the Uptake of Gaseous Ammonia and Amines onto C3 – C7 Solid Dicarboxylic Acids
Authors: M. Fairhurst, M. J. Ezell and B. J. Finlayson-Pitts
Keywords: amines, dicarboxylacids, ionic liquids, reactivity, uptake coefficients
Abstract: While atmospheric particles affect health, visibility and climate, the details governing their formation and growth are poorly understood on a molecular level. A simple model system for understanding such interactions is the reaction of bases with acids, both of which are common constituents of atmospheric particles. In the present study, uptake coefficients for the reactions of gas phase ammonia, methylamine, ethylamine, dimethylamine and trimethylamine with a series of solid dicarboxylic acids (diacids) were measured at 296 ± 1 K using a Knudsen cell interfaced to a quadrupole mass spectrometer. The uptake coefficients (?) for a given amine follow an odd-even trend in carbon number of the diacid, and are larger for the odd carbon diacids. Values range from g = 0.4 for ethylamine on malonic acid (C3) to less than ~10-6 for ammonia and all amines on adipic (C6) and pimelic (C7) acids. Basicity or structure of the amines/ammonia alone do not explain the effect of the base on uptak
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Article Title: New Mechanism of Extractive Electrospray Ionization Mass Spectrometry for Heterogeneous Solid Particles
Authors: S. Kumbhani, T. Longin, L. M. Wingen, C. Kidd, V. Perraud, B. J. Finlayson-Pitts
Keywords: EESI solvent, kinetic factors
Abstract: Real-time in situ mass spectrometry analysis of airborne particles is important in several applications, including exposure studies in ambient air, industrial settings, and assessing impacts on visibility and climate. However, obtaining molecular and 3D structural information is more challenging, especially for heterogeneous solid or semisolid particles. We report a study of extractive electrospray ionization mass spectrometry (EESI-MS) for the analysis of solid particles with an organic coating. The goal is to elucidate how much of the overall particle content is sampled, and determine the sensitivity of this technique to the surface layers. It is shown that, for NaNO3 particles coated with glutaric acid (GA), very little of the solid NaNO3 core is sampled compared to the GA coating, whereas for GA particles coated with malonic acid (MA), significant signals from both the MA coating and the GA core are observed. However, conventional ESI-MS of the same samples collected on a Teflon...
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Article Title: Probing surfaces of atmospherically relevant organic particles by easy ambient sonic-spray ionization mass spectrometry (EASI-MS)
Authors: L. M. Wingen, B. J. Finlayson-Pitts
Keywords: EASI-MS, organic particles
Abstract: Both ambient and laboratory-generated particles can have a surface composition different from the bulk, but there are currently few analytical techniques available to probe these differences. Easy ambient sonic-spray ionization mass spectrometry (EASI-MS) was applied to solid, laboratory-generated particles with core-shell morphologies formed from a variety of dicarboxylic acids. The soft ionization facilitated parent peak detection for the two compounds, from which the depth probed could be determined from the relative signal intensities. Two different configurations of a custom-made nebulizer are reported that yield different probe depths. In the “orthogonal mode,” with the nebulizer ~10 centimeters away from the particle stream and at a 90° angle to the MS inlet, evaporation of the nebulizer droplets forms ions before interaction with the particles. The probe depth for orthogonal mode EASI-MS is shown to be 2 – 4 nm in these particle systems. In the “droplet mode”, the nebulizer and
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Article Title: Understanding interactions of organic nitrates with the surface and bulk of organic films: implications for particle growth in the atmosphere
Authors: A. C. Vander Wall, P. S. J. Lakey, E. Rossich Molina, V. Perraud, L. M. Wingen, J. Xu, D. Soulsby, R. B
Keywords: organic nitrates, gas uptake, diffusion,partition coefficients
Abstract: Understanding impacts of secondary organic aerosol (SOA) in air requires a molecular-level understanding of particle growth via interactions between gases and particle surfaces. The interactions of three gaseous organic nitrates with selected organic substrates was measured at 296 K using attenuated total reflection Fourier transform infrared spectroscopy. The organic substrates included a long chain alkane (triacontane, TC), a keto-acid (pinonic acid, PA), an amorphous ester oligomer (poly(ethylene adipate), PEA), and laboratory-generated SOA from ?-pinene ozonolysis. There was no uptake of the organic nitrates on the non-polar TC substrate, but significant uptake occurred on PEA, PA, and ?-pinene SOA. Net uptake coefficients (?) at the shortest reaction times accessible in these experiments ranged from 3×10-4 to 9×10-6 and partition coefficients (K) from 1×107 to 9×104. Trends in ? did not quantitatively follow trends in K, suggesting that the intermolecular forces involved in gas
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Article Title: Role of Gas-Phase Halogen Bonding in Ambient Chemical Ionization Mass Spectrometry Utilizing Iodine
Authors: Jane A. Ganske, Lisa M. Wingen, Véronique Perraud, Barbara J. Finlayson-Pitts
Keywords: halogen bonding, plasma discharge ionization, ambient ionization, organic acids, nitric acid, halogens
Abstract: We report ambient ionization mass spectra utilizing tincture of iodine and a piezoelectric discharge gun (PDG) to generate the ionizing reagents. Analytes include Cl2, Br2, HNO3, the C1-C9 saturated monocarboxylic acids, benzoic acid, 2,2-dimethylpropanoic acid, 9-decenoic acid, and trichloroacetic acid. Nitric acid and the organic acids show unexpected peaks corresponding to [2M-2H+I]-. For HNO3, the new ion formed is interpreted as the [NO3-…IONO2] complex. For the organic acids, the [2M-2H+I]- peaks are interpreted as [RC(O)O-…IOC(O)R] complexes formed by reaction of RC(O)O- with acyl hypoiodites (RC(O)OI). It is proposed that the association of (1) Cl2 and Br2 with I-, (2) IONO2 with NO3- ions and (3) RC(O)OI with carboxylate ions occurs via non-covalent halogen bonding. The results suggest the possibility that halogen bonding may play a role in chemical transformations in the atmosphere, particularly in particles where concentrations of iodinated species may be significant.
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Article Title: Multiphase chemistry in the troposphere: It all starts … and ends … with gases
Authors: Barbara J. Finlayson-Pitts
Keywords: gas, condensed phase, uptake, interactions, pesticides
Abstract: When the phenomena of smog and acid deposition were first recognized, it was largely gas phase chemists and photochemists who leapt into the fray to untangle the sources and chemistry involved. Over time, the importance of multiphase chemistry was recognized, as illustrated in a dramatic manner with the discovery of the Antarctic ozone hole. Since then, it has become clear that multiphase chemistry is central to both the lower and upper atmosphere, and that this deeply intertwines interactions between the gas and condensed phases in the atmosphere. As a result, it can be argued that multiphase atmospheric chemistry begins.... and ends.... with gases. This paper is based on the 2018 Polanyi Medal award presentation, and traces research carried out in the author's laboratory on multiphase chemistry over a number of decades. These processes remain one of the areas of greatest uncertainty in understanding and predicting atmospheric composition, air quality and climate change.
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Article Title: Novel ionization reagent for the measurement of gas?phase ammonia and amines using a stand?alone atmospheric pressure gas chromatography (APGC) source
Authors: Véronique Perraud, Xiaoxiao Li, James N. Smith, Barbara J. Finlayson-Pitts
Keywords: N-methyl2-pyrrolidone, atmospheric pressure ionization, amines, ammonia
Abstract: Contaminants present in ambient air or in sampling lines can interfere with the target analysis through overlapping peaks or causing a high background. Gas phase N-methyl-2-pyrrolidone (NMP) emitted from a PALL HEPA filter located in the inlet stream was shown to serve as an effective ionizing agent for amines and ammonia. Ammonia and some alkylamines efficiently form a [NMP+amine+H]+ cluster with NMP upon chemical ionization at atmospheric pressure. The extent of cluster formation depends largely on on the proton affinity of the amine compared to that of NMP. Aromatic amines (aniline, pyridine) and diamines (putrescine) were shown not to form cluster ions with NMP. The use of NMP as an ionizing agent with stand-alone APGC provided high sensitivity for ammonia and the smaller amines. The main advantages, in addition to sensitivity, are direct sampling into the APGC source and avoiding uptake on sampling lines which can be a significant problem with ammonia and amines.
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Article Title: Evidence for a kinetically controlled burying mechanism for growth of high viscosity secondary organic aerosol
Authors: Allison C. Vander Wall, Véronique Perraud, Lisa M. Wingen, Barbara J. Finlayson-Pitts
Keywords: secondary organic aerosol growth, alpha-pinene,ozone, organic nitrates,burying mechanism
Abstract: The uptake of three organic nitrates into semi-solid SOA particles formed by ?-pinene ozonolysis either with or without an OH scavenger was investigated. Uptake of selected organic nitrates (2-ethylhexyl nitrate (2EHN); ?-hydroxypropyl nitrate (HPN); ?-hydroxyhexyl nitrate (HHN)) into impacted SOA particles was interrogated by attenuated total reflectance (ATR)-FTIR. In this case, equilibrium was reached and partition coefficients were measured. In separate experiments, SOA particles were exposed on-the-fly to gas phase organic nitrates.Finally, each organic nitrate was incorporated into the SOA as the particles formed and grew. The incorporation of the RONO2 was much larger in this case (during growth), exceeding equilibrium values determined by exposure after growth. This enhanced uptake of organic nitrates is hypothesized to be due to a new "burying" mechanism for SOA growth, which is not currently incorporated into models of laboratory experiments or field measurements.
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Article Title: Enhanced Gas Uptake during ?-Pinene Ozonolysis Points to a Burying Mechanism
Authors: Allison C. Vander Wall, Lisa M. Wingen, Véronique Perraud, Yue Zhao, Barbara J. Finlayson-Pitts
Keywords: secondary organic aerosol, organic nitrates, particle growth
Abstract: Understanding how gases interact with and are incorporated into atmospheric secondary organic aerosol particles is crucial for predicting particle effects on climate and human health. This work examined how three gaseous organic nitrates (ON) are taken up into viscous particles formed from the ozonolysis of ?-pinene (AP). Experiments were performed in a flow reactor at room temperature under dry conditions either with or without an OH scavenger present, with constant ozone and variable AP concentrations. Each ON was introduced independently into the flow reactor and was present during particle formation/growth. ON gas phase concentrations were determined by GC-MS and particle phase concentrations were measured by HR-ToF-AMS. Partition coefficients (KSOA) for each ON were independent of the initial AP concentration, except for 2-ethylhexyl nitrate which was undetectable in the particles at the lowest AP concentration. Measured KSOA values were larger than those previously determin
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Publication Location:

Article Title: Open questions on the chemical composition of airborne particles

Authors: Barbara J. Finlayson-Pitts, Lisa M. Wingen, Véronique Perraud, Michael J. Ezell

Keywords: particle formation and growth, secondary organic aerosol

Abstract: Airborne particles have significant impacts on health, visibility and climate. An overview of what is known about particle chemical composition is presented, along with open questions and challenges that are central to relating composition to their life cycles and impacts.

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Partners

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No other collaborators were involved.

I certify that the information in the report is complete and accurate:
Signature: Barbara Finlayson-Pitts
Signature Date: 12/11/21 3:01PM

Final Report

ARO # W911NF1710105

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Major Goals: The overall goal of this project was to elucidate the role of the surface in airborne particle systems during uptake of organic gases as well as to understand the 3-D composition in these systems in terms of differences between surface and bulk composition. Specific goals were:

- To develop and apply mass spectrometry techniques for differentiating molecular surface composition from that of the bulk for model laboratory systems, and apply these to more complex systems to understand surface and bulk composition during oxidation reactions.
- To understand gas-surface interactions in complex, multiphase systems in order to explain mechanisms of particle growth that lead to nonuniformities in composition between the surface and the bulk.

Accomplishments: The following has been accomplished:

I. Mass Spectrometry Techniques.

- EASI is an ambient ionization method in which a solvent that passes through a nebulizer capillary is surrounded by a high velocity sheath gas flow. Several model organic particles were generated in core-shell configurations for EASI analysis. In the last report, we described surface and bulk analysis using this technique for glutaric acid particles coated with malonic acid. We showed that EASI could probe the top ~ 4 nm of the particles in the surface-selective mode and accurately interrogated the bulk in that mode. Similar results were obtained for succinic acid core particles coated with malonic acid and pimelic acid core particles coated with malonic acid with coating/core ratios of 25-40 for coatings of 0-30 nm.

A particle system that was difficult to coat was that of succinic acid core particles with oxalic acid as a coating compound. This C2 dicarboxylic acid was too volatile to appreciably condense onto succinic acid particles. Oxalic acid coatings were not detected by SMPS, from which a coating thickness was estimated to be <2 nm based on the SMPS detection limit. This coating measurement was consistent with EASI measurements in orthogonal mode that resulted in coating/core ratios of <0.02, i.e. detection of the predominantly succinic acid core, thus reinforcing the surface-sensitivity of the EASI-MS orthogonal analysis method. We estimate that as the coating thickness increased to approximately 4 nm, the orthogonal mode no longer detected the core of the particles

Further applications of EASI for other particle systems are underway in our laboratory, including heterogeneous ozonolysis of particles composed of solid or liquid unsaturated compounds. Detection of ozonolysis products at the surface and in the bulk with the same analytical technique would lend significant insight into heterogeneous chemistry under conditions of low and high viscosity.

- Matrix Assisted Laser Desorption Ionization (MALDI) mass spectrometry is currently being investigated as a potential surface sensitive method. A thin coating of a MALDI matrix compound is proposed to allow energy absorption from the MALDI laser to the particles followed by transfer to the immediately adjacent region in the particle subsurface and provide a surface sensitive measurement.

Core-shell particles are generated from organic compounds as described above, with the addition of a second coating using a common MALDI matrix compound, 2,5-dihydroxybenzoic acid (DHB). These doubly coated particles have been generated for a few different systems, such as tartaric acid (TA, a diol dicarboxylic acid) coated with adipic acid (C6 diacid) or TA coated with pinonic acid (a product of α-pinene ozonolysis), followed by a second coating with DHB. MALDI measurements of DHB directly coated on core particles (i.e., single coating) indicate that these small molecules are readily detected as sodium and potassium adducts, despite MALDI's typical use as a large molecule method. A core-shell particle system with a second coating of DHB will allow us to evaluate the MALDI probe distance into the particles. An undergraduate student has been trained using the coating system and carrying out SMPS and MALDI measurements.

- The compound N-methyl-2-pyrrolidone (NMP) was found to be released from PALL HEPA filters and, unexpectedly, provided a sensitive method for detection and measurement of amines and especially ammonia which is notoriously difficult to detect at ppb concentrations. NMP efficiently forms adducts with ammonia or alkylamines, $[M+NMP+H]^+$ at atmospheric pressure. The proton affinity of the amine of interest controlled the extent of NMP adduct formation and hence a major advantage of this approach is increased sensitivity to ammonia and amines.

II. Probing Gas-Surface Interactions.

- Evidence for a new mechanism for particle growth was developed during experiments on SOA formation in a large volume, slow flow reactor. Highly viscous, semi-solid SOA was generated in the flow reactor from α-pinene ozonolysis and gas-phase 2EHN, HPN, or HHN was introduced to the SOA throughout its initial particle formation and growth. In a second set of experiments, the SOA was generated in the absence of any organic nitrates, and these fully-grown particles were impacted on an ATR crystal and exposed to the same organic nitrates for uptake measurements. A comparison of the two sets of experiments showed that the fraction of each organic nitrate gas taken up into the growing particles was larger than that taken up in the fully-grown particles at equilibrium.

A partition coefficient that is larger than expected based on equilibrium suggests an enhanced uptake in which gases become trapped during particle formation and growth. This evidence for a "burying" mechanism was published in *Environ. Sci. Processes Impacts* and has important implications for how particle growth and partitioning are represented in air quality models, especially for highly viscous particles. Ambient particles are highly viscous under many environmental conditions, thus an assumption of equilibrium partitioning, which only holds for low viscosity liquid particles, falls short of accurately describing how gases interact with semi-solid particles. Additionally, the trapping of gases in particles is expected to lengthen the chemical or photochemical lifetimes of the gas. Potential release of these trapped components downwind may affect their regional and global distributions as particles undergo long-range transport.

- The mechanism of gases becoming trapped inside particles as they form and grow was further examined under a variety of SOA precursor concentrations to understand the role of particle mass concentration and composition. A range of <40 µg m^{-3} to ~800 µg m^{-3} mass loading was studied as this was expected to cover a wide range of molecular burying candidates. The measured partition coefficients of all three organic nitrates were again found to be larger than their equilibrium partitioning values over all conditions. The results showed no dependence of the enhanced partitioning on precursor α-pinene concentration or particle mass loading. The distribution of gas phase ozonolysis products was examined using a kinetic model, the Master Chemical Mechanism, which indicated that the type and polarity of potential burying candidates do not change significantly over a wide range of conditions, while the total number concentration changes significantly. The results suggest that the number concentration of burying species is more important than their molecular weight or oxygen content. Effective uptake coefficients of the organic nitrates, γ_{ON}, increased with increasing α-pinene concentration and particle mass concentration. One exception was the alkyl nitrate, 2EHN, which was not detected in the particles formed at the lowest α-pinene concentration. This less polar organic nitrate likely has less affinity for the surface of the particles formed at the lower concentrations. Particle composition measurements showed that the particles formed under the lowest α-pinene concentrations are smaller and more oxygenated than those formed at the other conditions.

Training: One undergraduate student (Joey Cheng), one graduate student (Allison Vander Wall), one postdoctoral researcher (Mica Smith), and three researchers (Lisa Wingen, Veronique Pérraud, and Michael Ezell) have contributed to this research as well as a former post-doctoral student (Yue Zhao) who is now a professor of chemistry at Shanghai Jiao Tong University. Five of the seven people carrying out this research are from underrepresented groups in STEM.

Dissemination: A total of 12 papers have been published in peer-reviewed journals. The results of this research have been incorporated into presentations given at universities and national meetings.

Honors: Francis P. Garvan–John M. Olin Medal of the American Chemical Society, 2017; 2017-2018 Distinguished Faculty Award for Research, University of California Irvine; 2018 Polanyi Medal, Royal Society of Chemistry; 2019 Environment Prize, Royal Society of Chemistry; 2021 Woman of the Year, 74th Assembly District, California

Tech Transfer: None

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    A. C. Vander Wall, L. M. Wingen, V. Perraud, Y. Zhao, and B. J. Finlayson-Pitts
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    B. J. Finlayson-Pitts, L. M. Wingen, V. Perraud and M. J. Ezell
    Commun. Chem. 3, Article number: 108 (2020) doi 10.1038/s42004-020-00347-4