

The Program of 37th Informal Symposium for Kinetics and Photochemical Process in the Atmosphere

California State University, Fullerton

February 19, 2021

Time	Event	Zoom Meeting ID
8:30 – 8:45 AM	Welcome and Introduction	812 8512 0166
8:45 – 9:30 AM	Invited Talk 1: Prof. Vicki Grassian <i>Multiphase Chemistry and Photochemistry Relevant to Marine Environments</i>	
9:30 – 9:35 AM	5 minute break	
9:35 – 10:20 AM	Invited Talk 2: Prof. Manabu Shiraiwa <i>Multiphase chemistry of organic aerosols and reactive oxygen species in the atmosphere</i>	
10:20 – 10:30 AM	10 minute break	
10:30 AM – 12:00 PM	Mini Talk Session 1A Moderator: Prof. Andrew Petit	834 3354 5041
10:30 AM – 12:00 PM	Mini Talk Session 1B Moderator: Prof. Daniel Curtis	812 8512 0166
12:00 – 1:00 PM	Lunch Break	
1:00 – 1:45 PM	Invited Talk 3: Dr. Sina Hasheminassab <i>2020 Air Quality in the South Coast Basin, CA: A Focus on COVID-19 Lockdown, Ozone Season, Wildfires and Fireworks Emissions</i>	
1:45 – 1:50 PM	5 minute break	
1:50 – 2:35 PM	Invited Talk 4: Prof. Roya Bahreini <i>Utilizing aerosol chemical composition measurements to identify aerosol sources and formation processes</i>	
2:35 – 2:45 PM	10 minute break	834 3354 5041
2:45 – 4:15 PM	Mini Talk Session 2A Moderator: Prof. Fu-Ming Tao	
2:45 – 4:15 PM	Mini Talk Session 2B Moderator: Prof. Zhuangjie Li	812 8512 0166
4:15 – 4:30 PM	Conclusion and 38 th ISKPPA	



The 37th Informal Symposium for Kinetics and Photochemical Processes in the Atmosphere

Mini Talk Presentation Schedule and Abstracts

February 19, 2021

10:30 am – 12:00 pm

Mini Talk Session 1A: pages 2-10

Mini Talk Session 1B: pages 11-19

2:45 pm – 4:15 pm

Mini Talk Session 2A: pages 20-27

Mini Talk Session 2B: pages 28-36



Mini Talk Presentation Session 1A

Moderator: Dr. Andrew Petit

Zoom Link:

<https://fullerton.zoom.us/j/83433545041?pwd=Ty9xdnE3UFBhR0NuMU43eVhBdXdsQT09>

Time	Presenter Name	Affiliation	Title of Mini Presentation	Page
10:30	Zachary Cornwell	UC Irvine, Department of Chemistry	Kinetics of Criegee intermediate reactions with ketones and diketones	3
10:40	Theodore Dibble	SUNY- Environmental Science and Forestry	Together But Not Separately: Ozone and OH Oxidize Hg(0) to Hg(II) in the Atmosphere	4
10:50	Jose Luis Guardado	California State University, Fullerton	Theoretical Study of the Electronic Quenching of NO (A) with H ₂ O	5
11:00	Zhuangjie Li	California State University, Fullerton	A Kinetics Study of the Reactions of OH and Cl with Octanal at 240 -340 K Using the Relative Rate/Discharge Flow/Mass Spectrometry Method	6
11:10	Alexis Robles	California State University, Northridge	Vacuum Ultraviolet Photolytic Destruction of Anesthetic agents	7
11:20	Michael von Domaros	UCI	Human Skin Oil Ozonolysis: The Atomistic View	8
11:30	Weihong Wang	UCI	Reactions of Ozone with Model Compounds for Emerging Contaminants	9
11:40	Xu Zhang	Caltech/JPL	Reaction of Methane and UV-activated Perchlorate: Relevance to Heterogeneous Loss of Methane in the Atmosphere of Mars	10

Kinetics of Criegee intermediate reactions with ketones and diketones

Zach Cornwell and Craig Murray

UC Irvine, Department of Chemistry

The rate constants of the reactions of the Criegee intermediate (CI) CH_2OO with acetone and α - and β -diketones have been measured in a flash photolysis flow reactor at 295 K and a total pressure of about 70 Torr. CH_2OO was produced photochemically and rates were measured by varying reactant concentrations while maintaining pseudo-first order conditions. A pulsed LED was used to measure broadband transient absorption spectra of CH_2OO and its byproducts. CH_2OO loss rates were determined by fitting time-dependent concentrations using a kinetic model that accounts for self-reaction and other loss processes. The rate constants for the reactions of CH_2OO with the α -diketones ($\sim 10^{-11} \text{ cm}^3 \text{ s}^{-1}$) are approximately 20–30 times larger than those for acetone and the β -diketones. The reactivity trend for these cycloaddition reactions can be understood using concepts from frontier molecular orbital theory. The reactions of ketones and diketones are too slow to have a significant impact on CI concentrations in the troposphere.

Together But Not Separately: Ozone and OH Oxidize Hg(0) to Hg(II) in the Atmosphere

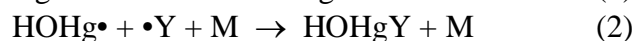
Theodore S. Dibble,(1) Rongrong Wu,(2) Chuji Wang,(2) Ivan Černušák,(3), Vladimir Kello,(3)
Camille K. Beckett,(1) and Ilena J. Kirby(1)

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Most atmospheric models of the gas-phase mercury assume that oxidation of Hg(0) to Hg(II) occurs in one step in reactions with either OH or ozone. However, the well-cited paper of Calvert and Lindberg (2005) pointed out that these assumptions were flawed, and subsequent evidence seemed to confirm their conclusion. Computational chemistry indicates that OH-initiated oxidation of Hg(0) occurs in two steps:



where $\bullet\text{Y} = \text{NO}_2, \text{HOO}, \text{ROO},$ halogen oxides, and other radicals (but not NO). The fast dissociation of HOHg \bullet (lifetime of ~10 ms at 298 K and 1 atm) strongly limits the efficiency of this process.

We propose an alternative process that can efficiently oxidize HOHg \bullet to an Hg(II) compound:



Reaction (3) is exothermic by about 35 kcal/mole. Evidence for a high rate constant for reaction (3) comes from both computations and experiment.

Experiments were carried out on the BrHg \bullet analogue of HOHg \bullet , since there seems to be no way to generate HOHg \bullet for kinetic studies, and computations indicate that these two radicals have very similar reactivity. These experiments suggest a rate constant for BrHg \bullet + O₃ that is ~10% of the collision rate constant. Experiments used laser flash photolysis of HgBr₂ vapor at 266 nm to generate BrHg \bullet in the presence of ozone. The abundance of BrHg \bullet was monitored by laser induced fluorescence at 256 nm with detection near 500 nm.

Computations find no activation barrier to this reaction using three functionals and multireference 2nd order perturbation theory. All calculations used a triple-zeta valence basis set with a pseudopotential to treat scalar relativistic effects in Hg. The absence of a barrier to HOHg \bullet + O₃ is consistent with the high rate constant observed in experiments on BrHg \bullet + O₃.

Since the abundance of ozone in the atmosphere is much higher than that of radicals, the reaction HOHg \bullet + O₃ means that oxidation of HOHg \bullet to HOHgO \bullet can outcompete dissociation of HOHg \bullet . The fate of HOHgO \bullet appears to be much the same as that of BrHgO \bullet (and OH); namely, abstraction of hydrogen atoms to form a stable Hg(II) compound:



competes with reaction with CO:



Theoretical Study of the Electronic Quenching of NO (A) with H₂O

Jose Luis Guardado and Andrew Petit

Department of Chemistry and Biochemistry, California State University Fullerton, Fullerton, CA 92831

Nitric Oxide (NO) radicals are important atmospheric pollutants produced by combustion systems. Laser-induced fluorescence (LIF) is a popular method used on NO ($X^2\Pi \rightarrow A^2\Sigma^+ 3s\sigma$) to detect NO and determine the conditions inside operational combustion energies. However, reliable measurements derived by NO fluorescence, ($A^2\Sigma^+ 3s\sigma \rightarrow X^2\Pi$) are compromised by the interactions of excited NO ($A^2\Sigma^+$) with other species commonly found in the same systems. For example, H₂O is known to readily cause collisional electronic quenching of NO ($A^2\Sigma^+$), with an electronic quenching cross section of 120 \AA^2 at 300K. The underlying photochemical mechanism responsible for this electronic quenching is not known. In order to identify the electronic quenching pathways of NO ($A^2\Sigma^+$) with H₂O, we use equation of motion-electron attachment-coupled cluster singles and doubles (EOM-EA-CCSD) to determine the long-range attractions and orientations that facilitate internal conversion. Through the analysis of adiabatic potential energy curves, we reveal that H₂O is capable of electronically quenching NO ($A^2\Sigma^+$) at specific orientations guided by long-range steering. Experimental work to verify our predictions through velocity map imaging is currently underway in Nathan Kidwell's laboratory at the College of William and Mary.

A Kinetics Study of the Reactions of OH and Cl with Octanal at 240 -340 K Using the Relative Rate/Discharge Flow/Mass Spectrometry Method

Rick Stoody and Zhuangjie Li

Department of Chemistry and Biochemistry, California State University Fullerton, Fullerton, CA 92831

The rate constant for reactions of OH and Cl radicals with octanal have been measured for the first time using the RR/DF/MS technique at the temperature range 240-340 K with 1,4-dioxane as reference compound. At 298 K the rate constant for reactions of OH and Cl radicals with octanal are determined to be:

$$k_{\text{octanal+OH}} = (2.97 \pm 0.15) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

$$k_{\text{octanal+Cl}} = (2.89 \pm 0.53) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The rate constant of reaction of octanal with OH was found to be negatively dependent on at 240-340 K, with an Arrhenius expression of $k_{\text{octanal+OH}} = (7.6 \pm 4.0) \times 10^{-11} \exp(390 \pm 148) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, suggesting that its reaction could proceed with the formation of pre-complex, octanal...OH. Within the experimental uncertainty, the reaction of octanal with Cl radical is found to be essentially independent on temperature in a temperature range of 253 – 330 K. Using k_{OH} and k_{Cl} at 277 K determined in the present work, the atmospheric lifetime of octanal is estimated to be 9.8 hours, with the OH being the dominate sink for the removal of octanal from troposphere in daytime.

Vacuum Ultraviolet Photolytic Destruction of Anesthetic agents

Kjertan Lyster, Mads P. Sulbaek Andersen, Alexis Robles

California State University – Northridge

The main driving force of climate change is the increasing abundance of CO₂ in our atmosphere, but smaller anthropogenic contributors do play a role in the overall radiative forcing of climate. Isoflurane (CF₃CHClOCHF₂), desflurane (CF₃CHFOCHF₃), and sevoflurane ((CF₃)₂CHOCH₂F) are strong greenhouse gases and see wide use as common inhaled anesthetic agents. Anesthesia is by far the most dominant source of these ethers in the atmosphere and it is relevant to consider these gases in connection to the profession's contribution to the radiative forcing of the climate. Most gasses are expelled by the patient during the medical procedure with little to no metabolism and is vented to the atmosphere. Previous studies have documented that emission of inhaled anesthetic agents make up a sizeable fraction of health care's total climate footprint . In the present work we investigate the use of high energy ultraviolet radiation to induce photochemical destruction of sevoflurane and isoflurane compounds. A temperature-controlled advanced photochemical simulation chamber with in-situ excimer-radiation lamps and multi-pass analytical optics was constructed for this experiment. The photolysis kinetics were measured using a relative-rate technique with reference compounds (dimethylether, DME) as a function of total pressure (N₂). We determined that isoflurane and sevoflurane undergo rapid photolytic destruction producing carbonyl fluoride and halogenated ketone and ester compounds.

Keywords: climate change, volatile anesthetics, isoflurane, sevoflurane

Human Skin Oil Ozonolysis: The Atomistic View

Michael von Domaros, Douglas J. Tobias

UCI

We use atomistic molecular dynamics simulations to study the transport and partitioning of ozone and human skin oil ozonolysis products in multiple layers of human skin and in the surrounding gas phase. We find remarkably low barriers against skin permeation for certain reaction products. Results feed into kinetic models describing the full, macroscopic transport of all involved species.

Reactions of Ozone with Model Compounds for Emerging Contaminants

Weihong Wang and Barbara J. Finlayson-Pitts

University of California Irvine

An increasing number of new compounds are being developed daily, especially in the agriculture and pharmaceutical industries. Once these compounds are put into use, they can remain in the soil (pesticides) and water systems (both pesticides and medications) for years, and fall into the class of emerging contaminants. One such group of organic compounds contains an amino and nitro group attached to a double bond. Examples of these multifunctional group compounds include the insecticide nitenpyram and the heartburn medications ranitidine and nizatidine. The degradation of these compounds has the potential to generate chemicals that are more or less toxic than their parent compounds. It is therefore important to understand the kinetics and mechanisms of their degradation on a molecular basis. One of their fates in the atmosphere is the reaction with oxidants, such as ozone. Our goal is to study the effect of amino and nitro functional groups on the alkene-ozone reaction mechanism and kinetics for compounds where both groups are attached to the vinyl carbon. Model compounds with amino and/or nitro groups are selected for lab studies. Preliminary results on studies of the reaction of ozone with one of the selected model compounds, 1-dimethylamino-2-nitroethylene, which has the amino and nitro group on opposite sides of the double bond, will be presented.

Reaction of Methane and UV-activated Perchlorate: Relevance to Heterogeneous Loss of Methane in the Atmosphere of Mars

Xu Zhang, David Berkinsky, Sathya R. Chitturi, Charles R. Markus, Frederick Grieman, Michio Okumura, Yangcheng Luo, Yuk L. Yung and Stanley P. Sander

Caltech/JPL

The absence of significant detectable signatures of organic molecules in the atmosphere and on the surface of Mars is a major unsolved puzzle. One possible explanation is that perchlorate-rich Martian soils, activated by solar ultraviolet (UV) radiation, create an environment favorable to the rapid oxidation of organics such as alkanes (including methane or CH₄). In this paper, we conducted studies on reactions of methane + perchlorate + UV at room temperature. Our results show that magnesium perchlorate (Mg(ClO₄)₂•6H₂O) surfaces exposed to UV light at wavelengths found on Mars catalyze the decomposition of methane (CH₄), resulting in the formation of carbon dioxide (CO₂) and volatile chlorine oxides. The CO₂ production under UV-activated perchlorate surfaces is up to 3 times as much as that under conditions without perchlorate or UV. In addition, under UV radiation, perchlorate (ClO₄⁻) decomposes to chlorate (ClO₃⁻) and chlorine oxides. Considering the accelerated oxidation of methane under UV-activated perchlorate, the lifetime of CH₄ on Mars is estimated to be much shorter than that derived from the gas-only chemical destruction.

Mini Talk Presentation Session 1B

Moderator: Dr. Daniel Curtis

Zoom Link:

<https://fullerton.zoom.us/j/81285120166?pwd=QTJnc0x5NTRXVUNibDhOS283UEUwUT09>

Time	Presenter Name	Affiliation	Title of Mini Presentation	Page
10:30	Anissa Barrera	California State University, Fullerton	Intercomparison of spectroscopic instrumentation for measuring the optical properties of atmospheric aerosol particles	12
10:40	Kunpeng Chen	University of California, Riverside	Solvent effects on extraction of secondary brown carbon constituents from nighttime oxidation of heterocyclic VOC precursors	13
10:50	Linden Conrad	Harvey Mudd College	Brown Carbon Production from Heterogeneous Reactions of Syringol in an Atmospheric Simulation Chamber	14
11:00	Alexandra Klodt	University of California, Irvine	The Effects of Ammonium on the Aging of Oxaloacetic Acid in the Atmospheric Aqueous Phase	15
11:10	Veronique Perraud	UC Irvine	Particles characterization from atomized mixtures of methanesulfonic acid and methylamine	16
11:20	Andrea Rohrbacher	University of California - Irvine	Potential Matrix Effects on the Heterogeneous Photochemistry of Neonicotinoid Pesticides	17
11:30	Megan Woods	The University of California, Riverside	In-Silico Investigation of EI Mass Spectra of Brown Carbon Aerosols	18
11:40	Ningjin Xu	UCR	Design and Characterization of a new OFR: The Particle Formation Accelerator (PFA)	19

Intercomparison of spectroscopic instrumentation for measuring the optical properties of atmospheric aerosol particles

Anissa A. Barrera, Stephanie Salas, Jorge A. Gonzalez, and Daniel B. Curtis

California State University, Fullerton

Aerosols are suspensions of liquid or solid particles in the atmosphere. It is thought that the scattering and absorption of solar radiation by aerosol particles can affect the Earth's climate, but the climate effects of many types of aerosols are poorly understood due to their diversity in size, composition, and source. Measuring the spectroscopic properties of atmospheric aerosol particles has traditionally been difficult due to their relatively low scattering and absorption cross sections, leading to the development of advanced spectroscopic techniques. This study performed an intercomparison of two commercially available instruments for measuring aerosol spectroscopic properties in order to better understand their precision. An Ambilabs Dual Wavelength Integrating Nephelometer, which measures the intensity of light scattered by particles, and an Aerodyne Cavity Attenuated Phase Shift extinction monitor (CAPS PMex), which measures a phase shift in modulated light passing through an optical cavity, were compared. The scattering coefficient and extinction coefficient for polystyrene latex (PSL) test aerosol particles were measured with the nephelometer and CAPS instrument, respectively. PSL particles were chosen because their optical properties are well known and because they only scatter light and do not absorb, so the two instruments should agree. Preliminary results from the study show excellent agreement between the two instruments, with an average correlation slope of $99 \pm 6\%$.

Solvent effects on extraction of secondary brown carbon constituents from nighttime oxidation of heterocyclic VOC precursors

Kunpeng Chen, Nilofar Raeofy, Raphael Mayorga, Roya Bahreini, Haofei Zhang, Ying-Hsuan Lin

Department of Environmental Sciences, University of California, Riverside, CA, USA;
Department of Chemistry, University of California, Riverside, CA, USA;
Environmental Toxicology Graduate Program, University of California, Riverside, CA, USA

Secondary brown carbon (BrC) aerosol is a potentially important contributor to positive radiative forcing on Earth, but the quantification of its influence on the global radiative budget remains uncertain due to incomplete characterization of its optical and chemical properties. Particularly, light absorption of secondary organic aerosols (SOA) from heterocyclic precursors, which are emitted abundantly in biomass burning, is little explored. Previous studies usually characterized BrC's optical properties by either online measurement at certain wavelengths or offline measurement of spectral profiles. In our study, we performed chamber experiments to generate secondary BrC from nighttime oxidation (i.e., in the presence of both ozone and nitrate radicals) of five heterocyclic VOC precursors (pyrrole, 1-methylpyrrole, thiophene, furan, and furfural). Optical properties of the SOA are investigated by both online measurement with a photoacoustic extinctionsmeter (PAX) at 375 nm and offline measurement with an ultraviolet-visible (UV-Vis) spectrophotometer (290-700 nm). The mass absorption coefficients (MAC) of SOA from these precursors show the following trend based on the PAX measurements: furfural > furan \approx pyrrole > thiophene > 1-methylpyrrole. However, in the offline UV-Vis measurements, samples extracted by methanol (MeOH) and acetonitrile (ACN) exhibit different results of MAC, depending on the type of precursors. For pyrrole SOA and 1-methylpyrrole SOA, MeOH extraction obtains higher MAC, while for furan SOA and furfural SOA, the results are contrary. For thiophene SOA, both solvents lead to similar MAC profiles. Functional group analysis by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) suggests that MeOH-extracted and ACN-extracted samples contain different compositions of multi-substituted unsaturated products. Since MeOH-extracted samples are typically used to fit optical parameters in recent climate models, our work suggests that these results should be interpreted with caution and non-extractable chromophores require further identifications.

Brown Carbon Production from Heterogeneous Reactions of Syringol in an Atmospheric Simulation Chamber

Linden Conrad, Ellie Smith, Professor Lelia Hawkins

Harvey Mudd College

The formation of brown carbon (BrC) in the atmosphere is a chemical process that affects both air quality and climate change through its effect on aerosol loading and transmitted solar radiation. Specific effects include reduction of visibility and local absorption of radiation; despite recent efforts, the global radiative effect of this material remains to be quantified. Using the CESAM (a multiphase atmospheric simulation chamber) at the Laboratory of Atmospheric Systems in Paris, France (LISA), we simulated heterogeneous syringol photochemistry with wet and dry aerosol particles. These organic compounds are abundant in the atmosphere, especially in areas impacted by biomass burning, from the incomplete combustion of lignin. Additionally, they are water-soluble which increases the likelihood they will be dissolved in atmospheric water droplets where aqueous phase chemistry and photochemistry can occur. The chamber allows for a more realistic approximation of heterogeneous BrC formation. There were three different humidity conditions tested, each in the presence and absence of artificial sunlight: dry aerosol, deliquesced aerosol, and cloud droplets. Brown carbon compounds demonstrate wavelength-dependent absorbance of solar radiation. UV/visible spectroscopy was used throughout the chamber experiments to monitor changes in optical properties of chamber aerosol by coupling to a Particle-Into-Liquid Sampler. Following previous studies, 365 nm was used to indicate the presence of brown carbon though absorbance measurements were collected from 250-700 nm. Single scattering albedo at 405 nm, 450 nm, and 600 nm were monitored by cavity attenuated phase shift (CAPS) as additional indicators of aerosol browning. Without light, syringol did not form brown carbon. Aerosol chemical composition was monitored by two aerosol mass spectrometers while gas phase chemistry was tracked using a proton transfer mass spectrometer. The overall oxidation state of all organic products was calculated from aerosol mass spectra and revealed a distinct shift towards more oxidized compounds under lit conditions. From preliminary data analysis, we found evidence that the BrC forming in the presence of hydroxyl radicals is chemically and optically similar to BrC formed without hydroxyl radicals, in the presence of light. This is contrary to previous work showing that syringol requires OH radicals or photosensitizers to initiate browning, in bulk studies. This may be evidence of syringol, or a first-generation product of syringol oxidation, acting as a photosensitizer which then begins the oligomerization of organics to form high molecular weight compounds absorbing in the BrC region, approximately 350nm to 450nm. There is no evidence of syringol partitioning into the aerosol phase under dark conditions. This supports the current proposed mechanism where a phenoxy radical is created, either by introduction to a hydroxyl radical or unidentified syringol photosensitizer, and then linked with other phenoxy radicals until stabilized. Before they become apparent in the aerosol, the organics are either in the gas phase or clinging to the chamber walls.

The Effects of Ammonium on the Aging of Oxaloacetic Acid in the Atmospheric Aqueous Phase

Alexandra L. Klodt, Kimberly Zhang, Jorge L. Fernandez, Michael W. Olsen, and Sergey A. Nizkorodov

University of California, Irvine

Oxaloacetic acid (OAA) and other 3-oxocarboxylic acids undergo a known decarboxylation reaction which can be catalyzed by ammonium and amines. We suggest that this process occurs in atmospheric water, and further that it likely controls the atmospheric lifetime of these molecules. To address this, pseudo-first-order rate constants were calculated by preparing 1 mM solutions of OAA and monitoring the extent of decarboxylation using UV-Vis absorption. The experiments were also conducted in the presence of varying concentrations of ammonium sulfate, ammonium chloride, ammonium bisulfate, and sodium sulfate to understand the catalysis of OAA's decarboxylation by ammonium over a broad range of conditions found in the atmosphere. At pH 3 to 4, the rate of decarboxylation was linearly dependent on ammonium concentration below 2.7 M, with the lifetime of OAA varying from 5 h in dilute solutions representing cloud/fog water to 1 h in the concentrated ammonium solutions representing neutralized aqueous particles. Above 2.7 M, additional ammonium had no further effect on OAA's lifetime. When solutions were acidified to pH values less than 2, the rate of decarboxylation was decreased regardless of ammonium's presence, suggesting OAA will have a lifetime of tens of hours in acidic aerosols. Finally, density functional theory was used to generate energy diagrams for the catalyzed and uncatalyzed decarboxylation. The free energy barrier height was calculated to be approximately 21 kcal/mol lower after reaction of OAA with ammonium. Comparing the measured rates of decarboxylation with estimated rates of OH oxidation suggests that decarboxylation will be the dominant loss pathway for OAA, and likely other 3-oxocarboxylic acids, in all types of atmospheric water simulated.

Particles characterization from atomized mixtures of methanesulfonic acid and methylamine

Veronique Perraud and B. J. Finlayson-Pitts

UC Irvine

Recent laboratory investigations show that sub-10 nm particles generated from gas phase acid-base reactions of sulfuric or methanesulfonic acids with amines exhibit an acid-to-base molar ratio higher than 1, suggesting that those particles are acidic. In contrast, larger particles were observed to be neutral (i.e. acid-to-base molar ratio = 1). Reference salt for these acid-amine systems are not commercially available (with the exception of ammonium sulfate), and rely on atomizing dilute solutions of the acid and the corresponding base. It is a priori expected that particles generated from this process would be stoichiometrically balanced, thus pH-neutral. However, we observed that those particles are acidic in nature, and may uptake adventitious ammonia present in the system. We present here an example of such measurement from atomized mixtures of methanesulfonic acid and methylamine.

Potential Matrix Effects on the Heterogeneous Photochemistry of Neonicotinoid Pesticides

Andrea Rohrbacher and Barbara J. Finlayson-Pitts

University of California – Irvine

The environmental fate of neonicotinoids (NNs), the world's most commonly used insecticide class, is a key regulatory issue due to their widespread distribution, mobility, and role in honeybee colony collapse disorder. In the natural environment, NNs are delivered in a variety of complex formulations and have been found on a plethora of different environmental surfaces. Their chemistry and photochemistry are commonly characterized using pure compounds, but it is not known if other species present in the commercial formulations will impact those results. Here, we explore the potential matrix effects on the environmental fates of two NN structural families, the nitroguanadines and the nitromethylenes, as represented by dinotefuran (DNF) and nitenpyram (NPM), respectively.

This work probes whether the two representative NNs in commercial formulations behave similarly to the pure reagents, both in KBr pellets for experimental comparison. The commercial formulations and the pure reagents were irradiated at room temperature using three different lamps with peak wavelengths ranging from 254 nm to 350 nm. Loss of the NN and product formation were followed using FTIR and DART mass spectrometry. The results are also compared to the thin film data and matrix effects on product formation, quantum yields, and atmospheric lifetimes are discussed.

In-Silico Investigation of EI Mass Spectra of Brown Carbon Aerosols

Megan Woods, Kunpeng Chen, Nilofar Raeofy, Roya Bahreini, and Ying-Hsuan Lin*

Department of Environmental Sciences, University of California Riverside

The increasing global population and industrial development have altered our climate drastically within the last century. Brown carbon (BrC) aerosols have recently attracted interest as a factor in climate forcing. BrC aerosols are light-absorbing organic particles suspended in the air, which are known to be produced from biomass burning events, fossil fuel combustion, and atmospheric transformation of volatile organic compound (VOC) precursors. Mass spectrometry-based analytical measurements have been widely used to speciate BrC aerosol constituents that are necessary for developing comprehensive climate models. However, due to the large variety and chemical complexity of BrC aerosols, there is a lack of authentic standards readily available to aid in the identification of these compounds. Utilizing Quantum Chemical Electron Ionization Mass Spectra (QCEIMS) to generate a theoretical EI mass spectrum, this work offers supplemental information in identifying unknown BrC molecules. By investigating the impacts of Gradual Gradient Approximation (GGA) functional methods such as PBE, BLYP, and B97D, as well as the new standalone GFn2-xTB method, we can determine the method with high accuracy and computational efficiency necessary to predict an EI spectra of molecules of interest. Preliminary results demonstrate that the combination of QCEIMS generated EI spectra, NIST mass spectral libraries, and experimental results acquired from aerosol mass spectrometer (AMS) measurements can allow for accurate determination of unidentified BrC constituents when authentic standards are not available.

Design and Characterization of a new OFR: The Particle Formation Accelerator (PFA)

Ningjin Xu; Don Collins

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2. College of Engineering - Center of Environmental Research and Technology (CE-CERT); University of California Riverside; Riverside, CA 92507

Oxidation flow reactors (OFRs) are valuable tools for studying the formation and evolution of secondary aerosol (SA) in the atmosphere. Here we present a new all-Teflon reactor, the Particle Formation Accelerator (PFA), that was designed, constructed, and characterized through both experimental measurements and CFD modeling. We describe some of the design elements that were used to reduce flow recirculation and gas and particle losses and wall interactions. We report laboratory characterization of the reactor, including hydroxyl radical production, UV intensity distribution, residence time distributions (RTDs) for gases and particles determined using both computational simulation and experimental verification, gas and particle losses, and a comparison of aerosol yields of α -pinene and m-xylene with those reported in the literature. By wrapping the reactor with highly UV-reflective material, an overall UV intensity comparable to that in other OFRs is achieved using a relatively low power output lamp. Near laminar flow velocity profiles of gases and particles are suggested by CFD simulations and confirmed by the RTD experimental results. The transmission efficiencies of non-reactive gases and of particles are greater than 90%. Particle loss was reduced by minimizing static charge on the Teflon surfaces, resulting in higher inferred aerosol yields of α -pinene and m-xylene. Preliminary measurements of SA production when sampling ambient air in Riverside, CA, U.S. showed that the mass concentration of SA formed in the reactor was up to 1.8 times the mass concentration of the ambient aerosol at the same time. In the future, we will focus our efforts on measurement of the composition of the particulate and gaseous products during one or more field studies to evaluate how well the PFA reactor simulates atmospheric chemistry that typically requires hours or days.

Mini Talk Presentation Session 2A

Moderator: Dr. Fu-Ming Tao

Zoom Link:

<https://fullerton.zoom.us/j/83433545041?pwd=Ty9xdnE3UFBhR0NuMU43eVhBdXdSQ09>

Time	Presenter Name	Affiliation	Title of Mini Presentation	Page
2:45	Franck Fu	W.M Keck Science Department	Impact of the COVID-19 Pandemic Lockdown on Air Pollution in 20 Major Cities around the World	21
2:55	Sahar Ghadimi	University of California, Riverside	Physiochemical Characterization of Heavy-Duty Vehicles Primary Particulate Emissions and Secondary Organic Aerosol (SOA) Using Diesel Fuel and Renewable Diesel	22
3:05	Savannah Lewis	Scripps Institution of Oceanography, UCSD	Do Seasons Matter for Aerosol from the Ocean?	23
3:15	Hossein Pazooki	University of California, Riverside	Composition and Source Characterization of Aerosols in an Environmental Justice (EJ) Community in California (Wilmington)	24
3:25	Linia Tashmim	University of California, Riverside	The role of Dimethyl Sulfide oxidation on prediction of air quality for polluted coastal areas around the world	25
3:35	Katie Tuite	UCLA	Impact of nitrous acid and formaldehyde on radical production in biomass burning plume	26
3:45	Zihan Zhu	University of California, Riverside	Vertical Ozone Profile Measurements in Riverside	27

Impact of the COVID-19 Pandemic Lockdown on Air

Franck Fu, Kathleen L. Purvis-Roberts and Branwen Williams

W.M. Keck Science Department, Claremont McKenna College, Pitzer College and Scripps College

In order to fight against the spread of COVID-19, the most hard-hit countries in the spring of 2020 implemented different lockdown strategies. To assess the impact of the COVID-19 pandemic lockdown on air quality worldwide, Air Quality Index (AQI) data was used to estimate the change in air quality in 20 major cities on six continents. Our results show significant declines of AQI in NO₂, SO₂, CO, PM_{2.5} and PM₁₀ in most cities, mainly due to the reduction of transportation, industry and commercial activities during lockdown. This work shows the reduction of primary pollutants, especially NO₂, is mainly due to lockdown policies. However, preexisting local environmental policy regulations also contributed to declining NO₂, SO₂ and PM_{2.5} emissions, especially in Asian countries. In addition, higher rainfall during the lockdown period could cause decline of PM_{2.5}, especially in Johannesburg. By contrast, the changes of AQI in ground-level O₃ were not significant in most of cities, as meteorological variability and ratio of VOC/NO_x are key factors in ground-level O₃ formation.

Physiochemical Characterization of Heavy-Duty Vehicles Primary Particulate Emissions and Secondary Organic Aerosol (SOA) Using Diesel Fuel and Renewable Diesel

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Heavy duty vehicles (HDVs) are one of the major contributors to urban air pollution. Despite enforcement of stringent standards for the reduction of primary PM emissions and gas phase organics emitted from the diesel trucks, the inadvertent secondary organic aerosols (SOA) formation – linked to adverse health impacts— remained disregarded. Exhaust after treatment systems, fuel types, and driving conditions are critical elements impacting the primary and secondary emissions. This study characterized the diluted emissions that were photo oxidized into the 30 m³ Mobile Atmospheric Chamber (MACH) from two HDVs when operated with renewable diesel (RD) and ultra-low sulfur diesel (ULSD). The HDVs were exercised over the cold start urban dynamometer driving schedule (UDDS) and the Heavy Heavy-Duty Diesel Truck (HHDDT) Cruise cycle using a chassis dynamometer. The HDVs were equipped with different exhaust after treatment systems, including diesel particulate filters (DPFs), selective catalytic reduction (SCR), and diesel oxidation catalysts (DOCs). The physiochemical properties of secondary aerosol were evaluated using a variety of particle and gas phase instrumentation after 5 hours photo oxidation process. Moreover, a detailed high-resolution mass spectral analysis with an HR-ToF-AMS was performed on both primary and secondary aerosols. The high-resolution mass spectra analysis of 4 organic classes (CH, CHO, CHN, and CHNO) exhibited that in the primary organic aerosol (POA) of UDDS-ULSD experiment, the organic CH class is the dominant fraction (61.0%), followed by the CHO class (29.0%), the CHN class (5.3%) and the CHNO class (1.9%). After 5 hours irradiation of the primary emissions from the UDDS-ULSD experiment, the organic CH class reduced to 48.9%, while the CHO and CHN classes significantly increased to 37.4% and 10.6%, respectively. The CHON remained the minor component with 1.0%. Analysis of POA in the UDDS-RD experiment demonstrated that the organic CHO class is the dominant fraction (51.5%), followed by the CH class (44.6%), with low contribution from the CHN (3.4%) and the CHON class (0.8%). Similarly, in the SOA (after 5 hours irradiation) from the UDDS-RD experiment, the organic CHO class increased to 64.4%, and the CH class reduced to 30.1%.

Moreover, for both fuel types, cruise mode produced lower primary and secondary emissions compared to the UDDS driving cycle. The higher formation of SOA was observed when the vehicles operated with ULSD and equipped with DPF compared to RD with the same after-treatment system. Inorganic ammonium nitrate (NH₄NO₃) aerosol formation was very low (negligible in some cases) in both primary and secondary emissions for the HDV without SCR after-treatment system, while the HDV equipped with advanced after treatment (DOC+DPF+SCR) produced higher tailpipe ammonia (NH₃) emissions, which further generated secondary ammonium nitrate particles upon reacting with HNO₃ in the chamber.

Do Seasons Matter for Aerosol from the Ocean?

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4 months of marine aerosol data were collected in the North Atlantic (November 2015, May 2016, September 2017, and March 2018) during the NAAMES research cruises. Primary marine aerosol was found to have similar organic functional group (OFG) composition in of 72-85% alcohol, 6-13% alkane, and 5-8% amine groups via FTIR. Carboxylic acid was present in the late spring and autumn, but rarely present in the winter and early spring campaigns, likely related to a combination of polar air masses and low PAR. The organic mass concentrations were not statistically different from each other ($p > 0.1$), suggesting that there is not a strong seasonal signal in either the organic composition or concentration in sub 1 μm samples in the North Atlantic region sampled. Generated primary marine aerosol (gPMA) seasonal averages showed little variation, however interesting seasonal changes emerged when the dataset was separated by latitude.

Composition and Source Characterization of Aerosols in an Environmental Justice (EJ) Community in California (Wilmington)

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A series of aerosol measurements were conducted in collaboration with the South Coast Air Quality Management District, in Wilmington, an Environmental Justice community in the Southern California Air Basin for three weeks during Fall 2019. The site was selected to examine the influence of nearby oil refineries, major highways, and the ports of Los Angeles and Long Beach on local air quality. Temporal concentration changes of various aerosol species were measured using a Compact Time-of-Flight Aerosol Mass Spectrometer (m-AMS, Aerodyne Research Inc.). The results showed that during the measurement period, the non-refractory composition of submicron aerosols was dominated by organics (average of $10.62 \mu\text{g}/\text{m}^3$), followed by nitrate ($5.32 \mu\text{g}/\text{m}^3$) and sulfate ($2.87 \mu\text{g}/\text{m}^3$). Diurnal presentation of major organic fractions using high-resolution (HR) mass spectral analysis indicates that the site was influenced predominantly by fresh hydrocarbon-like (C_xH_y^+ family) species, followed by slightly oxygenated organics ($\text{C}_x\text{H}_y\text{O}^+$ family). Furthermore, ratios of the measured NO^+ and NO^{2+} along with values during ammonium nitrate sampling was used to calculate the organic fraction of the nitrates and suggest on average 30% contribution to total nitrate from organonitrates during the measurements. Moreover, HR analysis of the mass spectra was used to qualitatively detect processes responsible for emissions of Sodium, Aluminum, Zinc, Magnesium, Manganese, Nickel, and Titanium (Na, Al, Zn, Mg, Mn, Ni, and Ti). For instance, one of the high sulfate events was further investigated using the combination of the results from Positive Matrix Factorization (PMF) and HR analysis. Detectable signals of organic fragments in the range of m/z 200- 270 in one of the factors (indicative of PAHs) and a corresponding increase in the concentration of Nickel (Ni) provided evidence for influence from flaring emissions in this period. Further work is needed to elaborate the impacts of aqueous chemistry and refractory species on the chemical composition of the aerosols at this site.

The role of Dimethyl Sulfide oxidation on prediction of air quality for polluted coastal areas around the world

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Oceanic emissions of dimethyl sulfide (DMS) and subsequent formation of sulfate aerosol represent a major source of uncertainty in understanding the climate and air quality impact of natural aerosol. Once DMS is in the atmosphere it is oxidized to form SO₂ and methane sulfonic acid (MSA). This SO₂ can be further oxidized leading to the formation of sulfate aerosol. These oxidized products and DMS itself plays a major role in controlling ambient air quality, and also contribute to uncertainty in the Earth's radiation budget due to an incomplete understanding of their formation pathways and chemical/microphysical properties. In many current air-quality models the oxidation mechanism of DMS in the troposphere is highly simplified and neglects important interactions between DMS and O₃ or halogenated species like bromine oxide (BrO). These simplifications contribute to uncertainties in the global DMS budget, as well as potential biases in estimates of SO₂, MSA, and sulfate abundance in the pre-industrial environment. The oxidation of DMS can also affect new particle formation, further influencing local air quality and climate. The major objective of this work is to integrate and evaluate two individual DMS oxidation schemes, including gas-phase and aqueous-phase oxidation reactions, using the GEOS-Chem global chemical transport model, and to examine mechanism impacts on urban-coastal sulfur budgets in terms of new particle formation and growth. Using these mechanisms, one of which includes the intermediates dimethyl sulfoxide (DMSO) and methane sulphinic acid (MSIA) while the other includes the previously unquantified product hydroperoxymethyl thioformate (HPMTF), it is possible to reduce biases in the prediction of key products such as SO₂ and MSA. The inclusion of these species and associated reactions are expected to improve the modeled representation of the sulfur cycle in the global marine troposphere, as well as the modeled representation of the sulfur budget over coastal areas around the world. Preliminary investigations using GC-TOMAS microphysics simulations show an overall reduction in sulfate aerosol formation with greatest regional impact on small aerosol number concentration. In very polluted regions, integrated DMS mechanism increases sulfate aerosol formation closest to major anthropogenic sulfur emission sources, with decreases further downwind. Overall, this can have important implication for the prediction of air quality and climate impacts around the world.

Impact of nitrous acid and formaldehyde on radical production in biomass burning plume

Katie Tuite, Nathaniel Brockway, Jennie Thomas, Jochen Stutz

UCLA

Biomass burning is one of the largest sources of primary and secondary pollutants to the global atmosphere, and has significant impacts to air quality. Formation of secondary pollutants like ozone and secondary organic aerosol is dependent on HO_x radical concentrations within plumes. Nitrous acid (HONO) and formaldehyde (HCHO) are thought to be two of the main radical sources in young smoke since they are directly emitted from fires and quickly photolyze to give OH and HO₂. HONO in particular can photolyze at higher wavelengths so is especially important in the low light conditions typical of thick smoke. Measurements of HONO within plumes are sparse, however, causing uncertainty in HONO's role in radical formation. The FIREX-AQ experiment provided an opportunity to study HONO and HCHO chemistry in biomass burning plumes throughout the United States. UCLA's airborne Differential Optical Absorption Spectroscopy (DOAS) instrument was deployed on the NASA DC-8 aircraft to collect remote sensing measurements of trace gases. Here we present HONO and HCHO observations from early plumes with a smoke age of a few hours or less. These measurements are used to investigate HO_x formation rates and better constrain plume radical budgets.

Vertical Ozone Profile Measurements in Riverside

Zihan Zhu, Don Collins

University of California, Riverside

The understanding of atmospheric processes and the corresponding influence on air quality relies on the comprehensive characterization of different atmospheric gas and particle-phase species in three dimensions. In addition to the traditional ground measurements, unmanned aerial vehicles (UAVs) have received increasing attention over the past few years for their potential use in the field study. This study presents the results from the routine measurement of the vertical profile of ozone over Riverside from August 2020 to November 2020. Total 616 vertical profiles of ozone concentration, PM 2.5, PM 10, temperature, and relative humidity were collected from surface to 500 m above ground level during early morning and late afternoon by use of embedded sensors on the UAV. The ozone profiles measured exhibit different features under different atmospheric conditions. The multi-month dataset was processed statistically.

Mini Talk Presentation Session 2B

Moderator: Dr. Zhuangjie Li

Zoom Link:

<https://fullerton.zoom.us/j/81285120166?pwd=QTJnc0x5NTRXVUNibDhOS283UEUwUT09>

Time	Presenter Name	Affiliation	Title of Mini Presentation	Page
2:45	Vahe Baboornian	University of California, Irvine	Humidity dependent viscosity and phase state of the photo-recalcitrant fraction of biogenically derived SOA	29
2:55	Nathaniel Brockway	UCLA AOS Department	Remote Sensing of Biomass Burning Emissions	30
3:05	Yumeng Cui	University of California, Riverside	Secondary Organic Aerosol Particles from Continuous-flow Chamber Experiments	31
3:15	Ying Li	University of California Irvine	Predictions of the glass transition temperature and viscosity of organic aerosols from volatility distributions	32
3:25	Nilofar Raeofy	University of California, Riverside	Chemical Characterization of Secondary Organic Aerosols from Nighttime Oxidation of Thiophene	33
3:35	Jiaqi Shen	University of California, Los Angeles	Ascorbate Oxidation by Iron, Copper and Reactive Oxygen Species: Review, Model Development, and Derivation of Key Rate Constants	34
3:45	Natalie Smith	UC-Irvine	Viscosity and liquid-liquid phase separation in healthy and stressed plant SOA	35
3:55	James (Young Suk) Yoon	UCLA	Investigating surface mixing's effect on HONO chemistry using the PACT-1D atmospheric model	36

Humidity dependent viscosity and phase state of the photo-recalcitrant fraction of biogenically derived SOA

Vahe J. Baboornian, Giuseppe Crescenzo, Yuanzhou Huang, Fabian Mahrt, Allan K. Bertram, Sergey A. Nizkorodov

University of California, Irvine

The viscosity and phase state of atmospheric aerosols are key components in predicting their atmospheric lifetimes and understanding their multiphase reactivity as well as effects on climate. Aerosols undergo photochemical aging while being transported throughout the atmosphere - particularly in the free troposphere where they can remain for longer. Recently, studies have shown that long term photodegradation of secondary organic aerosol (SOA) results in a noticeable difference in composition and the formation of a non-degrading, or photo-recalcitrant fraction of SOA. The viscosity and phase state of this non-degrading fraction is currently unknown and is crucial to fully understand its implications on climate and the atmosphere. To address this, we experimentally measured the humidity dependent viscosity, diffusion rates, and phase of the photo-recalcitrant fraction of biogenically derived SOA. Our results show that photochemically aged particles have increased viscosity as much as 5 orders of magnitude compared to control samples and undergo liquid-liquid phase separation at lower relative humidity values. These experimentally determined viscosities overlap well with parameterization model predictions based on the composition of the recalcitrant fraction determined by high resolution mass spectrometry analysis.

Remote Sensing of Biomass Burning Emissions

Nathaniel Brockway, Katie Tuite, Jochen Stutz

UCLA AOS Department

Biomass burning plumes can produce large amounts of ozone and SOA that can be transported hundreds of kilometers from the source. Secondary pollutant production is largely dependent upon radical chemistry. Therefore, the two largest sources of HO_x, HONO and HCHO, greatly influence the chemistry of biomass burning plumes.

HONO, in particular, provides an early source of radicals in biomass burning smoke due to its fast photolysis. This fast photolysis also makes measurements of HONO emissions difficult, as in-situ observations are made after photolysis has occurred.

The UCLA Mini-DOAS instrument was deployed onboard the NASA DC-8 during FIREX-AQ for this reason. This is a remote sensing instrument that can measure UV-Vis absorbers in the youngest smoke directly emitted from a fire. Here, I will present the methods used to remotely measure trace gases in biomass burning plumes, our analysis techniques, and our current understanding of HONO emission from biomass burning.

Secondary Organic Aerosol Particles from Continuous-flow Chamber Experiments

Yumeng Cui, Roya Bahreini

University of California, Riverside

Photochemical chamber experiments are widely used to study the gas-phase and particle-phase chemistry, and aerosol formation. The results from laboratory chamber studies have been widely applied to atmospheric models to understand the ambient organic aerosols and estimate their radiative effect. The traditional batch chamber experiments are usually carried out with certain amounts of hydrocarbon, oxidant, NO/NO₂ and other reactants; however, oxidation conditions may not remain the same throughout the experiment. On the other hand, continuous flow chambers that include continuous/stepwise injection of the oxidant and/or reactants could control the reaction conditions better. In this work, we examine the influence of the injection scheme on chemical and optical properties of the resulting secondary organic aerosol (SOA) particles. Specifically, we will compare results from batch photooxidation reactions of 1-methylnaphthalene and longifolene in the presence of HONO and NO (effective OH concentration $\sim 3.6 \times 10^7$ molecules cm⁻³) with those under a continuous flow of H₂O₂ and stepwise injections of NO (effective OH concentration $\sim 1.1 \times 10^7$ molecules cm⁻³). The chemical and optical properties of the resulting SOA are analyzed with multiple online instruments including a compact time-of flight aerosol mass spectrometer (C-ToF-mAMS) and a photoacoustic extincionimeter (PAX-375) and provide details on nitro organic/organ nitrate formation, single scattering albedo (SSA) and mass absorption coefficient (MAC) of the SOA.

Predictions of the glass transition temperature and viscosity of organic aerosols from volatility distributions

Ying Li, Douglas A. Day, Harald Stark, Jose L. Jimenez and Manabu Shiraiwa

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Volatility and viscosity are important properties of organic aerosols (OA), affecting aerosol processes such as formation, evolution and partitioning of OA. Volatility distributions of ambient OA particles have often been measured, while viscosity measurements are scarce. We have previously developed a method to estimate the glass transition temperature (T_g) of an organic compound containing carbon, hydrogen, and oxygen. Based on analysis of over 2400 organic compounds including oxygenated organic compounds as well as nitrogen- and sulfur-containing organic compounds, we extend this method to include nitrogen- and sulfur-containing compounds based on elemental composition. In addition, parameterizations are developed to predict T_g as a function of volatility and the atomic oxygen-to-carbon ratio based on a negative correlation between T_g and volatility. This prediction method of T_g is applied to ambient observations of volatility distributions at eleven field sites. The predicted T_g of OA under dry conditions vary mainly from 290 K to 339 K and the predicted viscosities are consistent with the results of ambient particle phase state measurements in the southeastern US and the Amazonian rain forest. Reducing the uncertainties in measured volatility distributions would improve predictions of viscosity especially at low relative humidity. We also predict the T_g of OA components identified via positive matrix factorization of aerosol mass spectrometer data. The predicted viscosity of oxidized OA is consistent with previously reported viscosity of SOA derived from α -pinene, toluene, isoprene epoxydiol (IEPOX), and diesel fuel. Comparison of the predicted viscosity based on the observed volatility distributions with the viscosity simulated by a chemical transport model implies that missing low volatility compounds in a global model can lead to underestimation of OA viscosity at some sites. The relation between volatility and viscosity can be applied in the molecular corridor or volatility basis set approaches to improve OA simulations in chemical transport models by consideration of effects of particle viscosity in OA formation and evolution.

Chemical Characterization of Secondary Organic Aerosols from Nighttime Oxidation of Thiophene

Nilofar Raeofy, Kunpeng Chen, Raphael Mayorga, Haofei Zhang, Ying-Hsuan Lin, Roya Bahreini

University of California, Riverside

NO₃-initiated oxidation of unsaturated heterocyclic volatile organic compounds (VOC) contributes to brown carbon (BrC) formation in biomass burning plumes (Jiang, et al., 2019). These oxidation reactions lead to the formation of condensable nitrogen- and sulfur-containing products that can act as chromophores of BrC aerosols. Here, we investigated the NO₃-oxidation products of thiophene (C₄H₄S) as a possible precursor for BrC formation. Chemical composition of the resulting secondary organic aerosols (SOA) was obtained using a mini-Aerosol Mass Spectrometer coupled with a compact time-of-flight detector (mAMS) and a Filter Inlet for Gases and AEROsols coupled to a chemical ionization high-resolution time-of-flight mass spectrometer (FIGAERO-CIMS). From the high-resolution mass spectrometric analysis from mAMS, we investigated the fragmentation patterns of different species with a specific focus on the nitrogen- and sulfur- containing families. The fraction of C_xH_ySO_z⁺ (dominated by CHS⁺ and C₂H₂S⁺) over total organic species decreased slightly with oxidation while that of C_xH_yN⁺ family increased. Detection of organosulfur fragments in mAMS was consistent with results from FIGAERO-CIMS which also showed trace amounts of organosulfur compounds present in the aerosol phase (e.g., C₄H₃NO₄S and C₄H₅NO₇S). SO₂⁺, SO₃⁺, HSO₃⁺, and H₂SO₄⁺ fragmentation patterns relative to SO⁺ were compared to those of ammonium sulfate to better understand formation of sulfur- containing species in this system. Finally, because nitrogen- and sulfur-containing SOA (Nguyen, et al., 2012) may contribute to light absorption, the chemical composition results will be compared with the time trace of optical properties (e.g., mass absorption coefficient (MAC) measured by a photoacoustic extincionimeter (PAX) at 375 nm) to elucidate BrC chromophores in the system.

Reference:

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Ascorbate Oxidation by Iron, Copper and Reactive Oxygen Species: Review, Model Development, and Derivation of Key Rate Constants

Jiaqi Shen, Paul T. Griffiths, Steven J. Campbell, Battist Uttinger, Markus Kalberer and Suzanne E. Paulson

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Ascorbic acid is among the most abundant antioxidants in the lung, where it likely plays a key role in the mechanism by which particulate air pollution initiates a biological response. Because ascorbic acid is a highly redox active species, it engages in a far more complex web of reactions than a typical organic molecule, reacting with oxidants such as the hydroxyl radical as well as redox-active transition metals such as iron and copper. The literature provides a solid outline for its chemistry, but there are large disagreements about mechanisms, stoichiometries and reaction rates, particularly for transition metal reactions. Here we synthesize this literature, develop a chemical kinetics model, and use seven sets of laboratory measurements to constrain mechanisms for the iron and copper reactions and derive key rate constants. We find that micromolar concentrations of iron(III) and copper(II) are more important sinks for ascorbic acid (both AH_2 and AH^-) than reactive oxygen species. The iron and copper reactions are catalytic rather than redox reactions, and have unit stoichiometries: $Fe(III)/Cu(II) + AH_2/AH^- + O_2 \rightarrow Fe(III)/Cu(II) + H_2O_2 + \text{products}$. Rate constants are 5.7×10^4 and $4.7 \times 10^4 \text{ M}^{-2}\text{s}^{-1}$ for $Fe(III) + AH_2/AH^-$ and 7.7×10^4 and $2.8 \times 10^6 \text{ M}^{-2}\text{s}^{-1}$ for $Cu(II) + AH_2/AH^-$, respectively.

Viscosity and liquid-liquid phase separation in healthy and stressed plant SOA

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Molecular composition, viscosity, and liquid-liquid phase separation (LLPS) were investigated for secondary organic aerosol (SOA) derived from synthetic mixtures of volatile organic compounds (VOC) representing emission profiles for Scots pine trees under healthy and aphid-herbivory stress conditions. Model “healthy plant SOA” and “stressed plant SOA” were generated in a 5 m³ environmental smog chamber by photooxidation of the mixtures at 50% relative humidity (RH). SOA from photooxidation of α -pinene was also prepared for comparison. Molecular composition was determined with high resolution mass spectrometry, viscosity was determined with the poke-flow technique, and liquid-liquid phase separation was investigated with optical microscopy. The stressed plant SOA had increased abundance of higher molecular weight species, reflecting greater fraction of sesquiterpenes in the stressed VOC mixture compared to the healthy plant VOC mixture. LLPS occurred in both the healthy and stressed plant SOA; however, stressed plant SOA exhibited phase separation over a broader humidity range than healthy plant SOA, with LLPS persisting down to $23 \pm 11\%$ RH. At RH $\leq 25\%$, both stressed and healthy plant SOA viscosity exceeded 108 Pa s, value similar to tar pitch. At 40% and 50% RH, stressed plant SOA had the highest viscosity, followed by healthy plant SOA and then α -pinene SOA in descending order. The observed peak abundances in the mass spectra were also used to estimate the SOA viscosity as a function of RH and volatility. The predicted viscosity of the healthy plant SOA was lower than that of the stressed plant SOA driven by both the higher glass transition temperatures and lower hygroscopicity of the organic molecules making up stressed plant SOA. These findings suggest that plant stress influences the physicochemical properties of biogenic SOA. Furthermore, a complex mixture of VOCs resulted in a higher SOA viscosity compared to SOA generated from α -pinene alone at $\geq 25\%$ RH, highlighting the importance of studying properties of SOA generated from more realistic multi-component VOC mixtures.

Investigating surface mixing's effect on HONO chemistry using the PACT-1D atmospheric model

James (Young Suk) Yoon, Katie Tuite, Jochen Stutz

UCLA

Photochemical smog is a prominent issue in urban basins, with OH's oxidizing ability being central in the tropospheric ozone production. Nitrous acid (HONO) is a OH precursor, with HONO photolysis being the dominant OH source during early morning. HONO has been the subject of recent interest due to the uncertainty of its heterogeneous surface formation mechanisms. This presentation investigates how surface mixing affects HONO chemistry, focusing on how sensitive HONO concentrations and surface chemistry are to changes in turbulent mixing. Using the PACT-1D atmospheric model, we ran sensitivity studies that varied the eddy diffusion coefficients (K_z) in the lowest 20 meters. We observed that increases in surface mixing resulted in elevated levels of HONO above the surface and that increased HONO levels were primarily due to decreased HONO deposition. Although total HONO surface production had a limited response to mixing changes, individual formation mechanisms were more sensitive during the day, with higher mixing decreasing HONO production from NO_2 mechanisms and increasing production from nitric acid photolysis and acid displacement. These findings demonstrate how changes in the atmosphere's physical properties can alter HONO levels and the relative significance of HONO surface mechanisms.