

Atmospheric Chemical Mechanisms Conference

Book of Abstracts

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Keynote: Considering Multiple Dimensions of Complexity in Atmospheric Chemistry Models

Invited Presentation, Oral Presentation,

Presented By: Kelley Barsanti, *University of California Riverside; National Center for Atmospheric Research*

Chemical mechanisms describe the reactivity of compounds in the gas phase. Due to computational constraints, most widely used chemical mechanisms have been simplified (i.e., reduced), such that a limited number of reaction pathways, intermediates, and products are considered when applied in air quality models. The reduction approaches largely were developed when extreme ozone formation events under high nitrogen oxides (NO_x) levels were the primary regulatory concern. Advances in emissions control technologies and successful regulatory and mitigation efforts have succeeded in shifting our atmosphere to a regime in which chemistry under lower NO_x levels has become increasingly important, multipollutant predictions at lower concentrations are required, and new sources of pollutants are emerging. Wildland fires are one such emerging source, and will be used here to illustrate multiple dimensions of complexity in the application, development, and reduction of chemical mechanisms for air quality modeling. The representation of hundreds of organic compounds by a limited number of model surrogates, the linkages between gas-phase chemistry and secondary organic aerosol formation, and the sensitivity of predicted air quality endpoints to complexity in model representation will be presented. This presentation reflects over a decade of collaborative research seeking to improve model representation of secondary pollutants, including from emerging sources and under evolving conditions.

Additional Authors: Samiha Binte Shahid, UC Riverside, Jia Jiang, UC Davis, Qi Li, UC Riverside, David Cocker, UC Riverside, Julia Lee Taylor, NCAR, Louisa Emmons, NCAR, John Orlando, NCAR, Christine Wiedinmyer, CIRES/NOAA, Robert Yokelson, University of Montana, William Carter, UC Riverside

Plenary: Deeper insight into atmospheric reaction systems from the laboratory: RO₂ isomerization and ROOOH formation

Invited Presentation, Oral Presentation,

Presented By: Torsten Berndt, *TROPOS Leipzig*

Biogenic and anthropogenic emissions are released into the Earth's atmosphere with a total annual strength in the order of 10⁹ metric tons of carbon. The detailed understanding of their oxidation pathways is still a challenging task. For example, in the last years it has been discovered that isomerization steps of peroxy (RO₂) radicals, which represent the key intermediates in the course of atmospheric oxidation, can outrun the "traditional" bimolecular

RO₂ radical reactions with NO or HO₂ radicals, resulting in a distinctly changed product distribution.

In our laboratory measurements, we use flow systems that allow for the investigation of the early stages of an oxidation reaction for close to atmospheric conditions. Direct monitoring of RO₂ radicals and resulting closed-shell products is carried out by chemical ionization mass spectrometry applying a set of different reagent ions. Detection limits for oxidized compounds can be as low as 10⁽³⁾ - 10⁽⁴⁾ molecules cm⁽⁻³⁾, i.e., below ppq level. The reaction conditions are chosen in such a way that solely the formation of initially formed RO₂ radicals and their unimolecular pathways can be studied. Addition of a second reactant allows to follow the product formation from a selected bimolecular RO₂ radical step. Possibilities and limits of this experimental approach are discussed.

Recent results on RO₂ radical isomerization and hydrotrioxide (ROOOH) formation in the OH + isoprene reaction are presented.

Additional Authors: Andreas Tilgner, TROPOS Leipzig, Erik H. Hoffmann, TROPOS Leipzig, Frank Stratmann, TROPOS Leipzig, Hartmut Herrmann, TROPOS Leipzig,

Atmospheric Chemistry in Public Health and Regulatory Applications

Characterizing the impact of volatile chemical products (VCPs) and cooking on air quality in major US cities

Invited Presentation, Oral Presentation,

Presented By: Matthew Coggon, *National Oceanic and Atmospheric Administration*

Declining emissions from motor vehicles in US cities has resulted in an urban atmosphere where understudied sources of pollution - such as consumer products, solvent use, and cooking emissions – are becoming the dominant source of urban VOCs. Recent work has shown that volatile chemical products (VCPs) are as important to urban VOCs as fossil fuel emissions. Chemical transport models used to simulate urban air quality often misrepresent the magnitude and chemistry of VCP emissions, which leads to uncertainty in simulations of ozone. For example, oxygenated VOCs such as glycols and glycol ethers are major ingredients in consumer VCPs, but their chemistry is often represented by lesser-reactive hydrocarbons in reduced chemical mechanisms. In this presentation, we will demonstrate the impact of VCP emissions and chemistry on air quality simulations of ozone and other secondary air pollutants in New York City. We will show that VCP emissions significantly contribute to maximum daily 8-hr ozone, and that the representation of VCP emissions using oxygenated VOC chemistry significantly impacts simulations of peroxy acyl nitrates (PANs), a reservoir for NO_x. We will also

present recent evidence that points to the important role that cooking VOCs have on urban reactivity. Cooking VOCs constitute another source of urban air pollution that requires further investigation.

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Accounting for the chemistry of reactive toxic VOCs for community level modeling

Invited Presentation, Oral Presentation,

Presented By: Zhen Liu, *California Air Resources Board*

Community level exposure modeling and health risks analysis may need to consider the chemistry of reactive toxic VOCs. While conducting full chemical transport modeling at a community level remains challenging, we utilize a hybrid approach that involves dispersion modeling and post-modeling adjustment derived by a 0-D or 1-D chemistry model using an explicit (MCM) or condensed (e.g., SAPRC07) chemical mechanism. Chemistry adjustment factors are estimated to reflect the effects from both photochemical loss and secondary production. Sensitivity modeling analysis shows that the extent of chemistry effect is a function of the residence time of individual toxic VOCs and their precursors within the community of interest. The upper bound of secondary production of carbonyls (e.g., formaldehyde and acetaldehyde) is estimated through mass balance calculations based on emission inventories and chemistry product yields. We will present results from two case studies in California and discuss the implications for future modeling of toxic VOCs at a community level.

Additional Authors: Pingkuan Di, CARB, Jeremy Avise, CARB

Long-term Trends of Impacts of Global Gasoline and Diesel Emissions on Air Quality and Human Health for 2000-2015

Oral Presentation,

Presented By: Ying Xiong, *Wayne State University*

Global economic development and urbanization during the past two decades have likely caused changes in vehicle tailpipe emissions associated with aerosols and trace gases. However, long-term trends of impacts of global gasoline and diesel emissions on air quality and human health are not clear. Here we employ the CESM CAM6-Chem in conjunction with the Community

Emissions Data System (CEDs) to quantify the long-term trends of impacts of global gasoline and diesel emissions on air quality and human health for the period of 2000-2015. Global gasoline and diesel emissions contributed to regional increases in annual mean surface PM_{2.5} concentrations by up to 17.5 and 13.7 $\mu\text{g}/\text{m}^3$, and surface O₃ concentrations by up to 7.1 and 7.2 ppbv, respectively, for 2000-2015. However, we found substantial declines of surface PM_{2.5} and O₃ concentrations over Europe, the US, Canada, and China for the same period, which suggested the co-benefits of air quality and human health from improving gasoline and diesel fuel quality and tightening vehicle emissions standards. Globally, we estimate the mean annual total PM_{2.5}- and O₃-induced premature deaths are 139,700-170,700 for gasoline and 205,200-309,300 for diesel, with the corresponding years of life lost of 2.74-3.47 and 4.56-6.52 million years, respectively. Diesel and gasoline emissions create health-effect disparities between the developed and developing countries, which are likely to aggravate afterwards.

Additional Authors: Yaoxian Huang, Wayne State University

Optimization of air pollutant control policy based on the nonlinearity of atmospheric chemistry

Invited Presentation, Oral Presentation,

Presented By: Jia Xing, Tsinghua University

Serious ambient PM_{2.5} and O₃ pollution is one of the most important current environmental challenges of China, necessitating an urgent cost-effective co-control strategy. Herein, we introduced a novel integrated assessment system to optimize the multiple air pollutant control strategy for the synergistic reduction of ambient pollution and associated impacts on human health and ecosystem. Focusing on the Beijing–Tianjin–Hebei cities and their surrounding regions, which experience the most serious PM_{2.5} and O₃ pollution in China, we determined that NO_x emissions reduction (64%–81%) is absolutely essential to meet the air quality standard no matter how much VOCs emission is reduced. However, the synergistic VOCs control is strongly recommended when considering substantially human health and crop production benefits. Notably, such benefits will be greatly reduced if the synergistic VOC reduction is delayed. NH₃ abatement still remain controversial in China for its effectiveness in reducing PM_{2.5} pollution and nitrogen deposition but with potential risk in enhancing acid rain. We further extended the response surface model to deposition and found that one third of Yangtze River Delta cities exhibit considerable large (15%-71%) NH₃ control potentials which become even greater when more strengthened controls are applied on SO₂ and NO_x. Greater NH₃ control potential towards to more strengthened air quality standards, leading to additional avoided premature deaths with limited cost.

Additional Authors: Dian Ding, Tsinghua University, Zhaoxin Dong, Tsinghua University, Shuxiao Wang, Tsinghua University

Chemical Regimes

Ozone photochemistry and free radical budgets in the Los Angeles basin: A comparison of ground-based observations in 2021 and 2010

Oral Presentation,

Presented By: Michael Robinson, *NOAA CSL*

Radical precursors and termination products are important factors to understanding sensitivities of ozone (O₃) production to nitrogen oxides (NO + NO₂ = NO_x) and volatile organic compounds (VOCs). During the summer of 2021, an extensive set of photochemical measurements were conducted at a ground site on the Caltech campus in Pasadena, CA to evaluate emissions and photochemistry in the Los Angeles (LA) basin. Here we present measurements of important radical precursors and compare them to observations from the CalNex 2010 field intensive. Major radical sources include formaldehyde (HCHO) and other aldehydes, nitrous acid (HONO), nitryl chloride (ClNO₂), ozonolysis of alkenes, and O(1D) + H₂O. In addition to radical precursors, radical termination products were measured, including peroxy acetyl nitrates (PAN), nitric acid (HNO₃), organic nitrates and organic peroxides. The comparison of radical precursors and termination products illustrates shifts in photochemical regime resulting from NO_x and VOC emissions changes over the past ten years in the LA basin, as well as other influences such as temperature, seasonality and day of week.

Additional Authors: J. Andrew Neuman, NOAA/CIRES, Patrick R. Veres, NOAA, James M. Roberts, NOAA, Matthew M. Coggon, NOAA, Lu Xu, NOAA/CIRES, Carsten Warneke, NOAA, Chelsea Stockwell, NOAA/CIRES, Jessica B. Gilman, NOAA, Aaron Lamplugh, CU-Boulder, Andrew W. Rollins, NOAA, Kristen L. Zuraski, NOAA/CIRES, Jeff Peischl, NOAA/CIRES, Shang Liu, CARB, Toshihiro Kuwayama, CARB, Jason Surratt, UNC, Steven S. Brown, NOAA

Chemistry of Reactive Organic Gases in Mega-cities of China: Insights from Vertical Gradient and Eddy Covariance Flux Measurements

Invited Presentation, Oral Presentation, Virtual

Presented By: Bin Yuan, *Jinan University*

The oxidation of reactive organic gases contributes to the formation of ozone and fine particles. A large number of organic gases with different formula, structure, and reactivity are emitted in urban regions from various sources (e.g., vehicles, solvent and fuel evaporation, plants). However, the chemistry of reactive organic gases and the subsequent effects to secondary pollution remain with large uncertainties. In recent few years, my group conducted vertical

gradient measurements and eddy covariance flux measurements in mega-cities of China, including Beijing, Shenzhen and Guangzhou. These measurements along with ground-based observations of reactive organic gases provide additional constraints on the chemistry of these species and their contributions to ozone and particle formation.

Additional Authors: Xiaobing LI, Jinan Univ., Yibo Huangfu, Jinan Univ., Xianjun He, Jinan Univ., Xin Song, Jinan Univ., Sihang Wang, Jinan Univ., Yubin Chen, Jinan Univ., Suxia Yang, Jinan Univ., Min Shao, Jinan Univ.

An exploration of changing ozone production under new chemical regimes in three cities

Invited Presentation, Oral Presentation,

Presented By: Beth Nelson, *University of York*

Understanding how changing chemical regimes impacts the formation of harmful secondary pollutants, such as ozone, is crucial in megacities and urban centres where most of the global population live. Chemical box models are important tools used to understand the detailed chemical processes occurring in any atmospheric environment. Where chemically detailed observational data is available, tailored box models can be used to investigate the key drivers for in situ ozone production.

Observational data from three recent field campaigns in Beijing, Delhi and Manchester has been used to constrain chemical box models and investigate in situ ozone formation. These models incorporate the near explicit Master Chemical Mechanism (MCM), which allows for the modelling of detailed oxidation chemistry. The concentrations of both volatile organic compounds (VOCs) and NO_x are varied, revealing insights into how ozone production may change under future chemical regimes, where different air quality and climate policies are implemented. This work investigates the current chemical regimes in the three cities and explores changes in ozone production under future emission scenarios. The sensitivity of ozone production to chemical species, both individually and grouped by class, is also examined. A detailed understanding of the chemical processes leading to ozone production will play a crucial role in informing on how future pollution and climate policies will impact urban air quality.

Additional Authors: James Lee, University of York, Andrew Rickard, University of York, Jim Hopkins, University of York, Jacqui Hamilton, University of York

THE DEVELOPMENT OF AN ISOPRENE MECHANISM FOR ANOXIC ATMOSPHERES AND THE IMPLICATIONS FOR TRANSMISSION SPECTRA FOR N₂-RICH EXOPLANETS

Oral Presentation,

Presented By: Alexander ARCHIBALD, *University of Cambridge & NCAS-Climate*

With continuing advances in exoplanetary detection and transmission spectra resolution, the accurate modelling of potential biological signatures (biosignatures) in exoplanet atmospheres has become an important area of scientific research. In this study, the first extended exoplanet mechanism for isoprene, a specialised biosignature with no known geochemical source, has been developed and implemented into ARGO, a one-dimensional numerical model. From simulations of four N₂-rich exoplanet atmospheres, isoprene was found to be the most promising isoprenoid biosignature.

The concept of isoprene as a photon sink is proposed, acting to slow CO₂ photolysis, and a possible transition from CO₂-initiated to isoprene-initiated CH₂O formation with increasing isoprene emissions is identified. The implications of these regimes for carbonyl transmission spectra at 5.7 μm are discussed, with the potential for alterations in transmission possible below Earth emissions of isoprene in simulations with the early Sun. Additionally, the contributions of isoprene decomposition products and CH₂O to the overall carbonyl optical depth are found to be comparable in some cases. The newly developed anoxic chemistry is found to dominate (>10¹⁴ times) over previously known isoprene (O₂-rich) kinetics; therefore, we encourage its integration into pre-existing numerical models, originally designed to model the atmosphere of modern Earth, in future studies of isoprene in exoplanet atmospheres.

Additional Authors: Thomas Elgar, University of Cambridge, Paul Rimmer, University of Cambridge

Fundamental Studies of Atmospheric Chemical Mechanisms

Speciated Monitoring of Organic Peroxy Radicals with Proton-Transfer Mass Spectrometry: First applications in the laboratory

Invited Presentation, Oral Presentation,

Presented By: Barbara Noziere, *KTH, Royal Institute of Technology*

In spite of important progress over the last decade, the chemistry of organic peroxy radicals ("RO₂") in Earth's atmosphere is still not fully understood. This presentation reports the

development of mass spectrometric approaches based on proton transfer ionization with the objective of monitoring individual RO₂ in the atmosphere.

First applications of these techniques to the investigation of RO₂ reactions and mechanisms in laboratory are also presented, in particular, the first study of RO₂ + alkene reactions under atmospheric conditions (298 K). A kinetic study, performed in a flow reactor and monitoring the consumption of individual RO₂ by alkenes, reported significantly larger rate coefficients (x10 to x100) than expected from high-temperature literature data. A product study then showed that the slow epoxide formation channel proposed in the literature was not the main reaction pathway under atmospheric conditions, but was bypassed by a faster peroxy radical formation channel. Thus, under atmospheric conditions these reactions are not kinetically limited by the epoxide formation but by the first (and faster) addition step, in agreement with our recent kinetic study. In the atmosphere, the RO₂ sinks due to their reactions with unsaturated compounds such as isoprene or terpenes would be more significant than expected until now from the literature data, and possibly non-negligible for some RO₂. Monitoring individual RO₂ is thus important even in laboratory investigations.

Additional Authors: O. Durif, E. Dubus, Department of Chemistry, KTH, Royal Institute of Technology, Stockholm, Sweden; F. Fache, Université Lyon 1, CNRS, UMR 5246, ICBMS, Villeurbanne, France

Reconciling Disparate Mechanisms for Oxidation of Hg(0) to Hg(II) in the Gas Phase

Oral Presentation,

Presented By: Theodore Dibble, *State University of New York - Environmental Science and Forestry*

Quantum calculations and experiment support a two-step oxidation of Hg(0) by Br via a BrHg• intermediate. BrHg• is sufficiently stable to react with NO₂, HOO, and other atmospheric radicals to form stable Hg(II) compounds. The analogous HOHg• intermediate in the OH-initiated oxidation of Hg(0) is much less stable, and had been thought to decompose rather than forming Hg(II), except in the uppermost troposphere.

We recently found that HOHg• can react with ozone to form a radical form of Hg(II), namely, HOHgO•. Assuming the same rate constant as that recently measured for the analogous BrHg• + ozone reaction, the fraction of HOHg• forming Hg(II) easily reaches 50% in the continental U.S. boundary layer and 100% above 6-8 km.

Many chemical transport models have assumed irreversible oxidation of Hg(0) to Hg(II) by OH and ozone, separately. These assumptions ignore the fact that no known thermodynamically and kinetically plausible mechanism can rationalize these oxidations under atmospheric

conditions. Models of mercury over continental areas tend to require these implausible reactions (as opposed to Br-initiated oxidation) to explain field observations. We expect that modelers will no longer need to invoke those unlikely mechanisms once they incorporate our new results: that OH and ozone, together in a two-step mechanism, can efficiently oxidize Hg(0) to Hg(II).

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Ozonolysis of α -pinene and Δ^3 -carene – influence of molecular structure on aerosol formation and chemistry

Invited Presentation, Oral Presentation,

Presented By: Marianne Glasius, Aarhus University, Denmark

In both experimental and model studies, α -pinene is often used as a standard monoterpene, but how well does it represent the chemistry of other monoterpenes? In a series of chamber studies combined with off-line analysis and quantum chemical calculations, we investigated the similarity in formation and composition of secondary organic aerosols (SOA) from ozonolysis of the structurally similar monoterpenes α -pinene and Δ^3 -carene. We observe that ozonolysis of α -pinene produces a higher particle number concentration than ozonolysis of Δ^3 -carene, while the SOA mass depends on experimental conditions such as the monoterpene-to-ozone ratio. More SOA mass was formed from both monoterpenes in experiments at 10C and 0C compared to 20C in line with previous work. Analysis by liquid chromatography coupled to quadrupole time-of-flight mass spectrometry shows that ozonolysis of Δ^3 -carene yields a simpler product distribution with fewer products in the particle phase compared to α -pinene, with the major product being the dicarboxylic acid cis-3-caric acid. Only few dimer esters were observed from Δ^3 -carene and at lower levels than for α -pinene. According to the quantum chemical calculations cis-3-caric acid is expected to be more efficient in condensing on already existing particles compared to the analogue cis-pinic acid from α -pinene, in good agreement with the experimental results. Recent results from studies of ozonolysis of mixtures of α -pinene and Δ^3 -carene will also be presented.

Additional Authors: Ditte Thomsen, Aarhus University, Lotte Dyrholm Thomsen, Aarhus University, Emil Mark Iversen, Aarhus University, Þuríður Nótt Björgvinsdóttir, Aarhus University, Sofie Falk Vinther, Aarhus University, Jane Tygesen Skønager, Aarhus University, Thorsten Hoffmann, Johannes Gutenberg University, Mainz, Bernadette Rosati, Aarhus University, Jonas Elm, Aarhus University, Merete Bilde, Aarhus University.

Investigating the Atmospheric Oxidation of Methylamine with Multiplexed Photoionization Mass Spectrometry: Insight into the Reactivity of C-centered and N-centered Radicals with O₂

Oral Presentation,

Presented By: Sommer Johansen, *Sandia National Laboratories*

CO₂ capture and storage relies heavily on amine-based adsorbents. This has resulted in an increase in emissions of these amines and their degradation products into the atmosphere, necessitating an in-depth understanding of their atmospheric oxidation pathways. Methylamine (CH₃NH₂) is a common degradation product of CO₂ capture agents and is also emitted through other natural and anthropogenic processes. Here, we present experimental results of the oxidation of CH₃NH₂ using multiplexed time-resolved photoionization mass spectrometry coupled to tunable synchrotron VUV radiation from the Chemical Dynamics Beamline at the LBNL Advanced Light Source. This sensitive probe method enables simultaneous measurements of multiple products and transient intermediates. CH₂NH₂ and CH₃NH were produced within a slow-flow quartz reactor tube through the reaction of CH₃NH₂ with either OH or Cl, generated by pulsed-laser photolysis of H₂O₂ and Cl₂, respectively, before reacting with O₂. Using selectively deuterated methylamine (CD₃NH₂), we were able to discriminate between the CH₂NH₂ and CH₃NH reaction channels. Potential energy surfaces were calculated with the program KinBot at the CCSD(T)-F12a/cc-pVDZ-F12// ω B97X-D/6-311++G(d,p) level of theory to assist with intermediate and product identification. We will discuss our efforts to quantify the reaction kinetics of this system, and what our results demonstrate about the differences in reactivity between the C-centered and N-centered radicals.

Additional Authors: Arkke Eskola, University of Helsinki, Leonid Sheps, Sandia National Laboratories, Judit Zador, Sandia National Laboratories, Kendrew Au, Sandia National Laboratories

Particle-Phase Accretion Forms Dimer Esters in Pinene Secondary Organic Aerosol

Oral Presentation,

Presented By: Christopher Kenseth, *University of Washington*

For more than a decade, multifunctional dimer esters have been identified using advanced MS techniques as significant components of SOA formed from oxidation of α/β -pinene, and have been implicated as key players in new particle formation and growth, particle viscosity, and cloud condensation nuclei activity. Particle-phase reactions of closed-shell monomers (e.g., esterification and peroxyhemiacetal/diacyl peroxide decomposition) and gas-phase reactions

involving early-stage oxidation products and/or reactive intermediates (e.g., SCIs, carboxylic acids, and RO₂) have been advanced as possible dimer ester formation pathways. Due to a lack of authentic standards, however, structures of the dimer esters are inferred from accurate mass/fragmentation data and, therefore, mechanistic understanding of their formation remains unconstrained. Here, informed by detailed structural analyses (MS and MS/MS, ¹³C and ¹⁸O isotopic labeling, and H/D exchange), we synthesize the first authentic standards of several major dimer esters identified in SOA from ozonolysis of α/β -pinene. Based on a series of targeted environmental chamber experiments using LC/ESI-MS for analysis of SOA molecular composition, we conclusively demonstrate that these dimer esters are formed through particle-phase chemistry and propose a unifying accretion mechanism that accounts for the observed regioselectivity, dynamics, and environmental dependencies (e.g., oxidant type and RO₂ fate) of ester formation.

Additional Authors: Nicholas Hafeman, Caltech, Samir Rezgui, Caltech, Yuanlong Huang, Caltech, Nathan Dalleska, Caltech, Brian Stoltz, Caltech, Paul Wennberg, Caltech, John Seinfeld, Caltech

Tunneling, Roaming, and Oligomerization Kinetics of Criegee Intermediates Elucidated through Theory and Experiment

Invited Presentation, Oral Presentation,

Presented By: Stephen Klippenstein, *Argonne National Laboratory*

The kinetics of Criegee intermediates (CI) are challenging to study experimentally due to their highly transient nature. Furthermore, the resonance between zwitterionic and singlet diradical forms, presents challenges for theoretical studies. In recent years, the experimental challenges have been met with in situ syntheses coupled with photoionization mass spectrometry to obtain direct measurements of the thermal rate constants. Furthermore, supersonic expansion based cooling of the nascent CI together with IR excitation and UV laser induced fluorescence based detection of OH has yielded energy resolved determination of the rate constants. Meanwhile, the implementation of high level theoretical methods, based on the coupling state-of-the-art electronic structure evaluations (including multireference methods as necessary) with sophisticated transition state theory and master equation treatments, has yielded high quality predictions for the kinetics. In this talk, we will review some of our recent joint theory and experiment studies (with experiments performed by the Lester, Caravan, and Taatjes groups) of the kinetics for a variety of CIs. These studies highlight the (i) role of a multistage sequence of roaming reactions, (ii) possibility for oligomerization through successive addition of CIs, and (iii) physical aspects (tunneling, multidimensional rotors, conformational dependence, and structural effects) of the initial H transfer step in the unimolecular dissociation.

Additional Authors: None

Recent Computational Results on RO₂ + R'O₂ Reactions

Oral Presentation,

Presented By: Theo Kurtén, *University of Helsinki*

The detailed mechanism of peroxy radical self- and cross reactions (RO₂ + R'O₂) remains elusive despite the importance of the process e.g. for aerosol-related atmospheric chemistry. Using multireference methods, we have confirmed that RO₂ + R'O₂ reactions inevitably proceed via RO₄R' tetroxides, which in turn rapidly decompose to yield triplet O₂ and a triplet complex of two alkoxy radicals. This complex can further decompose to free alkoxy radicals, react to form carbonyl and alcohol products, or undergo an intersystem crossing (ISC) leading to ROOR' formation. In sufficiently complex systems, additional reaction channels, e.g. formation of ROR' products through RO scission reactions, may also be competitive.

The results of our recent computational work can be condensed into three conclusions:

- 1) The overall rate of RO₂ + R'O₂ is determined by the formation rate of the RO₄R'.
- 2) If the barrier to RO₄R' is low, this rate can be roughly estimated using simple MD techniques. When the barrier is high, transition state calculations can be applied – however high-level methods are needed to assess the barrier.
- 3) The branching ratio for ROOR' formation is determined primarily by the ISC rate of alkoxy complex intermediates. This rate, which requires expensive multireference calculations to evaluate, varies by up to 10 orders of magnitude depending on the RO₂ and on the complex conformer. This is much larger than the variation of the competing dissociation and H-shift rates.

Additional Authors: Christopher Daub, U. Helsinki, Mikael Ehn, U. Helsinki, Lauri Franzon, U. Helsinki, R. Benny Gerber, Hebrew University Jerusalem, Thomas Golin Almeida, U. Helsinki, Galib Hasan, U. Helsinki, Otso Perakyla, U. Helsinki, Matti Rissanen, U. Helsinki, Vili-Taneli Salo, U. Helsinki, Rashid Valiev, U. Helsinki, Itai Zakai, Hebrew University Jerusalem

Changes in composition and volatility of biogenic secondary organic aerosol from nitrate radical oxidation during night-to-day transition

Invited Presentation, Oral Presentation, Virtual

Presented By: Claudia Mohr, *Stockholm University*

The nitrate radical (NO₃) represents a significant night-time oxidant that is present downstream of polluted environments. Reactions with biogenic volatile organic compounds (BVOCs) can lead to the formation of biogenic secondary organic aerosol (BSOA). In this talk I will focus on novel results regarding 1) the composition of NO₃-derived BSOA and how it evolves as a result of particle-phase reactions in the dark, 2) the impacts of light exposure on the chemical composition, and 3) the volatility of BSOA formed in the dark and its changes through transition to light conditions. The insights on chemical changes at molecular level result from smog chamber experiments, where a suite of state-of-the-art instrumentation including a chemical ionization mass spectrometer with a filter inlet for gases and aerosols (FIGAERO-CIMS) and an extractive electrospray ionization time-of-flight mass spectrometer (EESI-TOF) was deployed. I will show that particle-phase composition changes as a function of particle-phase reactions during dark aging represent an important atmospheric aging pathway, and that photolysis causes photodegradation of a substantial fraction of BSOA. I will also discuss strategies for improving the predictive power of the volatility parameterizations, particularly in relation to the contribution from the nitrate group. The results from the chamber experiments will be complemented by and contrasted with ambient observations.

Additional Authors: Claudia Mohr, Cheng Wu, David Bell, Emelie Graham, Amelie Bertrand, Sophie Haslett, Urs Baltensperger, Imad El Haddad, Radovan Krejci, Ilona Riipinen

Formation of Accretion Products in the Self-Reaction of Ethene-Derived Hydroxy Peroxy Radicals

Oral Presentation,

Presented By: Sara Murphy, *California Institute of Technology*

Quantifying the relative importance of various peroxy radical pathways is crucial to understanding of the effect of anthropogenic and biogenic emissions on air quality. In the troposphere, possible bimolecular reactions of peroxy radicals include reactions with NO_x, HO_x, and other peroxy radicals. Previously, it was believed that the self-reaction of peroxy radicals in the gas-phase proceeded primarily via two pathways, forming alkoxy radicals or an alcohol and carbonyl. However, recent studies have suggested that a third pathway, forming peroxides, may proceed at rates far greater than previously expected. In this study, we measure the rate of formation of the accretion product from ethene-derived peroxy radical self-reactions using

CF3O- GC-CIMS. We demonstrate that the accretion product is formed in the gas-phase and confirm its identity by comparison to synthetic standards of the ROOR. Our results are consistent with recent suggestions that the formation of these accretion products is more important in the chemistry of the troposphere than previously recognized.

Additional Authors: John Crouse, Caltech, Nicholas Hafeman, Caltech, James Park, Caltech, Samir Rezgui, Caltech, Brian Stoltz, Caltech, Paul Wennberg, Caltech

SOA and volatile product formation from the nighttime oxidation of various terpenes, and the ICARUS database

Invited Presentation, Oral Presentation,

Presented By: Tran Nguyen, *UC Davis*

A diversity of terpenes (C₁₀H₁₆) is emitted by plants during both daytime and nighttime. Their reactions with the nitrate radical (NO₃) can represent important formation pathways for both secondary organic aerosol (SOA) and organonitrates, which in turn provide critical reservoirs or sinks for NO_x. However, the volatile product and aerosol formation of these reactions are poorly understood mechanistically, and are often heavily simplified in atmospheric models through the lumping of terpene reactants and the omission of product species. Here, we use atmospheric chamber studies to investigate the nighttime oxidation of nine abundantly emitted terpenes and pinonaldehyde, under conditions designed to mimic the biogenic-anthropogenic chemistry regime of the Southeast US, including high humidity (>60%), mixed NO₃/O₃ oxidation, and RO₂ reactivity dominated by HO₂ and RO₂. Control ozonolysis experiments enable the isolation of SOA and product yields from the NO₃ pathway. We propose mechanisms consistent with the products observed. We discuss the implications for terpene lumping methods in atmospheric models and provide model constraints for organonitrate and SOA production mixed biogenic/anthropogenic regions.

We also discuss the open-access discovery and sharing of atmospheric chamber data in the ICARUS database (<https://icarus.ucdavis.edu>) for model mechanism development, with a demonstration of database capabilities and typical data management workflows.

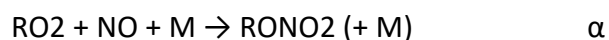
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Formation yields of organic nitrates in reactions of organic peroxy radicals with NO

Oral Presentation,

Presented By: John Orlando, *Atmospheric Chemistry Observations and Modeling (ACOM) Laboratory, NCAR*

Ozone formation in the troposphere occurs via the oxidation of volatile organic compounds (VOC) in the presence of nitrogen oxides (NO_x). Central to this process is the reaction of organic peroxy radicals (RO₂) with NO, a reaction that can occur through two pathways:



As the formation of organic nitrates occurs in parallel to NO₂ (and hence ozone) production, larger values of α coincide with reduced ozone production efficiency. Further, formation of organic nitrates (particularly as overall NO_x emissions decrease) is known to be a major NO_x sink, thus controlling NO_x levels and distributions. Despite many studies over the years regarding organic nitrate yields from numerous RO₂ (particularly those derived from alkanes), uncertainties remain.

In this study, we have conducted systematic lab studies of the yields (α) of organic nitrates formed in the oxidation of the alkanes. The work includes linear and branched species containing 5-8 carbon atoms. We demonstrate that, while nitrate yields increase with molecular size, the structure of the radical (1ry, 2ry, 3ry) has no effect. As an extension of that work, studies of ketones and ethers are being conducted, and preliminary results on these species will also be presented.

The work will provide input for more accurate modeling of air quality, and provide more confidence in mitigation strategies designed to limit the formation of ozone and other secondary pollutants.

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Oxidation of naphthalene in atmosphere: A computational perspective

Oral Presentation, Virtual

Presented By: Prasenjit Seal, *Tampere University*

Anthropogenic volatile organic compounds often dominate the urban atmosphere. Amongst them, naphthalenes are one of the most abundant aromatic hydrocarbons those are reactive in ambient atmospheres. Although benzene and toluene usually considered to be the primary anthropogenic precursors in secondary organic aerosol (SOA) formation, studies also reveal the importance of these polycyclic species. One of the chemical sink of naphthalenes in the atmosphere are their reactions with atmospheric oxidants like OH, HO₂, NO, etc. radicals and so studies of its oxidation are of paramount importance in understanding the role in aerosol formation. In this work, we focus our attention to the possible pathways leading to naphthalene oxidation in atmosphere and thereby aiming to predict formations of highly oxygenated organic molecules (HOM). Density functional theory was used as the prime investigating tool to obtain the optimized geometries of the species involved. Further refinement of the energies were made for certain systems of interest at coupled cluster level of theory and their rate constants were also estimated using master equation simulations. Our recent NO₃- inlet mass spectrometric observations also justify the possibility of HOM formation from naphthalene oxidation and hence strengthen our proposed mechanistic pathways.

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Ring-opening yield and auto-oxidation rate of the first-generation hydroxy peroxy radical (C₁₀H₁₇O₃) from OH-oxidation of α-pinene and β-pinene

Oral Presentation,

Presented By: Joel Thornton, *University of Washington*

Monoterpene oxidation contributes significantly to particle number and mass concentrations due, in part, to the ability of their peroxy radicals to undergo autoxidation leading to highly oxygenated molecules. We report on the yield of the isomer of the hydroxy peroxy radical formed from the OH radical addition to the C=C double bond, thought to be responsible for the majority of OH-initiated monoterpene-derived HOM. The OH addition leads to the opening of the C-4 ring and formation of a new C=C double bond with the shift of the alkyl radical center. We constrain the yield and autoxidation rate of this isomer by using isotopically-labeled precursors such as D₃-α-pinene and by directly measuring peroxy radicals and their fate in

competition with the reaction with nitric oxide at a fixed reaction time (~0.7 s). Based on observation of sequentially oxygenated peroxy radicals, organic nitrates, and alkoxy radical fragmentation products, and quantum chemical calculations of alkoxy radical fates, we find that the yields of the ring-opened first-generation peroxy radical isomers are 0.05 to 0.2 and 0.06 to 0.25 for α -pinene and β -pinene, respectively. The autoxidation rates of the corresponding peroxy radical are 2.7 and 0.4 per sec, respectively. These rates and yields are lower than recent determinations but in general agreement with HOM yields determined from independent methods and in a range where OH driven monoterpene HOM formation will be atmospherically important.

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Organic Aerosol Multiphase Aging: Rethinking the Chemical Mechanism under Atmospherically Relevant Conditions

Oral Presentation,

Presented By: Haofei Zhang, *University of California, Riverside*

Multiphase oxidative aging is a ubiquitous process for atmospheric organic aerosols (OA). But for decades, the process was considered too slow to impact air quality and climate on atmospherically relevant timescales based on results from laboratory studies. Here we show that OA heterogeneous oxidation may be 2 – 3 orders of magnitude faster when the gas-phase oxidant, hydroxyl radicals are at atmospheric levels. Direct laboratory measurements coupled with kinetic simulations suggest that an autoxidation mechanism mediated by particle-phase peroxy radicals greatly accelerates OA heterogeneous oxidation, with enhanced formation of organic hydroperoxides, alcohols, and fragmentation products. With autoxidation, we estimate that the OA oxidation timescale in the atmosphere may be only a few hours to several days. Thus, heterogeneous oxidation of OA can have more significant atmospheric and climate impacts than previously expected. Furthermore, our findings reveal the nature of heterogeneous aerosol oxidation chemistry in the atmosphere and may reconcile the discrepancies between atmospheric observations and laboratory studies on OA aging.

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Identification and Quantitation of Products Formed from the Reaction of Alkenoic Acids with OH Radicals in a Low NO_x Environment

Oral Presentation,

Presented By: Anna Ziola, *University of Colorado Boulder*

According to results from the CalNex 2010 and LAAQS 2020 field campaigns, the concentration of mid-day NO, a prominent component in many VOC (volatile organic compound) oxidation mechanisms, decreased in Los Angeles by about 75% during the decade between campaigns. Although there have been many studies of VOC oxidation in high NO_x environments, less is known about this chemistry in the absence of NO_x. Here we present results of environmental chamber studies in which a series of alkenoic acids (linear 1-alkenes with a terminal carboxyl group) were reacted with OH radicals formed by H₂O₂ photolysis while using an iodide chemical ionization mass spectrometer (I-CIMS) to identify products. Because the I-CIMS is very sensitive to carboxylic acids, the presence of this functional group tag provided an easy way to detect both the parent VOC and the products. When possible, authentic standards of identified products were synthesized and used to calibrate the I-CIMS for product quantitation, allowing us to determine mechanistic branching ratios for some reaction pathways. The studies explore the effects of carbon chain length and oxidation regime (RO₂ + RO₂ and RO₂ + HO₂) on products, mechanisms, and secondary organic aerosol formation from the oxidation of alkenes, a major class of VOC emissions, in a low NO_x environment.

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Mechanism Development and Reduction

Comparing GECKO-A and MechGen as a basis for evaluation of simplified mechanisms

Invited Presentation, Oral Presentation,

Presented By: Julia Lee-Taylor, *NCAR*

Regional atmospheric chemical-transport models require chemical mechanisms that are greatly simplified in order to reduce operational computational demands. These reduced mechanisms must satisfactorily represent not only the influence of the precursor mixture on the tropospheric gaseous oxidative environment, but also its ability to form secondary organic aerosol. We have developed a framework for comparing two explicit benchmark models, GECKO-A, the “Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere” and MechGen, the “SAPRC Mechanism Generation System” in terms of bulk properties of their product mixtures. We present comparisons between the two model systems of parameters including OH and NO₃ reactivity, and volatility and Henry’s law coefficient distributions. We

compare bulk functional group analyses to diagnose differences between the model systems. We intend to use this framework to evaluate the output of simplified mechanisms against that of the explicit benchmark models.

Additional Authors: John Orlando, NCAR; Kelley Barsanti, UC Riverside; William Carter, UC Riverside; Samiha Shahid, UC Riverside; Bernard Aumont, ____

Recent advances in SARs for the unimolecular chemistry of peroxy radicals

Invited Presentation, Oral Presentation,

Presented By: Luc Vereecken, *Forschungszentrum Jülich GmbH*

It is increasingly recognized that the chemistry of peroxy radicals, RO₂, is more complex than previously thought. The current research focus has shifted towards atmospherically relevant environments with lower NO_x concentrations, where the RO₂ lifetime can easily exceed tens of seconds, and unimolecular chemistry of the RO₂ radicals becomes important. This chemistry leads to formation of products that differs significantly from that in high-NO_x environments; the observed formation of highly oxidized molecules, HOMs, through autoxidation processes, and their subsequent impact on SOA formation and growth, is a clear indication of this rich RO₂ chemistry.

Incorporating these RO₂ processes in atmospheric kinetic models is demanding due to the complexity of the chemistry, and speciated experimental observation of the RO₂ radicals remains difficult given the plethora of RO₂ radical species and isomers being formed. To guide the construction of kinetic models, several structure-activity relationships (SARs) were recently formulated based on an extensive set of theoretical kinetic calculations. The SARs span a wide range of RO₂ substitutions, and focus on the H-migrations and ring closure reactions that allow autoxidation of VOCs. It is found that unsaturated groups and oxygenated functionalities can lead to fast reactions with rates exceeding 1 s⁻¹, while fast "scrambling" interconversion reactions between RO₂ isomers by H-migration further increase the autoxidation chain length.

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A Broad View of Structure-Activity Relationship Performance for Alkanes and Haloalkanes

Oral Presentation,

Presented By: Max McGillen, *CNRS*

As a subset of the gas kinetic database, the alkanes and haloalkanes possess some remarkable properties. Considering that they each share a common reaction mechanism with atmospheric oxidants, this group displays a wide range of reactivity. Furthermore, because of long-standing concerns over their effects upon climate, the ozone layer and climate, they have attracted a large amount of interest since the 1970s. As a result, there is a wealth of information that is known about them in terms of their kinetics, spectroscopy, thermodynamics and many other properties besides.

The performances of the structure-activity relationships (SARs) and linear free-energy relationships (LFERs) that are available to the alkanes and haloalkanes are investigated. Well-known approaches such as the group-additivity approaches of Atkinson and co-workers and DeMore are found to perform well. However, there are many other methods including the LFERs between oxidants; with ionization potential; bond-dissociation energy; and other thermochemical approaches. These estimation methods also demonstrate good predictive power.

Combining these developments with a new electrotopological approach that is unique to this study, a new level of coverage of the prediction-space of this family of compounds is achieved, and the possibility of an ensemble SAR prediction of rate coefficients is explored.

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Designing chemical mechanisms for ozone and secondary organic aerosol endpoints

Oral Presentation,

Presented By: Havala Pye, *US Environmental Protection Agency*

Chemical mechanisms are traditionally designed to predict ozone and related gas-phase endpoints, and mass is often duplicated for purposes of predicting secondary organic aerosol (SOA). In this work, we use the recently developed Community Regional Atmospheric Chemistry Multiphase Mechanism (CRACMM) to show that coupling gas-phase radical chemistry and SOA formation can have benefits for representing the full range of atmospheric reactive organic carbon (ROC). We find that considering SOA and retaining intermediate and lower volatility emissions expands the coverage of primary ROC mass by 40%. In addition, considering SOA

products in gas-phase mechanisms sequesters HOX, decreasing ozone formation compared to default assumptions. In cases where traditional gas-phase products were previously represented as smaller carbon-number products, consideration of SOA also improves conservation of carbon mass throughout the system. Furthermore, linking SOA formation to gas-phase products allows CRACMM to represent SOA precursors not included in earlier generation mechanisms. Newly included precursors, such as phenolic, furanone, and aldehyde species that are produced in later generations from species such as benzene and terpenes, further increase the amount of SOA that can be captured in models.

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Multi-phase chemistry surrogate modeling with a recurrent neural network

Oral Presentation,

Presented By: Xiaokai Yang, *University of Illinois Urbana-Champaign*

Modeling atmospheric chemistry and physics is computationally expensive, and the computation cost arises mainly from solving high-dimensional systems of stiff differential equations. Previous work has demonstrated the promise of machine learning (ML) to accelerate air quality model simulations but has suffered from numerical instability during simulations of seven days or longer. Here we use a recurrent neural network-based multi-phase chemistry surrogate model to predict the concentrations of air pollutants. First, we couple the near-explicit gas-phase Master Chemical Mechanism (MCM) with the state-of-art Particle-resolved

Monte Carlo Model for Simulation Aerosol Interactions and Chemistry (PartMC-MOSAIC). The combined multi-phase chemical mechanism has more than 6,000 species and 16,000 chemical reactions. Second, we use an autoencoder to learn a compressed representation of the state of the chemical system to reduce memory usage and computational expense. Third, we structure our surrogate modeling framework as a series of first-order reactions for each chemical species, where each reaction rate and equilibrium concentration are predicted by a neural network. Preliminary training results on a small dataset of five cases and one day's simulation are promising; we are currently working to scale up our training workflow to realize the full potential of this approach.

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Detailed multiphase chemistry modelling of methylamines with CAPRAM

Oral Presentation,

Presented By: Erik Hoffmann, *Leibniz Institute for Tropospheric Research (TROPOS)*

Methylamines (MAs) are important atmospheric organic nitrogen compounds. Laboratory and field studies demonstrated their importance for new particle formation, increase of secondary organic aerosol mass and the aerosol acidity. However, high uncertainties exist regarding these effects because the complex multiphase interactions of MAs are not yet studied by near-explicit atmospheric chemistry models.

Therefore, a detailed multiphase MA chemistry mechanism, the CAPRAM Amine module, has been developed to describe the oxidation of ammonia (NH₃), monomethylamine (MMA), dimethylamine (DMA) and trimethylamine (TMA). Overall, the mechanism contains 537 reactions, thereof 233 gas-phase reactions 52 phase transfer processes, and 252 aqueous-phase reactions.

Box model simulations of marine and remote environments were performed investigating the chemical multiphase processing of MAs and their products under both cloud and non-cloud conditions. Simulations indicate that uptake is a main loss term for DMA whereas it is gas-phase oxidation for TMA. The chemical rates analyses revealed that during cloud conditions TMA, DMA and MMA are degraded into DMA, MMA and NH₃, respectively. Furthermore, autoxidation processes dominate the gas-phase oxidative fate of DMA and TMA. Because of the importance of DMA and TMA for new particle formation, the uncovered processes have to be included into higher-scale atmospheric chemistry models.

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An Online-Learned Neural Network Chemical Solver for Stable Long-Term Global Simulations of Atmospheric Chemistry

Invited Presentation, Oral Presentation,

Presented By: Makoto Kelp, *Harvard University*

A major computational barrier in global modeling of atmospheric chemistry is the numerical integration of the coupled kinetic equations describing the chemical mechanism. Machine-learned (ML) solvers can offer order of magnitude speedup relative to conventional implicit solvers but past implementations have suffered from fast error growth and only run for short simulation times (<1 month). A successful ML solver for global models must avoid error growth over yearlong simulations and allow for reinitialization of the chemical trajectory by transport at every time step. Here, we explore the capability of a neural network solver equipped with an autoencoder to achieve stable full-year simulations of tropospheric oxidant chemistry in the global 3-D GEOS-Chem model. We find that online training of the ML solver within GEOS-Chem is important for accuracy, whereas offline training from archived GEOS-Chem inputs/outputs produces large errors. After online training, we achieve stable 1-year simulations with 5x speedup compared to the standard Rosenbrock solver with global tropospheric normalized mean biases of -0.3% for ozone, 1% for hydrogen oxide radicals, and -5% for nitrogen oxides. There are however large regional biases for ozone and NO_x under remote conditions where chemical aging leads to error accumulation. These regional biases remain a major limitation for practical application, and ML emulation would be more difficult in a more complex mechanism.

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An adaptive auto-reduction solver for speeding up integration of chemical kinetics in atmospheric chemistry models: implementation and evaluation within the Kinetic Pre-Processor (KPP) version 3.0.0

Invited Presentation, Oral Presentation,

Presented By: Haipeng Lin, *Harvard University*

Integration of chemical kinetics is a major computational bottleneck in the modeling of atmospheric chemistry. Chemical mechanisms for models typically include hundreds of coupled species, but a large fraction of the simulation domain typically does not require the complexity of the full mechanism. We develop an adaptive auto-reduction chemical solver which reduces

any mechanism on the fly based on local conditions, partitioning species as “fast” or “slow” based on their production and loss rates. We use a dynamically defined partitioning threshold based on the production and loss rates of species central to the mechanism. We implement this solver as an option in a new version 3.0.0 of the Kinetic Pre-Processor (KPP) chemical solver software package, allowing it to be immediately applicable to any atmospheric chemistry mechanism using KPP, maintaining the same diagnostic and output capabilities as the full mechanism, and without requiring changes when the chemical mechanism is updated. We apply this adaptive solver to the GEOS-Chem global 3-D model and demonstrate a 32% reduction in solver time while maintaining a mean error lower than 1% for key species in the troposphere.

Additional Authors: Michael S. Long, Harvard University, Robert M. Yantosca, Harvard University, Rolf Sander, Max Planck Institute of Chemistry, Lu Shen, Peking University, Daniel J. Jacob, Harvard University

Modeling at multiple scales of chemical complexity and spatial resolution

Developing a new ocean-atmosphere exchange model to calculate iodine emissions and better constrain their role in tropospheric chemistry

Invited Presentation, Oral Presentation,

Presented By: Ryan Pound, *University of York*

Marine emissions of iodine play an important role in regulating tropospheric photochemistry. In the troposphere iodine chemistry removes approximately as much O₃ as is created by isoprene. The largest source of atmospheric iodine is from inorganic ocean emissions of HOI and I₂. HOI and I₂ production in the ocean surface microlayer (SML) is initiated by O₃ deposition to the ocean and is dependent on physical, chemical, and biological processes. Despite iodine's importance in atmospheric chemistry and a growing body of research on this, many uncertainties in iodine emissions still remain. We will present a new, multi-level model of the SML which couples O₃ dry deposition to SML chemical and physical processes to calculate the atmospheric flux of HOI and I₂. We parameterize this model to allow implementation of an improved representation of iodine fluxes into the atmosphere in a 3D chemistry transport model (GEOS-Chem). This more advanced representation of iodine emissions is used to further constrain and understand the role of iodine in global tropospheric photochemistry.

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Urban and Remote cheMistry modELLing with the new chemical mechnaism URMELL

Oral Presentation,

Presented By: Marie Luttkus, *Leibniz Institute for Tropospheric Research (TROPOS)*

For a better representation of NMVOC chemical degradation a new chemical mechanism has been developed suitable for Urban and Remote cheMistry modELLing (URMELL). URMELL is based on the chemical mechanism ECHAM6.3-HAM2.3-MOZ1.0 JAM version 002b (Schultz et al. 2017). The mechanism was first updated using the latest recommendations of kinetic reaction rate constants as well as oxidation products mainly using IUPAC and MCMv3.3.1 as well as recent publications (e.g. Cox et al., 2020; Jenkins et al., 2018 & 2019; Mellouki et al., 2021; Sheps et al., 2017; Vereecken et al., 2021; Wennberg et al., 2018). The central focus of the mechanism development has been the integration of a comprehensive anthropogenic (mainly aromatics) and biogenic (mainly isoprene) VOC degradation scheme focusing on the formation of SOA compounds enabling a direct SOA determination. About 90 possible substances have been identified, whereby the volatility of the substance decrease with increasing level of functionalisation with hydroperoxides showing the most significant SOA forming potential. Here, an explicit SOA module has been established and applied in a CTM to investigate the BVOC/O₃/NO_x/SOA interrelations.

Additional Authors: Ralf Woke, TROPOS, Andreas Tilgner, TROPOS, Erik Hans Hoffmann, TROPOS

Climate forcing from vegetation emissions strongly influenced by the chemical mechanism employed.

Oral Presentation, Virtual

Presented By: James Weber, *University of Sheffield*

Emissions of biogenic volatile organic compounds (BVOCs) affect climate via formation of organic aerosols and their influence on cloud properties, and via atmospheric oxidation changes influencing the greenhouse gases ozone and methane. Despite recent scientific advances, there remains considerable uncertainty between model simulations in the net impact BVOCs have on climate.

One contributor to this uncertainty is the description of BVOC chemistry (i.e. the chemical mechanism), hitherto minimally assessed in a climate context. Using the Earth system model UKESM1 we quantify the influence of chemistry by comparing the climate response to a doubling of BVOC emissions in a pre-industrial (PI) atmosphere with standard and state-of-science chemistry mechanisms. The net feedback from BVOCs is positive in UKESM1, regardless

of the mechanism used. The negative feedback from enhanced aerosol scattering is outweighed by positive feedbacks from increases in ozone and methane, and changes to aerosol-cloud interactions (ACI). Contrary to prior studies, we show the ACI response is driven by reductions in cloud droplet number concentration (CDNC) via oxidant-driven suppression of gas phase SO₂ oxidation. However, with the state-of-science mechanism the feedback is 43% smaller due to lower oxidant depletion yielding smaller methane increases and smaller CDNC decreases. This illustrates the significant influence of the chemical mechanism on the climatic impact of BVOC emission changes.

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Modeling the multiphase chemistry of isoprene-related organic hydroxy hydroperoxides and epoxides with MCM/CAPRAM

Oral Presentation,

Presented By: Andreas Tilgner, *Leibniz Institute for Tropospheric Research (TROPOS)*

Oxidation of isoprene under low NO_x conditions leads to formation of oxygenated organic hydroperoxides, ISOPOOHs and ISOP(OOH)₂, and epoxides (IEPOX) that chemically interact with deliquesced particles and clouds. A CAPRAM mechanism module is developed focusing on the multiphase chemistry of these compounds.

For ISOPOOHs/ISOP(OOH)₂ the module contains phase transfer, aqueous photolysis, thermal decomposition, S(IV) oxidation and OH oxidation. In the base mechanism, no Fenton-like reactions for ISOPOOH/ISOP(OOH)₂ are considered due to potentially uncertain reaction rate coefficients. But for sensitivity studies recently published constants were tested. For IEPOX, uptake, aqueous OH oxidation of IEPOX and its reaction products were included. In total, the module contains 12 gas-phase and 142 aqueous-phase reactions as well as 20 phase transfer processes.

The CAPRAM module was coupled to the multiphase mechanism MCMv3.3.1/CAPRAM4.0. Subsequently, detailed box model studies were performed for remote non-permanent cloud scenarios.

The simulations show that ISOPOOH and IEPOX chemistry contribute substantially to aqSOA formation. Sensitivity studies demonstrate that Fenton-like chemistry of ISOPOOH has high impact on aqueous-phase HO_x. Thus, aqSOA yield under remote conditions depends on multiphase chemistry of isoprene oxidation products and Fenton-like chemistry. The studies

exhibit the need for more kinetic and mechanistic process knowledge to build more sophisticated mechanisms.

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Plans For Enhanced Research Capabilities for Atmospheric Chemistry within NOAA's Unified Forecasting System

Invited Presentation, Oral Presentation,

Presented By: Rebecca Schwantes, *NOAA Chemical Sciences Laboratory*

NOAA's Unified Forecasting System (UFS) is a community-based Earth modeling system that plans to provide a framework to efficiently incorporate research advances into NOAA's operational forecasts. Currently, the simplified aerosol scheme, GOCART, is incorporated into the UFS with minimal gas-phase chemistry. We will discuss our plans for adding innovative research capabilities for improving chemistry and aerosol processes and thereby predictions of air quality and atmospheric composition into the UFS. These enhanced research capabilities will include: 1) Options to use gas and aerosol chemical mechanisms of varying complexity. 2) Ability to easily couple different mechanisms to different physics options. 3) Development of a more flexible emissions processing system. 4) Further investment of model evaluation tools like MELODIES-MONET (<https://melodies-monet.readthedocs.io>) that efficiently compare model results against a variety of observations. These capabilities will be added into a flexible, easy to modify, and well-documented infrastructure. In this work, we will use the Model Independent Chemistry Module, which is a component of the Multi-Scale Infrastructure for Chemistry and Aerosols, led by NCAR. By discussing our plans, we hope to get input early in the process on whether these enhancements will meet the needs of the research community, so as to ensure the UFS accomplishes one of its main goals to efficiently update NOAA's operational forecasts with research advances.

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New and Emerging Air Pollutants (HAPs, VCPs, PFAS)

Observations of Chlorinated Amines in an Urban Atmosphere in Summer and Winter

Invited Presentation, Oral Presentation, Virtual

Presented By: Jon Abbatt, *University of Toronto*

In this work, we present the first quantified analyses of chlorinated amines – monochloramine (NH₂Cl), dichloramine (NHCl₂), trichloramine (NCl₃) – in the outdoor atmosphere. In particular, we used both proton-transfer-reaction mass spectrometry and iodide ion chemical ionization mass spectrometry to detect these molecules in downtown Toronto during campaigns in the summer of 2020 and the winter of 2021. Mixing ratios were especially high in the summer, repeatedly approaching ppbv levels during the nighttime for both NH₂Cl and NHCl₂. Mixing ratios during the daytime and in the winter were generally quite a bit lower, at the pptv level. The mixing ratios of NCl₃ were at the 1 to 10 pptv level for most time periods. It is likely that NCl₃ readily photolyses in sunlight, most likely forming Cl atoms which are able to initiate oxidation reactions in the atmosphere. We demonstrate that the daytime measurements of NCl₃ imply that it is a photolytic Cl-atom source of comparable strength to more traditional Cl-atom sources, such as ClNO₂. The primary sources of the chloramines detected at this sampling location are not known. Whereas they can be released by water purification facilities and swimming pools, the transient nature of the NCl₃ signals and its short calculated photolytic lifetime suggest a highly local source, perhaps due to chlorine-related cleaning and disinfection activities.

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A Better Representation of VOC chemistry from VCP and Cooking emissions in WRF-Chem

Invited Presentation, Oral Presentation,

Presented By: Qindan Zhu, *Cooperative Institute for Research in Environmental Sciences and the NOAA Chemical Sciences Laboratory*

Volatile organic compounds (VOCs) fuel the production of air pollutants like ozone and particulate matter (PM) through reactions with hydroxyl radicals (OH) and nitrogen oxides

(NO_x). The representation of VOCs chemistry remains challenging in reduced chemical mechanisms due to its complexity in speciation and reactions. We are developing a chemical mechanism compatible with WRF-Chem that better represents VOC chemistry in urban areas such as Los Angeles. This chemical mechanism, RACM2_BERK_VCP, is based on RACM2_Berkeley mechanism and includes more complex oxygenated VOC chemistry to address the impact of VCP and cooking emissions. We then incorporate the TUV photolysis scheme, a more complex SOA_VBS scheme, and aerosol uptake reactions to better represent photolysis, aerosol, and ozone. We also add five new species, D4 siloxane, D5 siloxane, p-Dichlorobenzene, and PCBTF as VCP tracers and nonanal as a cooking emission tracer. We evaluate how well this RACM2_BERK_VCP mechanism simulates VOC chemistry and ozone in WRF-Chem by comparing it against the airborne VOC measurements during RECAP-CA field campaign, as well as surface ozone (O₃) monitors from Airnow network in June 2021, LA. We discuss how O₃ changes due to different VOC emission sectors and provide insights on VOC emission control strategy for ozone regulations. We also show that adding missing VOC reactivity is important for models to accurately represent OH.

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Chemical characteristics of indoor aerosol particles and surface films

Oral Presentation,

Presented By: Rachel O'Brien, *University of Michigan*

Indoor surfaces and the films on them play important roles in indoor air quality due to the high surface area to volume ratios in our homes. These films are formed from the deposition of aerosol particles and the sorption of semi-volatile organic compounds and are thus often complex mixtures of organic chemicals. The composition of these films will play a role in their behavior indoors, so an improved understanding of the important chemical classes found in these films will help model predictions for partitioning of organic chemicals in indoor air. Important sources for chemicals in these films are cooking, cleaning, and aerosol particles from outdoors including wildfire smoke. Cooking can be a large source for semi-volatile and lower volatility organic compounds. Cleaning processes can generate aerosol particles and leave behind lower volatility material on indoor surfaces. Depending on the distance of the building from the fire, biomass burning organic aerosol particles (BBOA) can reach indoor spaces at different levels of aging. Here, we investigate the chemical composition of surface films formed on impermeable surfaces during different activities. We also investigate the correlations between this composition, and the composition of size resolved aerosol particles collected at the NIST (National Institute of Standards and Technology) Net-Zero Energy Residential Test Facility during the CASA (Chemical Assessment of Surface and Air) field campaign.

Additional Authors: Amy Hrdina, MIT; Emily Legaard, William & Mary; Churchill Wilkinson, William & Mary; Kathryn Mayer, Colorado State; Sumit Sankhyan, CU Boulder; Dustin Poppendieck, NIST; Delphine Farmer, Colorado State; Marina Vance CU Boulder

Volatile Organic Compounds inside Homes Impacted by Smoke from the Marshall Fire

Invited Presentation, Oral Presentation,

Presented By: Joost de Gouw, *University of Colorado Boulder*

The Marshall Fire in Colorado started as a grass fire on 30 December 2021, grew uncontrollably in hurricane-force winds, and burned more than 1,000 homes and commercial buildings in different parts of Boulder County within hours. Smoke from the fires infiltrated into undamaged homes surrounding the burnt areas, left ash and soot behind, and impacted indoor air quality very noticeably to the evacuees returning to their homes. Our group started making measurements of volatile organic compounds (VOCs) inside smoke-impacted homes within days after the fire and these continued for about five weeks. We found that levels of VOCs gradually decreased until February, when they had become indistinguishable from levels that are normally observed inside homes. The Marshall Fire was largely fueled by building materials, furniture, vehicles, and other man-made materials rather than by vegetation. As a result, VOCs that are non-typical for biomass burning can be expected and some evidence is reported. People were advised to increase ventilation and add filtration by activated carbon to their homes, and the effectiveness of these measures is illustrated. We also made measurements before, during and after professional home restoration efforts and will present how these impacted indoor VOC concentrations.

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Personal care product VOC emissions: Indoor air quality impacts and estimated inhaled dosage from use

Oral Presentation,

Presented By: Amber Yeoman, *The University of York*

Historically, air quality concerns have focussed on outdoor air pollution. Interest in indoor air pollution has only more recently been piqued, particularly since the Coronavirus pandemic. As we spend on average 90% of our time indoors the quality of the air we breathe is important to our wellbeing. A major contributor to indoor air pollution is the VOCs stemming from the use of personal care products (PCPs). Whilst exposure to these pollutants can cause negative health

effects in all, the risk is significantly greater for those applying products to themselves due to the close proximity of application area to the inhalation exposure pathway (nose and mouth), particularly for facial products. Solvents and fragrance compounds dominate emissions, but more surprising contaminant species such as benzene and toluene are also present. Utilizing Quadrupole-Time of Flight Gas Chromatography/Mass Spectrometry (Q-TOF GC/MS), Selected-Ion Flow-Tube Mass Spectrometry (SIFT-MS), and an innovative in-house built applicant respiration replica we identify and quantify VOC emissions from facial PCPs and replicate real-life use to determine the resulting inhalation risks. This talk outlines the investigative process, experimental setup, key VOCs identified and their emission factors, and negative outcomes from a health perspective to both product applicants and those breathing ambient indoor air.

Additional Authors: Alastair Lewis, NCAS, UoY, Marvin Shaw, NCAS, UoY, Stephen Andrews, NCAS, UOY

Drivers of Perfluorocarboxylic Acid (PFCA) Gas-Particle Partitioning: Modeled Properties and Observational Constraints

Oral Presentation,

Presented By: Trevor VandenBoer, *York University*

The atmospheric fate of perfluorocarboxylic acids (PFCAs) is attracting increasing attention due to the role of the atmosphere in global transport of these hazardous chemicals. There is a gap in our understanding of their gas-particle partitioning, limited by available measurements, and accurate partitioning properties. We model phase partitioning of C2-C14 PFCAs in the atmosphere including deprotonation and phase partitioning equilibria among air, aerosol liquid water, and particulate water-insoluble organic matter using a range of model-derived PFCA properties. Water and organic matter content are systematically varied across a full range of atmospheric conditions. Except during severe organic matter pollution episodes, shorter-chain PFCAs are predicted to mainly partition between air and aqueous phases, while for C12 and longer PFCAs, organic matter becomes the dominant particle phase sink. The partitioning framework underestimates the particle fraction of C2-C8 PFCAs compared with several ambient observations, with discrepancies increasing for longer-chain PFCAs. One to three orders of magnitudes higher particle/gas equilibrium ratios are required to fulfill the agreement. The discrepancy could result from externally mixed dust components, non-ideality of aerosol liquid water, and missed interactions between organic matter and charged PFCA molecules. High time resolution measurements of ambient PFCAs are needed to improve environmental fate modeling of ambient PFCAs.

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Sulfur Oxidation Advancements – Improving mechanisms and modelling

Assessing and improving the DMS oxidation mechanism in the MCM and CRI-Strat

Oral Presentation,

Presented By: Lorrie Jacob, *University of Cambridge*

Dimethyl sulfide (DMS), which originates from phytoplankton, is the major natural source of sulfur compounds in the atmosphere. The oxidation products of DMS can form aerosols, which contribute to the formation of clouds, making them important for rain and the radiative balance of the planet. Additionally, due to DMS naturally occurring above oceans, an oxidation product of DMS, methanesulfonic acid (MSA), has been used to determine sea ice extent in ice cores up to 300 years in the past. However, due to gaps in the oxidation pathway of DMS, there are large uncertainties in the modelling of MSA formation.

This project works with the box model BOXMOX, an extension to the KPP, incorporating the Master Chemical Mechanism (MCM) and CRI-Strat, to assess the mechanisms in light of gas-phase experiments, both in NO_x and NO_x-free conditions. Additionally, the effect of additional reactions to CRI-Strat was explored.

Through comparing the model outputs with the experiments, the models were found to have similar results in the NO_x-free conditions, and accurately modelled dimethyl sulfoxide (DMSO) and sulfur dioxide (SO₂). In the experiments with NO_x, the model outputs differed from each other, and the experiments. MSA was overestimated, and SO₂ was both over and underestimated by the models. The addition of a DMSO₂ formation reaction had the biggest effect on the model runs, allowing CRI-Strat to model the experiment more closely.

Additional Authors: Chiara Giorio, University of Cambridge, Alex Archibald, University of Cambridge

Sulfur radical formation from the tropospheric irradiation of aqueous sulfate aerosols

Oral Presentation,

Presented By: Kelvin Bates, *UC Davis*

The sulfate anion radical (SO₄•⁻) is known to be formed in the autoxidation chain of sulfur dioxide, and from minor reactions when sulfate or bisulfate ions are activated by OH radicals, NO₃ radicals, or iron. Here we report a new source of SO₄•⁻, from the irradiation of the liquid water of sulfate-containing organic aerosol particles under natural sunlight and laboratory

ultraviolet radiation. Irradiation of aqueous sulfate mixed with a variety of atmospherically relevant organic compounds degrades the organics well within the typical lifetime of aerosols in the atmosphere. Products of the $\text{SO}_4^{\bullet-}$ + organic reaction include surface-active organosulfates and small organic acids, alongside other products. Scavenging and deoxygenated experiments indicate that $\text{SO}_4^{\bullet-}$ radicals, instead of OH, drive the reaction. Ion substitution experiments confirm that sulfate ions are necessary for organic reactivity, while the cation is nearly irrelevant. The reaction proceeds at pH 1-6, implicating both bisulfate and sulfate in the formation of photoinduced $\text{SO}_4^{\bullet-}$. Certain aromatic species may further accelerate the reaction through synergy. This new reaction may impact our understanding of atmospheric sulfur reactions, aerosol properties, and organic aerosol lifetimes when inserted into aqueous chemistry model mechanisms.

Additional Authors: James Cope, UC Davis, Lillian Tran, UC Davis, Karizza Abellar, UC Davis, Tran Nguyen, UC Davis

Chamber studies of the oxidation of DMS, DMDS, and DMSO: Mechanism and aerosol formation

Oral Presentation,

Presented By: Matthew Goss, *Massachusetts Institute of Technology*

The use of chemical ionization mass spectrometry has enabled recent advances in our understanding of the oxidation of dimethyl sulfide (DMS), which is central to the atmospheric sulfur cycle and secondary aerosol formation over the oceans. Here we apply these same approaches to study the oxidation of two related compounds, dimethyl disulfide (DMDS) and dimethyl sulfoxide (DMSO). DMDS and DMSO are themselves atmospherically-relevant organosulfur compounds, and due to the presence of common intermediate species, they can also shed light on the DMS oxidation mechanism. Using chamber studies monitored with chemical ionization mass spectrometry and aerosol mass spectrometry, this work examines total gas- and particle-phase product distribution from the low- and high-NO oxidation of DMDS and DMSO. The evolving concentrations of reactants and products give new insight into the oxidation mechanisms of these two compounds, while also offering clues into the aerosol formation channels of the DMS oxidation mechanism.

Additional Authors: Qing Ye, National Center for Atmospheric Research, Yaowei Li, Harvard University, Frank Keutsch, Harvard University, Jesse Kroll, Massachusetts Institute of Technology

Investigation of the OCS formation from the oxidation of DMS in marine-like conditions.

Invited Presentation, Oral Presentation,

Presented By: Anna Novelli, *Institute of Energy and Climate Research, IEK-8: Troposphere, Forschungszentrum Jülich*

Carbonyl sulfide (OCS) is the most abundant sulfur-containing gas in the Earth's atmosphere playing a pivotal role as precursor to sulfate aerosol in the stratosphere. In the troposphere, dominant sources of OCS are oceans and anthropogenic emissions while consumption by the terrestrial biosphere is the largest sink. The marine environment is the dominant source region for OCS with comparisons between observations and models indicating that there is either an over-estimation of the terrestrial OCS sink or an unaccounted source over the tropical oceans.

New chemical paths have been found for the peroxy radical formed from the oxidation of DMS by the OH radical that may impact the yield of OCS. We performed experiments in the atmospheric simulation chamber SAPHIR to elucidate the DMS oxidation chemical mechanisms focusing on the paths leading to the formation of OCS. The experiments were performed at atmospherically relevant conditions initiating the DMS oxidation with OH and Cl radicals and with measurements of precursors, radicals, OCS and oxidation products.

An unexpected high yield of 7% for OCS was found for all experimental conditions. Concentrations of measured species were compared to results from a detailed chemical mechanism, which includes new chemical paths derived a-priori from theoretical calculations with the observed OCS being underestimated. We suggest additional paths and adjustment of rate coefficients to bring measurements and model results into agreement.

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Lighting Talks & Poster Presentations

Computational Investigation of the Reaction Routes for 3(RO...OR') Intermediates Formed in Peroxy Radical Self- and Cross-Reactions

Lighting Talk, Poster Presentation

Presented By: GALIB HASAN, *University of Helsinki*

Gas phase dimer (accretion product) formation is regarded as a significant reaction in the atmosphere because it can lead to the formation of very-low volatility highly oxygenated organic molecules (HOMs), which later form aerosol particles. On the other hand, organic peroxy radical (RO₂) are the key intermediates in the chemistry of the atmosphere. One of the main sink reactions of RO₂ is the recombination reaction RO₂ + R'O₂. This reaction goes through an intermediate complex (RO...3O₂...OR') and three major reaction channels: 1) R₂H=O + R'OH 2) ROOR', and 3) RO₂+ R'O₂.

In our study, we performed a systematic conformation search on the 3(RO...R'O) cluster and tried to estimate the kinetics of the three channels. We have found that all these channels are indeed competitive (with typical rates of at least greater than 10⁶ s⁻¹, and many have rates exceeding 10¹⁰ s⁻¹) in the atmosphere. This suggests that the computationally proposed novel RO₂ + RO₂ reaction mechanism is qualitatively compatible with experimental results on accretion product formation and may thus play a key role in the formation of organic aerosols.

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Investigating fundamental structures in atmospheric chemical reaction mechanisms

Lighting Talk, Poster Presentation

Presented By: Sam Silva, *The University of Southern California*

Techniques from the discrete mathematical field of graph theory can provide a potential new set of tools for quantifying the structure and dynamics of the atmospheric chemical system. This has been shown by prior work, which demonstrated that mechanism analyses through the lens of graph theory reproduces existing knowledge in the field. Here, we go beyond reproduction of existing knowledge to explore what graph theoretical analysis can tell us about

mechanism structure and dynamics. We present new structural analysis of atmospheric chemical mechanisms focused on so-called “graph motifs” in mechanisms of varying complexity.

Motifs in reaction mechanisms are repeat patterns of interactions between compounds. The prevalence of all possible connection patterns for a given number of compounds are explored and compared to a random baseline. This analysis technique allows us to characterize the basic building blocks of atmospheric chemical mechanisms and relate them to mechanism dynamics. Our work indicates key differences in motif prevalence across mechanisms. For example, a subset of motifs related reciprocal reactions (reactions where at least one of the reactants and the products are the same) are much more common in reduced form mechanisms. We additionally explore the implications of these motifs on the dynamics of the chemical system to enable further insight into mechanism behavior.

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Use of OH/VOC ‘site-specific’ rate coefficient data to test, train and constrain structure-activity relationships.

Lighting Talk, Poster Presentation

Presented By: John Orlando, *Atmospheric Chemistry Observations and Modeling Laboratory, NCAR*

Fully explicit models (e.g., GECKO-A, MechGen, MCM) operate in part on structure-activity relationships (SARs), rules that are used to generate rate coefficient (k) data for reactions that have not been experimentally studied. For OH/VOC reactions, the most popular form is the ‘Atkinson-type’ SAR in which each unique site of attack on a VOC is parameterized as a ‘base k ’ multiplied by additional parameters that account for neighboring group effects, and the full set of parameters is optimized using available (total) k ’s from lab studies. However, until now, while these parameterizations have proved useful for predicting total k ’s, they have not been tested for their ability to predict branching ratios (or ‘site-specific’ k ’s) for OH attack on a VOC.

Our group has already published a comprehensive, digital, freely available, ‘living’ compilation of evaluated k ’s for gas-phase reactions of OH with about 1350 VOC. Here we collect an additional 175 branching ratios (based on lab-derived quantitative product data) for inclusion in the database. These are predominantly obtained for OH/VOC abstraction reactions where unique products are formed from reaction at a particular site in the parent VOC. Comparisons will be made between these branching ratios (or site-specific k ’s) and those predicted by the SARs used in developing GECKO-A and MechGen. The results of these comparisons will be used to the extent possible to suggest improvements to currently existing SARs.

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Reduction strategies for the automatic generation of SOA mechanism using GENOA

Lighting Talk, Poster Presentation

Presented By: Zhizhao Wang, CERE, ENPC

The degradation of volatile organic compounds (VOC) in the troposphere leads to the formation of secondary organic aerosols (SOA) and is therefore crucial to 3D air quality modeling (AQM). Although detailed VOC mechanisms like MCM can accurately describe the influence of VOC chemistry on SOA formation, they cannot be directly applied to SOA simulations in AQM due to the overwhelming computational costs.

Thus, we developed GENOA (GENERator of the reduced Organic Aerosol mechanism), which automatically reduces complex SOA mechanisms into smaller mechanisms with fewer species.

The GENOA training involves searching for potential reduction attempts using predefined reduction strategies (e.g., lump species, remove species/reactions), and evaluating their effects on SOA concentrations under selected representative atmospheric conditions (e.g., conditions under different chemical regimes). Automatically, the process can be conducted serially (search/evaluate one reduction at a time) or parallelly (search/evaluate multiple reductions and select the best one). It can also be customized by user-specified parameters and tracked explicitly.

GENOA has been applied to the degradation mechanisms of sesquiterpene, toluene, and monoterpene, reducing the number of condensable species from 356 to 6, 103 to 10, and 738 to 43, respectively, with an average error increase of less than 4% in the OD testing on more than 10,000 conditions. Their performances in 3D modeling are currently investigated.

Additional Authors: Florian Couvidat, INERIS France, Karine Sartelet, CERE ENPC

Volatile Chemical Product Contributions to the Urban Secondary Organic Aerosol Burden in the United States

Lighting Talk, Poster Presentation

Presented By: Shantanu Jathar, Colorado State University

Volatile chemical products (VCPs) are a large source of oxygenated volatile organic compound (OVOC) emissions into the urban atmosphere, yet the oxidation chemistry of OVOCs leading to SOA formation remains uncertain. In this work, we leveraged high NO_x environmental chamber data gathered at the University of California Riverside to develop parameters to represent SOA formation from a suite of VCP OVOCs. These VCP OVOCs included glycols, glycol ethers, oxygenated aromatics, and acetates. The SOA parameters were developed using SOM-TOMAS, a kinetic model that simulates the oxidation chemistry, thermodynamic properties, and microphysics of SOA. The SOA parameters were able to reproduce time-dependent SOA mass concentrations and oxygen-to-carbon (O:C) ratios observed in the chamber experiments. These parameters for OVOCs along with historical parameters for volatile hydrocarbons were used to develop a box model to study urban SOA formation. Consistent with recent work, the box modeling results confirmed that VCPs account for more than half of all urban SOA formed from anthropogenic sources in Los Angeles, CA and New York City, NY. Of the SOA attributed to VCP use, more than three quarters of it arose from oxidation of VCP hydrocarbons (alkanes, aromatics, monoterpenes being dominant) and less than a quarter came from VCP OVOCs (terpenoids, glycol ethers being dominant). Ongoing work is focused on understanding fossil fuel contributions to anthropogenic SOA in other US cities.

Additional Authors: Sreejith Sasidharan, Colorado State University, Yicong He, Colorado State University, Qi Li, University of California Riverside, David Cocker, University of California Riverside, Karl Seltzer, US Environmental Protection Agency, Brian McDonald, National Oceanic and Atmospheric Administration, Jeffrey R. Pierce, Colorado State University

Development and evaluation of an improved mechanism for the oxidation of dimethyl sulfide in the UKCA model

Lighting Talk, Poster Presentation

Presented By: Alexander ARCHIBALD, *University of Cambridge*

Dimethyl sulfide (DMS) is an important trace gas emitted from the ocean. The oxidation of DMS is important for global climate through the role DMS plays in setting the sulfate aerosol background in the troposphere. However, the mechanisms of DMS oxidation are very complex and have proved elusive to accurately determine in spite of decades of research. As a result the representation of DMS oxidation in global chemistry-climate models is often greatly simplified.

Recent field observations and laboratory studies have prompted renewed efforts in constraining the uncertainty in the oxidation mechanism of DMS as incorporated in global chemistry-climate models. Here we build on recent laboratory and observational evidence and develop a new DMS mechanism for inclusion in the UKCA chemistry-climate model. We

compare our new mechanism to the existing UKCA mechanism and to a range of recently developed mechanisms reported in the literature through a series of global and box model experiments. Our box model experiments highlight that there is significant variance in simulated secondary oxidation products of DMS across mechanisms used in the literature, with divergence in the sensitivity of these products to temperature exhibited. Our global model studies show that our updated and improved DMS scheme performs better than the current scheme when compared against observations. However, sensitivity studies underscore the need for further laboratory and observational constraints.

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Seasonal variation of PM_{2.5} and PM₁₀ bound polycyclic aromatic hydrocarbons in Dhaka, Bangladesh: Source apportionment and health risk assessment

Lighting Talk, Poster Presentation, Poster Competition

Presented By: Saif Shahrukh, *Bangladesh Council of Scientific and Industrial Research*

An investigation was carried out to analyze the seasonal variation, potential pollution sources, and health risk of PM_{2.5} and PM₁₀-bound 16 USEPA priority PAHs over seven urban traffic intersection sites of Dhaka during monsoon (June-September 2021) and winter (December-February 2022) seasons using GC-MS. Source apportionment of particle-bound PAHs were carried out using diagnostic ratios (DRs) of PAHs and positive matrix factorization (PMF) model. Health risk assessment was made based on B[a]P equivalent (B[a]P_{eq}), lifetime lung cancer risk (LLCR), respiratory deposition dose (RDD), lifetime average daily dose (LADD), and incremental lifetime cancer risk (ILCR). A clear seasonal variation was observed at all the sites, with the higher values in winter due to higher emissions and less scavenging. Proportions of high-molecular-weight PAH compounds (i.e., 5- and 6-ring) increased with decreasing particle size. DRs and PMF identified vehicular emission as the leading source of these species followed by biomass and coal combustion. Regional and trans-boundary incursion of pollutants was also identified with the help of back trajectories. Maximum contribution towards the carcinogenicity was found for Benzo (a) pyrene [B(a)p]. The average total BaP equivalent concentrations (BaP_{eq}) during monsoon and winter seasons were much higher than the WHO guideline of 1 ng/m³. The ILCR values over the sampling sites were found at acceptable limit (10⁻⁶-10⁻⁴) given by the USEPA.

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Atmospheric Chemical Reaction Mechanism Dependence on the Environment and Stellar Radiation

Lighting Talk, Poster Presentation, Poster Competition

Presented By: Alexandra Deal, *CU Boulder/CIRES*

Chemical mechanisms relevant to planetary atmospheres, including the contemporary and ancient Earth, are highly susceptible to the environment. For example, water is considered a necessary precursor for life yet many biotically relevant reactions are thermodynamically forbidden in bulk water (the “water paradox”). However, recent evidence shows that water-air interfaces are auspicious reaction environments for these reactions. Organic molecules concentrate at these interfaces, forming films with distinct compositions, morphologies, and optical and chemical properties, potentially resulting in a novel array of products. Furthermore, water-air interfaces and organic films would have ample access to starlight which provides a driving force for chemistry via energy transduction from stellar radiation to high energy chemical bonds. However, this chemistry is extremely sensitive to the environment and the stellar radiation spectrum, making fundamental mechanistic studies important to understand chemical reactions in all atmospheres.

We use examples from the dark chemistry and photochemistry of α -oxoacids and α -hydroxyacids to illustrate the similarities and differences in their reaction mechanisms in different phases and under various stellar irradiative environments. By examining fundamental chemical reaction mechanisms of these molecules in atmospherically relevant environments, we begin to build a more general understanding of the available processes in diverse atmospheres.

Additional Authors: Veronica Vaida, *CU Boulder/CIRES*

Atmospheric oxidation of imine derivative of piperazine initiated by OH radical.

Lighting Talk, Poster Presentation, Poster Competition

Presented By: Thomas Golin Almeida, *University of Helsinki*

Piperazine is a widely used amine as a solvent in carbon-capture (CC) technologies, which seek to mitigate the impact of fossil-fueled energy production on the climate. Concerned with the impact on air quality that atmospheric emissions of such amine may have, studies have observed the cyclic imine 1,2,3,6-tetrahydropyrazine (THPyz) to be its major photo-oxidation product. However, almost nothing is known about the fate of this imine. In fact, very few studies have focused on the atmospheric chemistry of imines in general, despite consistently appearing as major products of amine oxidation. In the presented work, we explored the reaction mechanism of THPyz oxidation initiated by OH radical, as well as the fate of the first-generation products, with quantum chemistry and theoretical kinetics methods. We predict that the major initial channels involve H-abstraction from a α -amino carbon, leading to subsequent formation of a second imine function. Typically carcinogenic compounds, nitrosamines are expected to have low but non-negligible yields, with a maximum value of ~3% under high NO_x regimes. Pathways involving attack of the OH radical on the imine group are minor but still relatively competitive. One of these pathways (H-abstraction from the imine C) leads to the formation of an isocyanate function, potentially also imparting toxicity to the product. Even though it is a minor channel for THPyz, it could be more competitive in the atmospheric oxidation of other imines.

Additional Authors: Theo Kurtén, University of Helsinki

Low-pressure yields of stabilized Criegee intermediates produced from ozonolysis of a series of alkenes

Lighting Talk, Poster Presentation, Poster Competition

Presented By: Lei Yang, UC Riverside

Ozonolysis of alkenes is an important oxidation pathway of alkenes in the troposphere because it is involved in the production of organic aerosol and OH radicals. The mechanism of ozonolysis of alkenes involves the formation of a primary ozonide (POZ), which then decomposes into a carbonyl and a carbonyl oxide (Criegee intermediate). Criegee intermediates are produced with a broad internal energy distribution. High-energy Criegee intermediates decompose into atmospherically important compounds (e.g. vinyloxy, OH radical). Stabilized Criegee intermediates (sCIs) undergo reactions to produce secondary ozonides and organic aerosols.

Cavity ring-down spectroscopy (CRDS) is utilized in combination with chemical titration with sulfur dioxide to quantify sCIs. The reactions are carried out under various flow and low-pressure conditions. Reference cross-sections of the products and reactants are fitted with spectral features to obtain product number densities. The yields of sCIs are measured at different low pressures, and the nascent yields are determined by extrapolation to zero pressure. Endocyclic alkenes show no sCI production at the pressures studied. Acyclic alkenes show pressure-dependent sCI yields. Formaldehyde oxide from the 1-alkenes studied has a high

nascent yield than larger CIs due to its relatively high energy barrier for dissociation. The information on the low-pressure yields from the current studies can be used as a benchmark for theoretical calculations.

Additional Authors: Mixtli Campos-Pineda, UC Riverside, Jingsong Zhang, UC Riverside

NO₃ Initiated Oxidation of Furan Compounds: Rate Coefficients, Gas-Phase Chemical Mechanisms and SOA Formation

Lighting Talk, Poster Presentation, Poster Competition

Presented By: Fatima AL ALI, *Université du Littoral Côte d'Opale*

Furan compounds are emitted in substantial quantities from biomass burning, greatly participating in OH and NO₃ reactivity.

In this work, we investigate the NO₃ reaction of furan, 2-methylfuran, 3-methylfuran, 2,5-dimethylfuran, and 2,3,5-trimethylfuran. Experiments were performed in CHARME simulation chamber at 294 ± 2 K, atmospheric pressure and under dry conditions (RH \approx 2%).

Rate coefficients were measured using the relative rate method and PTR-ToF-MS for monitoring of furan and reference compound concentrations vs. time. Oxidation product characterization and quantification were done using spectrometric (PTR-ToF-MS, TD-GC-MS, GC-MS, LC-MS-MS) and spectroscopic (FTIR) techniques allowing mechanism elucidation. SOA formation was followed by SMPS.

Hence, the nighttime atmospheric removal of furan compounds upon reaction with NO₃ is an important sink, with rate coefficients of 1.91 to 16.7×10^{-11} cm³ molecule⁻¹ s⁻¹. The mechanistic studies show that two major reaction pathways drive the NO₃ reaction with methylated-furan: NO₃ addition to carbon-2/5 of the ring and H-abstraction from the methyl(s) group(s).

Additional Authors: Cécile COEUR, ULCO, Nicolas HOUZEL, ULCO, Alexandre TOMAS, IMT NORD EUORPE, Manolis N. ROMANIAS, IMT NORD EUROPE.

Investigation of nighttime chemistry of trans-2-hexene in the atmospheric simulation chamber SAPHIR

Lighting Talk, Poster Presentation, Poster Competition

Presented By: Michelle Färber, *Forschungszentrum Jülich*

Investigations of nighttime chemistry of selected alkenes such as trans-2-hexene, performed in the atmospheric simulation chamber SAPHIR at Forschungszentrum Jülich, Germany, revealed a discrepancy between measured and modelled HO₂ and RO₂ radical concentrations at high and medium levels of nitrogen dioxide (NO₂, 40 ppbv) and ozone (O₃, 25 ppbv), respectively. Such chemical conditions have been observed in cities characterised by high pollution such as London, UK, and Beijing, China.

To further investigate the chemistry of organic peroxy radicals (RO₂) from trans-2-hexene at these conditions, we performed a series of O₃+NO₂ experiments in the atmospheric simulation chamber SAPHIR. The experiments were conducted for a range of NO₂ concentrations and temperatures (0 to 40 ppbv and 5 to 35 °C, respectively) to test the chemistry between the RO₂ radical and NO₂ which is the main reaction partner for RO₂ at these experimental conditions.

For the ozonolysis (NO₂=0) of trans-2-hexene, we find a good agreement between measured and modelled radical concentrations. However, with increasing NO₂ concentration discrepancies appear due to the lack of RO₂+NO₂ reaction paths for most of the implemented RO₂ in the model used. Due to the limited knowledge about both forward and backward reaction rates for the RO₂+NO₂ reaction, we derived a backward reaction rate obtained from our results and its impact on the modelled radical concentrations will be discussed in the presentation.

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Unimolecular reactions of hydroxy-substituted Criegee Intermediates

Lighting Talk, Poster Presentation, Poster Competition

Presented By: Lauri Franzon, *University of Helsinki*

The chemistry of stabilized Criegee intermediates (sCI) is a subject of great interest to atmospheric chemistry as these form from ozonolysis, one of the most common atmospheric oxidation reactions. Studies on sCI reactions have however mainly focused on sCI:s formed from the ozonolysis of pure hydrocarbons. Unsaturated alcohols are the most common heteroatom-including alkenes in the atmosphere, and thus the unimolecular reactions of OH-substituted sCI:s are worth studying.

This work is a computational investigation of thermal reaction rates for six simple OH-substituted sCI:s. Intramolecular H-shifts from the OH to the carbonyl oxide (COO) are compared to the most likely unimolecular reactions of the corresponding non-substituted sCI:s.

Conformer analysis was performed for the sCI:s using Molecular Mechanics, and all conformers were characterized based on the relative positions of the OH and COO. The geometries of important conformers were optimized using wB97X-D/aug-cc-pVTZ, and electronic energy corrections were calculated using CCSD(T)-F12/VDZ-F12. CCSDT(Q) corrections were calculated for a select small molecules to better account for multi-configurational character. Reaction rates were calculated using the Eyring equation with Eckart tunneling corrections.

Our results indicate that the H-shift from the OH is the main reaction pathway for all sCI:s with a suitable conformer, and that unimolecular reactions are likely to dominate for most simple OH-substituted sCI:s.

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Structure-activity relationship to predict Arrhenius parameters of OH addition to unsaturated volatile organic compounds under atmospheric conditions

Lighting Talk, Poster Presentation, Poster Competition

Presented By: Lisa Michelat, *ICARE-CNRS Orleans*

Hydrofluoroolefins (HFOs) and related haloalkenes are a family of man-made compounds replacing ozone-depleting substances that are increasingly emitted to the atmosphere as a

result of their numerous industrial applications. Electrophilic OH addition in the gas phase represents the main environmental sink for these unsaturated compounds, where the degree and type of halogenation strongly affects their chemical reactivity. This leads to a diversity of behavior that has been a challenge for structure-activity relationships (SARs). In this work, we investigate and extend the potential of existing SARs to estimate OH rate coefficients under atmospheric conditions. Starting from the position of substituents across the double bond, our SAR-based approach coupled with theoretical calculations provides predictions of the temperature-dependent OH addition rate coefficient, $k(T)$, of haloalkenes over a temperature range of 200–400K. We present improvements in accuracy and diversity upon existing approaches for estimating these kinetic data. We will investigate the potential for this method to be applied towards other substitutions, e.g., nitrates or carbonyls, to provide a general tool that can be easily used to predict the reactivity of most atmospheric compounds of interest.

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Chemical surrogate modeling with uncertainty quantification using a Bayesian Neural ODE

Lighting Talk, Poster Presentation, Poster Competition

Presented By: Lin Guo, *University of Illinois at Urbana-Champaign (UIUC)*

Neural Ordinary Differential Equations (N-ODE) have shown promise in emulating models of atmospheric chemistry. Here we create a probabilistic (Bayesian) N-ODE to create a chemical mechanism with uncertainty quantification. We emulate a photochemical box model of atmospheric ozone formation with 10 reactions, 13 species, and external inputs of solar radiation, emission, and deposition. We use Stochastic Gradient Langevin Dynamics (SGLD) for model training. For cases where the solar radiation is constant and emission/deposition are disabled, the posterior mean gives accurate predictions with validation error (RMSE) 5.6×10^{-2} ppm and testing error (RMSE) 6.1×10^{-2} ppm (trained on 300 simulations of 30 min duration, validated on 100 simulations of 30 min duration and tested on 40 min duration). For cases with variable solar radiation and emission and deposition enabled, the model can probabilistically capture the periodicity of the system when trained on a single 4-day simulation and projected to its 7-day extension. Model performance remains good when trained on up to ~ 250 simulation examples. Future work will focus on scaling our training workflow to larger datasets.

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Comparison of Common Vapor Pressure Estimation Methods through Modeling of Alkene OH/NO_x Systems

Lighting Talk, Poster Presentation, Poster Competition

Presented By: Emmaline Longnecker, *University of Colorado, Boulder - Chemistry Department*

Modeling of atmospheric reactions is an important tool in understanding the current and future impacts of human activity on the environment. Vapor pressure is a key parameter in modeling these reactions, as it largely determines the ability of a species to transition from the gas to particle phase. However, the vapor pressures of many atmospherically relevant molecules are still poorly constrained. To aid modeling efforts, several group contribution methods have been developed for estimating compound vapor pressures. The current study evaluates how four of these methods: SIMPOL, EVAPORATION, SPARC, and Nannoolal, impact the modeled predictions of secondary organic aerosol (SOA) yields for the reactions of C₈-C₁₄ 1-alkenes and C₉-C₁₅ 2-methyl-1-alkenes with OH radicals in the presence of NO_x. The models were created in the kinetics modeling software KinSim and include rate constants measured by Atkinson and co-workers, quantitative reaction mechanisms developed by our research group from several previous environmental chamber studies of product yields, as well as gas-particle and gas-wall partitioning. The modeled SOA yields were compared to the measured values, and the large range of agreement exemplifies the impact of vapor pressure in modeling atmospheric reactions and indicates the need for further development of estimation methods.

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Developing methods for efficient transport and chemistry calculations in forecasting applications

Lighting Talk, Poster Presentation, Poster Competition

Presented By: Obin Sturm, *NASA GMAO*

The Goddard Earth Observing System Composition Forecast (GEOS-CF) produces global predictions of atmospheric chemical constituents using the GEOS-Chem chemistry module at a resolution of 0.25 degrees. Due to its multiple dimensions of complexity, i.e., chemical detail and high spatial resolution, GEOS-CF is computationally demanding.

We explore various strategies for accelerating GEOS-CF model simulations, including (1) reducing chemical complexity in transport calculations, (2) reducing spatial detail in chemistry calculations, and (3) pre-conditioning the chemical solver.

Timing experiments indicate that though advecting a reduced set of chemical species lessens the computational burden of transport calculations, this strategy has limited potential to shorten the wall time of GEOS-CF runs. Instead, the largest speedup potential is in the reduction of the load imbalance in chemistry calculations. Load imbalances are primarily driven by chemistry calculations in twilight regions, where grid cells far from chemical pseudo-equilibrium transition to new regimes. We explore methods to accelerate chemistry computations under twilight conditions, including running stratospheric chemistry at a coarser resolution or feeding an initial solution to the chemical solver (pre-conditioning). We find that these strategies can reduce wall time substantially while retaining most of the chemical complexity in the system. Such solutions are particularly attractive for forecasting applications.

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Influence of application method on disinfection byproduct formation during indoor cleaning: an example of phenol chlorination during bleach cleaning

Lighting Talk, Poster Presentation, Poster Competition

Presented By: Leif Jahn, *University of Texas at Austin*

Large-scale disinfection methods that have become increasingly common following the COVID-19 pandemic utilize techniques such as electrostatic precipitators, foggers, or "no touch devices" that generate and disperse disinfectant-laden droplets. These devices are designed to work with a variety of disinfectants including those based on peroxides, reactive chlorine species, and quaternary ammonium compounds. Compared to traditional disinfection techniques such as mopping, the dispersal of droplets may alter disinfection byproduct formation and the partitioning of compounds away from or to the disinfectant. In this work we applied bleach within an environmental chamber containing several tables and chairs using a high-volume spraying device or an ultrasonic humidifier. Gas-phase species were measured using a Vocus 2R PTR-ToF-MS. We observe gas-phase phenol concentrations to decrease as bleach is applied, indicating partitioning of phenol to the disinfectant, which is accompanied by the formation of a variety of multi-generation polychlorinated phenolic disinfection byproducts that volatilize from airborne droplets. Greater byproduct formation was observed during experiments with a larger phenol background. The byproducts identified have been observed during prior wastewater disinfection work but primarily under slightly acidic to near neutral pH conditions, not representative of bulk bleach with a pH ~11-12, suggesting unique aspects to these reactions within airborne droplets.

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Sulfate and carbonyl sulfide production from aqueous processing of dimethyl sulfide oxidation products

Lighting Talk, Poster Presentation, Poster Competition

Presented By: Christopher Jernigan, *CIRES*

The oxidation products of dimethyl sulfide (DMS) contribute to the production and growth of cloud condensation nuclei (CCN) in the marine boundary layer. Laboratory and field measurements have demonstrated that DMS is oxidized by OH radicals to the stable intermediate hydroperoxymethyl thioformate (HPMTF), which is both globally ubiquitous and efficiently lost to multiphase processes in the marine atmosphere. Currently, the condensed phase chemistry included in chemical transport models relies on the assumption that HPMTF is irreversibly lost to atmospheric surfaces arresting carbonyl sulfide (OCS) production and forming sulfate at unit yield. At present, there are no experimental measurements of the connection between sulfate and carbonyl sulfide production from the aqueous processing of HPMTF. Using a custom-built bubbler apparatus combined with chemical ionization mass spectrometry (CIMS), a OCS analyzer and ion chromatography, we report the yield of OCS and sulfate. While we did not directly observe the condensed-phase mechanisms of HPMTF in this experiment, the relative yields of OCS and sulfate provide mechanistic insight on the hydrolysis mechanism of HPMTF.

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Kinetic Studies of the Pressure and Temperature Dependence of OH+SO₂ in the Presence of Water Vapor

Lighting Talk, Poster Presentation, Poster Competition

Presented By: Megan Woods, *California Institute of Technology*

The oxidation of sulfur dioxide (SO₂) by the hydroxy radical (OH) is the dominant pathway in the formation of sulfate particles. The formation of these particles is a foundation for aerosol growth, formation, and cloud droplet nucleation. These processes play a critical role in our tropospheric radiation budget and therefore our climate. As a result, it is imperative to accurately characterize the kinetics of the title reaction to understand its influence on our troposphere and climate. Currently, there is only one study which explores the temperature range of OH+SO₂ and observes the collisional efficiency of atmospherically relevant bath gasses nitrogen (N₂, 50-750 Torr, 230-333K), and water vapor (H₂O 50 Torr total pressure, 273-333 K). In consequence, it is essential to further expand on this work and investigate the influence of

N₂ and H₂O on the reaction rate constant at temperatures and pressures relevant to the troposphere. To elucidate knowledge gap, laser photolysis-laser induced fluorescence (LP-LIF) will be employed to observe OH+SO₂+M at the temperature range 230-293 K and a pressure range of 50 – 750 Torr of N₂ and 273-298K and 50-500 Torr total pressure with fractional H₂O = (0-4) × 10⁻¹⁷ molec/cm³. The collected data may provide new insight into the enhancement of the rate coefficient for OH+SO₂ in the presence of H₂O that have been previously reported. The potential tropospheric impact will be discussed.

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Chemical characteristics, long-range transport and health risks of PM_{2.5}-bound trace elements over a regional background location in Northern India

Poster Presentation

Presented By: Pooja Manwani, *Indian Institute of Technology Bombay*

This is a placeholder text. Additional information will be forthcoming

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Atmospheric Chemistry Classics: Exploring Recent Trends in Surface Ozone

Poster Presentation

Presented By: Anke C. Noelscher, *University of Bayreuth*

With the aim to reduce tropospheric production rates of ozone and hence improve air quality, its precursors nitrogen oxides and aromatic volatile compounds have been regulated in many states worldwide since several decades. Despite the successful reduction of these precursors' emissions, tropospheric ozone levels in many urban and suburban areas exhibit positive, rising trends (e.g. Yan et al., 2019). This highlights the complexity and non-linearity of the mechanisms leading to photochemical ozone production.

Here, we present our analysis of the temporal and spatial trends of ozone along with its regulated precursors. We selected contrasting sites in Southern Germany with various degrees of air pollution: For example, at a site in Munich with high traffic nitrogen monoxide decreased at a rate of 2.2 µg/m³ per year over the course of the last 30 years, whereas ozone concentrations increased by about 0.6 µg/m³ annually (data source: UBA). In contrast, at a site

located remotely within a spruce forest, we observed stagnating low levels of nitrogen oxides and persistent high levels of ozone reaching more than $100 \mu\text{g}/\text{m}^3$, therefore exceeding WHO air quality guidelines, during the summer of 2022. For further analysis, we combined spatial and temporal scales to bridge over long-term trends (decades), seasons, weekly and diurnal variability, and to highlight dependencies on the underlying chemical mechanisms regarding regional and local contributions to ozone production.

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Short-term studies of PM_{2.5} characteristics using SEM-EDX over Old Delhi region, India

Poster Presentation

Presented By: Shobhna Shankar, *IGDTUW*

In this study, PM_{2.5} samples were analysed for morphological and elemental characteristics for the duration January-June, 2021, using Scanning Electron Microscope coupled with Energy Dispersive X-Ray (SEM-EDX). The elements determined in this study were Cl, S, Al, Ca, K, Fe, Zn, Na, Mg, N, Tb, Ti, Ni, F, Cd, Cu, Mn, P and Cr (excluding C, Au, Si and O) of which Cl, S, Al, Ca, K, Fe, Zn, Na and Mg were the major constituents. The results revealed that variation in particles' shapes whether definite or irregular, columnar or spherical, flaky or aggregate or crystal-accumulation were achieved on the basis of the major constituting element, majorly Ca-rich, S-rich, Cl-rich and Fe-rich. Interestingly, the physical characteristics of the particles varied with variation in elemental composition. The elemental composition was found to vary with time and source of origin. Ti, Tb and Cd need more analytical studies for their percent contribution and to assess risk or impact on health.

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Trace H₂S Promotes Organic Aerosol Production and Organosulfur Compound Formation in Planetary Haze Photochemistry Experiments

Poster Presentation

Presented By: Eleanor Browne, *University of Colorado Boulder & Cooperative Institute for Research in Environmental Sciences*

Trace sulfur gases and planetary organic haze, produced by CH₄ photochemistry, are ubiquitous in planetary atmospheres of the solar system and likely exoplanets. Their respective chemistries are also thought to be key in the understanding of the early Earth atmosphere. Investigation of

sulfur chemistry has largely focused on the production of inorganic sulfur and has neglected the formation of organosulfur compounds. However, evidence from present-day studies shows that organosulfur contribute substantially to haze. Here, we performed laboratory studies to explore how the addition of trace amounts of H₂S (0.5-5 ppmv) affects haze analogs produced from the ultraviolet photochemistry of CH₄ and CO₂/CH₄ gas mixtures in N₂. We analyzed the aerosol product composition and size in real time using a quadrupole aerosol mass spectrometer (Q-AMS) and a scanning mobility particle sizer (SMPS). We find that the inclusion of trace amounts of H₂S in the precursor mixture significantly enhances the formation of organic aerosol mass, particle effective density, and leads to the formation of organosulfur compounds. Thiol-ene chemistry is proposed as a possible organosulfur formation mechanism. The altering of organic haze particle amount, size, and composition further suggests that trace amounts of H₂S can impact how an organic haze affects climate, habitability, and prebiotic chemistry.

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Secondary Organic Aerosol (SOA) formation from the gas-phase reaction of guaiacol with NO₃ radicals

Poster Presentation

Presented By: Fatima AL ALI, *Université du Littoral Côte d'Opale*

Guaiacol (2-methoxyphenol) is a major representative compound emitted by wood combustion consequently to the pyrolysis of lignin. With an atmospheric lifetime of 1 min with NO₃, guaiacol has a high reactivity during night and is the main degradation pathway with the hydroxyl reactivity during day time.

In this work, we investigate the SOA formation from the NO₃ reaction of guaiacol. Experiments were performed in CHARME and LPCA-ONE atmospheric simulation chamber at 294 ± 2K, atmospheric pressure and under dry conditions (RH < 2%).

Guaiacol gas concentration was measured using a PTR-ToF-MS and SOA formation was followed by a SMPS. After the full oxidation of gaseous guaiacol, SOA were collected on quartz filters and analyzed on a ESI-LC-QToF-MSMS to determine the aerosol chemical composition and the relative abundance.

Experiments in both chambers showed good agreement for SOA formation from guaiacol and NO₃ with yield values ranging from 0.01 and 0.21. Nineteen organic compounds (86 including isomers) have been identified in the SOA mainly represented by nitro-aromatic compounds confirming previous studies on NO₃ reactivity with guaiacol derivatives. Nevertheless, and to our knowledge, it's the first work concerning guaiacol to show compounds with molecular

structures with one, two or three aromatic rings. A mechanism has been proposed to explain the formation of most compounds, especially the multiple aromatic rings compounds.

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First Direct Kinetic Studies of Four-Carbon, Resonance-Stabilized Criegee Intermediates Formed from Isoprene Ozonolysis

Poster Presentation

Presented By: Rebecca Caravan, *Argonne National Laboratory*

Isoprene is the most abundant non-methane hydrocarbon emitted into Earth's atmosphere. Ozonolysis of isoprene produces MVK-oxide ((CH₂=CH)(CH₃)COO) and MACR-oxide ((CH₂=C(CH₃))CHOO) – four-carbon, resonance-stabilized Criegee intermediates. We have utilized the novel photolytic schemes of the Lester group to conduct the first direct experimental kinetic studies of these intermediates. We will present results from experimental and theoretical studies of the reactions of MVK-oxide and MACR-oxide with atmospherically pertinent species, and discuss how these results impact our understanding of their role in Earth's lower atmosphere. We will also compare their reactivity with that of MECI ((CH₃CH₂)(CH₃)COO), which has the same carbon-backbone as MVK-oxide but lacks resonance stabilization.

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Detection of Ambient Concentrations of Hydroxyl Radical using Broadband Cavity-Enhanced Absorption Spectroscopy

Poster Presentation

Presented By: Callum Flowerday, *Brigham Young University (BYU)*

The hydroxyl radical (OH) is responsible for the initiation of formation of a range of secondary pollutants in the atmosphere such as ozone and secondary organic aerosols. As such, it is a species of interest in monitoring and modelling of both biogenic and anthropogenic emissions. While methods of OH monitoring do exist, they tend to involve large, non-portable instruments and often do not measure OH directly but involve chemical ionization or the measurement of known products of reaction with OH. This work describes the development of a spectrometer utilizing broadband cavity-enhanced absorption spectroscopy (BBCEAS) to directly measure OH in the atmosphere.

BBCEAS uses a high finesse optical cavity with highly reflective mirrors (>99.8% reflectivity) to create a long pathlength that provides the ability of in situ sampling. This portable BBCEAS spectrometer was made with an open cavity giving it the ability to directly measure ambient concentrations of OH radical. The instrument currently has a 3-sigma limit of detection for OH, determined using an environmental chamber, of 5×10^8 molecules cm^{-3} using a 2.5 m base length cavity and a 30 min averages. Further improvements are being made to improve

resolution and base pathlength to lower the detection limit to ambient atmospheric concentration levels.

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Acetonyl peroxy and hydro peroxy self- and cross- reactions: Temperature-dependent kinetics parameters, branching fractions, and chaperone effects

Poster Presentation

Presented By: Fred Grieman, *Jet Propulsion Laboratory, California Institute of Technology*

Acetone, one of the most abundant OVOCs in the atmosphere, leads to the formation of $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$ radicals. The cross-reaction between $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$ and HO_2 is either a temporary reservoir reaction forming $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{OOH}$ or a radical propagation pathway forming $\text{OH} + \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}$. In this study, we have determined the temperature dependent kinetics parameters, branching fractions, and chaperone effects of the cross- and self-reactions between $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$ and HO_2 using Infrared Kinetic Spectroscopy (IRKS). As in our previous room temperature study, the IRKS system employed two tunable diode lasers, and a near-UV probe to measure three species (OH , HO_2 and $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$) independently and simultaneously on the μs time scale. The radical temporal profiles were analyzed to determine rate coefficients and uncertainties using the Markov Chain Monte Carlo (MCMC) algorithm to systematically determine the rate coefficients and their uncertainties. The acetone chaperone effect on the HO_2 self-reaction was determined for the first time.

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Ions diffuse slower than water in mixed organic/inorganic aerosol particles

Poster Presentation

Presented By: Liviana Klein, *ETH Zurich*

Internally mixed organic/inorganic aerosols have been the focus of numerous studies in recent years. Nevertheless, ion diffusivities, important for calculations of evaporation rates and gas-to-particle partitioning in these systems, are still poorly understood.

In this study, we determine the ion and water diffusivities of an atmospherically relevant surrogate system containing sucrose and NH_4NO_3 – a ubiquitous semi-volatile inorganic compound. We measure evaporation rates of single particles, levitated in an electrodynamic balance (EDB), in an environment of varying relative humidity (RH). We further fit the experimental results with a particle-shell model to determine diffusion coefficients of water molecules and of the inorganic ions. At elevated and rapidly changing RH, water quickly evaporates such that mass transfer limitations are not easily detected. In contrast, at dry conditions (< 30% RH) the evaporation rates of NH_3 and HNO_3 are significantly lower compared to what is expected for internally well-mixed particles. Our modeling results show that at low humidities the diffusion coefficients of the ions are orders of magnitude lower than that of water. This is an interesting finding which has not been reported in the literature to date and has implications on our understanding of gas-to-particle partitioning.

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WiFEX: Walk into the warm fog over Indo Gangetic Plain region

Poster Presentation

Presented By: Rachana Kulkarni, *self*

The presence of persistent heavy fog in northern India during winter creates hazardous situations for transportation systems and disrupts the lives of about 400 million people. The meteorological factors responsible for its genesis and predictability are not yet completely understood in this region. WiFEX is a first-of-its-kind multi-institutional initiative dealing with intensive ground-based measurement campaigns for developing a suitable fog forecasting capability under the aegis of the smart cities mission of India. Between the 2015–2020 winters, measurement campaigns were conducted at the Indira Gandhi International Airport, New Delhi, covering more than 90 dense fog events. The field experiments involved extensive suites of in-situ instruments and gathered simultaneous observations of micro-meteorological conditions, radiative fluxes, turbulence, droplet/aerosols microphysics, aerosol optical properties, fog water-chemistry, and vertical thermodynamical structure to describe the environmental stability in which fog develops. These field observations helped to interpret the strengths and deficiencies in the numerical modeling framework. Four scientific objectives were pursued: (a) life cycle of optically thin and thick fog, (b) microphysical properties in the polluted boundary

layer, (c) fog water chemistry, gas/aerosol partitioning during fog life-cycle, and (d) numerical prediction of fog.

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Decoding VOC Photooxidation on a Molecular Level – A Novel Ensemble of Methods to Generate, Analyze, and Characterize Multifunctional Oxidation Products in the Gas and Particle Phase

Poster Presentation

Presented By: Finja Löher, *University of Bayreuth*

Tropospheric photooxidation of volatile organic compounds (VOCs) is closely associated with the formation of secondary organic aerosols (SOAs) and ground-level ozone. To elucidate underlying reactions, a molecular view on evolving multifunctional oxidation products is as useful as it is demanding.

Here, we report first results from a newly integrated set-up enabling i) the controlled generation of photooxidation products, ii) their isomer-resolved analysis, and iii) assessments of their yields, gas-particle partitioning coefficients, and OH rate constants. For studying the photooxidation of anthropogenic and biogenic model VOCs (e.g. toluene, α -pinene), we performed experiments in a Teflon bag and a glass flow reactor at different temperatures, humidity levels, and NO_x concentrations. The oxidized products were determined by SPME-GC-MS using a two-step derivatization scheme (Borrás et al. 2021) which extended the analytical range towards traditionally challenging compounds like aldehydes, ketones, carboxylic acids, and alcohols. Gas-phase products were monitored on-line while SOAs were collected and separated with cascade impactors prior to off-line analysis. As supplement, the relative rate method (Kato et al. 2011) provides an effective and coherent approach to assess the reaction of the emerging compounds with OH radicals.

Jointly, these methods enable observations of the production and fate of atmospheric photooxidation products as key indicators of prevalent mechanisms.

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Assessment of size-segregated heavy metals dosimetry modeling in HRT: Auto repair garage.

Sneha M, Ramsundram N, Elangovan R

Poster Presentation

Presented By: Sneha M, *Kumaraguru College of Technology*

This research is the first step toward a more profound understanding of the inhalation of size-segregated PM in auto repair garages (ARG). The workers in ARG are exposed to aerosols, particulate matter, carbon monoxide, welding fumes, inorganic solvents, isocyanates in paints, heavy metal poisoning, and toxic chemical fumes. In the previous study, the ambient air quality of the ARG was monitored, and inferred that PM₁₀ and PM_{2.5} has exceeded the permissible limit. Elemental characterization was performed to detect the presence of 20 heavy metals. Al, B, Ba, Fe, and Zn were found to be significant. This finding is curated to address the previously unaccounted phenomena, the size-segregated PM (PM_{2.5}, PM₁, PM_{0.5}, PM_{0.25}) is been monitored in the ARG. From this, the presence of each heavy metal in the various size ranges is analyzed by ICP-MS and EDAX. The dosimetry model (MPPD) is performed to understand the total, regional, and lobar deposition in HRT. It was found that out of 247.6 $\mu\text{g m}^{-3}$ (PM₁₀) the heavy metals constituted about 12.6 $\mu\text{g m}^{-3}$. The inhalation concentration of the exposed workers in ARG is about 39.95 $\mu\text{g m}^{-3}$ per year (Al: 6.01 $\mu\text{g m}^{-3}$, B: 11.16 $\mu\text{g m}^{-3}$, Ba:12.85 $\mu\text{g m}^{-3}$, Fe: 0.71 $\mu\text{g m}^{-3}$, Zn: 9.21). Thus, this study will be an eye opener for the researchers in understanding the site-specific deposition of the particles in HRT, the nature of the heavy metal – hydrophilic/hydrophobic, its reaction with the mucus region, and its oxidative state.

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Vibrational Photochemistry and Dissociation of Peroxyformic Acid

Initiated by Visible Light

Poster Presentation

Presented By: Josue Perez, *University of California San Diego*

Peroxyformic acid (PFA) is an organic hydroperoxide formed in the atmosphere through several different pathways including the gas phase reaction of O₃ with chloroethene and the photo-oxidation of hydrocarbons. It is also a common industrial disinfectant used in both the food and medical industries. Photodissociation through the absorption of visible light is an important loss mechanism for atmospheric hydroperoxides (R-O-OH) at high solar zenith angles, where UV light is unavailable. Photodissociation of PFA leads to the production of OH radicals via the rupture of the weak hydroperoxide O-O bond. Here we present results from the visible light

induced unimolecular dissociation of peroxyformic acid initiated by exciting the molecule in the vicinity of its fifth OH stretching overtone state (6vOH) in the vicinity of 620nm. Using laser induced fluorescence (LIF), we have detected the resulting OH fragments from these near thresholds unimolecular dissociation experiments and have determined the partitioning of the available energy into its internal and translational degrees of freedom. Using available literature data for the heat of formation of the parent PFA molecule and the resulting OH +HCO₂ fragments, the O-O bond dissociation energy (D₀) in PFA is estimated to be ~45.1 kcal/mol. Thus, excitation of room temperature PFA molecules in the region of 620nm leaves the OH + HCO₂ fragments with roughly 3 kcal/mol of available energy.

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Nonisothermal nucleation in the gas phase is driven by cool subcritical clusters

Poster Presentation

Presented By: Bernhard Reischl, *University of Helsinki*

The classical view of nucleation in the gas phase assumes isothermal conditions where the nucleating clusters are in thermal equilibrium with their surroundings. However, in all first-order phase transitions, latent heat is released, potentially heating the clusters and suppressing the nucleation. The question of how the released energy affects cluster temperatures during nucleation as well as the growth rate remains controversial. To investigate the nonisothermal dynamics and energetics of homogeneous nucleation, we have performed molecular dynamics simulations of a supersaturated vapor in the presence of thermalizing carrier gas. The results obtained from these simulations are compared against kinetic modeling of isothermal nucleation and classical nonisothermal theory. For the studied systems, we find that nucleation rates are suppressed by two orders of magnitude at most, despite substantial release of latent heat. Our analyses further reveal that while the temperatures of the entire cluster size populations are elevated, the temperatures of the specific clusters driving the nucleation flux evolve from cold to hot when growing from subcritical to supercritical sizes and resolve the apparent contradictions regarding cluster temperatures. Our findings provide unprecedented insight into realistic nucleation events and allow us to directly assess earlier theoretical considerations of nonisothermal nucleation.

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The gas-phase formation mechanism of iodic acid: a catalytic role of iodine in particle formation

Poster Presentation

Presented By: Rainer Volkamer, *University of Colorado Boulder*

Iodine is a micronutrient, and a reactive trace element in atmospheric chemistry that destroys ozone and nucleates particles. Iodine oxoacids (e.g., iodic acid, HIO₃) and higher iodine oxide polymers (I_xO_y) present viable pathways to iodine particle formation. While much research has investigated the formation of I_xO_y species, the formation mechanism of iodic acid is missing. The lack of an understanding about iodic acid formation makes it difficult to assess the relevance of both pathways in iodine particle formation in the atmosphere. This presentation discusses chamber experiments at CLOUD, box modeling, and quantum chemical calculations to investigate the formation mechanism of iodic acid. A mechanism is proposed, and tested against field observations. The new mechanism provides a missing link between iodine sources and particle formation in atmospheric models. Since particulate iodate is readily reduced, recycling iodine

back into the gas-phase, our results suggest a catalytic role of iodine in aerosol formation.

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New Measurements of Glyoxal Yields from Acetaldehyde Oxidation

Poster Presentation

Presented By: James Warman, *University of Leeds*

Volatile organic compounds (VOCs) introduced into the atmosphere either through primary emissions or secondary chemistry play a crucial role in air quality and climate change. Whilst satellite measurements of VOCs are desirable for advancing our understanding of the chemistry and emissions both locally and globally, the large quantity and broad, overlapping spectra of the majority of VOCs make observations of direct VOC emissions impossible. Glyoxal (GL) and formaldehyde (FA) are two notable exceptions; ratios of GL:FA can provide information on primary emissions if the chemistry of GL and FA formation is understood.

One such precursor, acetaldehyde, particularly relevant to the marine boundary layer (MBL), is thought to produce GL through a minor OH abstraction channel from the methyl site. Modelled GL mixing ratios in the MBL consistently under predict experimental values, indicating a missing source of GL that may be mitigated through acetaldehyde chemistry. Measurements conducted within the University of Leeds HIRAC (Highly Instrumented Reactor for Atmospheric Chemistry) apparatus provide evidence for the production of GL, however demonstrate a significantly

lower yield (0.11 ± 0.02 %) than expected from the Master Chemical Mechanism (2.6 %). These results suggest an increased discrepancy between modelled and measured GL mixing ratios, providing a need for further investigation into the missing GL source in the MBL.

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Understanding How Representative Laboratory Simulation is for Ambient Chemical Processes through a Compound-Specific Approach

Poster Presentation

Presented By: Lindsay Yee, UC Berkeley

Organic aerosols (OA) contain a myriad of individual chemical constituents. Their chemical composition varies based on many factors including sources of primary OA as well as the chemical and environmental conditions under which secondary OA are formed. This creates a significant challenge to chemically characterize all the potential compounds that arise in ambient OA, as most of these compounds are uniquely created in the atmosphere and few authentic standards are available. We have obtained laboratory and field samples of OA on quartz filters representing a variety of sample types and chemical regimes (e.g. biomass burning, terpene oxidation, natural, rural, and urban environments). We resolved thousands of unique compounds among samples analyzed using two-dimensional gas chromatography with high-resolution time-of-flight mass spectrometry. We are curating over 24,000 mass spectra to be added to the open-access electron impact mass spectral database known as the University of California, Berkeley, Goldstein Library of Organic Biogenic and Environmental Spectra (UCB-GLOBES). Analyses of this database show thus far that laboratory oxidation experiments are far more chemically diverse than our ambient datasets, yet to date we still only see at most ~40% of ambient dataset overlap with laboratory datasets. Our analysis provides additional insight into how representative laboratory simulation may be for ambient chemical processes.

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Atmospheric Photolysis of CF₃CHO: A Source of HFC-23?

Poster Presentation

Presented By: Mads Sulbaek Andersen, *California State Univeristy*

CF₃CHO is an atmospheric degradation product of several chlorofluorocarbon (CFC) alternatives, including some commercially important hydrofluoroolefins (HFOs). The photolysis of CF₃CHO has three principal pathways:



There is conflicting information on the CF₃CHO photolysis in the literature. Campbell et al. (DOI 10.21203/rs.3.rs-199769/v1) recently announced that they have observed a 308 nm - quantum yield of $\Phi_2 = 0.010 \pm 0.005$, meaning that actinic photolysis of CF₃CHO would be a source of CF₃H, HFC-23. CF₃H has a large global warming potential of GWP₁₀₀ =12,960 and could in effect present a significant additional secondary contribution to the radiative forcing of climate from the parent CFC alternative.

We have investigated the photolysis kinetics and products of CF₃CHO under photolysis conditions relevant to the troposphere and the stratosphere. Experiments show that actinic photolysis produces CF₃ radicals, which under atmospheric conditions gives dominantly COF₂. No formation of CF₃H was observed under these conditions in contradiction to results published most recently. Photolysis using 254 nm radiation gives CF₃H in a significant yield, in addition to CF₃ radicals. The photochemical lifetime of CF₃CHO and the CF₃H yields are discussed with respect to troposphere and stratospheric conditions and in context of the environmental impact of important CFC substitutes.

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Chekimomi: a tool for enabling FAIR kinetic models

Poster Presentation

Presented By: Luc Vereecken, *Forschungszentrum Jülich GmbH*

Chemical kinetic modeling is a critical tool in atmospheric chemistry research, where it is used in many applications such as the design and interpretation of experiments, or regional and global modelling. The kinetic models are build from experimental data, theoretical predictions, and structure-activity relationships, and thus reflect our current knowledge on the studied chemical system.

Many kinetic solvers exist for the kinetic coupled differential equations, each with their own notational style and capabilities, and integrated in (locally developed) tool chains for e.g.

handling experimental data, analyzing model results, parameter optimization, or visualization. However, these different notational styles and tool chains are not directly interoperable, and literature model data is typically not reproducible in another tool chain without significant (manual) effort.

We have developed an open source modularized model handler, Chekimomi, which is able to help in the transcription of chemical models. It supports differences in notational styles, rate coefficient equations, chemical identifiers, photochemistry, etc., and can support local variations in the tool chains. By simplifying exchange of kinetic data, Chekimomi is a useful tool for publishing chemical models and rate data in a FAIR way (Findable, Accessible, Interoperable, Reproducible). Efforts are ongoing to expand the supported styles, tool chains, chemical identifiers and human-readable export formats.

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Automated Mechanism Reduction Algorithm Applied to Isoprene Chemistry

Poster Presentation

Presented By: Forwood Wiser, *Columbia University*

Automated chemical mechanism reduction has been applied to complex combustion mechanisms in order to reduce the computational effort needed to run them. The isoprene atmospheric chemical mechanism is highly complex and is a good candidate for automated reduction due to the extensive use of reduced isoprene mechanisms, but no automated reduced mechanisms have been tested so far. In this work, the Caltech isoprene mechanism was reduced using an automated reduction algorithm. After additional manual adjustments, the resulting mechanism outperformed the published RACM isoprene mechanism while containing only 9 isoprene species and 17 reactions. This method shows significant promise in the development of mechanism reduction algorithms for atmospheric chemistry.

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Multi-day Evolution of Organic Aerosol Mass and Composition from Biomass Burning Emissions

Poster Presentation

Presented By: Abraham Dearden, *Colorado State University*

Biomass burning is an important source of primary organic aerosol (POA) and volatile organic compounds (VOCs) to the atmosphere. Yet there are uncertainties surrounding the oxidation chemistry of POA and VOCs leading to SOA formation. Lim et al. (2019) performed 50+ photooxidation experiments on biomass burning emissions using a small environmental chamber (~150 L) at the Fire Sciences Laboratory in Missoula MT. In this work, we used a kinetic model, SOM-TOMAS (Statistical Oxidation Model-Two Moment Aerosol Sectional), to simulate the physicochemical evolution of organic aerosol (OA) in 15 of these chamber experiments. SOM-TOMAS simulates the oxidation chemistry, thermodynamics, and microphysics of OA, in addition to accounting for rapid dilution and wall losses. For most experiments the model was able to simulate the time-dependent evolution of the OA mass concentration but systematically underestimated the change in the OA O:C ratio with time. Simulations indicated that the same VOC classes that have previously been found to be important for SOA formation in smoke (oxygenated aromatic, heterocyclic, and semi-volatile compounds) at shorter photochemical ages (<12 hours) are also relevant at longer photochemical ages (~1 day to ~1 week). Heterogeneous oxidation, oligomerization, and assumptions about phase state modestly influenced the OA mass evolution. Ongoing work is focused on linking these laboratory insights to aircraft-based field measurements (e.g., WE-CAN, FIREX-AQ).

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Multi-scale modeling of air quality and mechanism comparison with MUSICA

Poster Presentation

Presented By: Louisa Emmons, *NCAR*

One of the key features in the design of the Multi-Scale Infrastructure for Chemistry and Aerosols (MUSICA) is the ability to easily change chemical mechanisms within an earth system model such as the Community Earth System Model (CESM). This capability is being developed with the Model Independent Chemistry Model (MICM), which is currently available in a box model (MusicBox) and being coupled to CESM. Another key design feature of MUSICA is the ability to simulate local-to-global scales within a single model. MUSICA_{v0} is a configuration of the CAM-chem global chemistry climate model with variable resolution refined over arbitrary regions of the globe. This presentation will illustrate these two components of MUSICA. Results from MusicBox with MICM will show the comparison of complex and simplified mechanisms, quantifying their ability to predict atmospheric composition and air quality metrics. Results from MUSICA_{v0} simulations with refined regions over the U.S., Asia and Africa will illustrate the value of integrating regional scale modeling in a global model.

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Impacts of Low-Level Jets on Surface Temperature

Poster Presentation

Presented By: Jonathan Hale, *UC Davis*

Low-Level Jets (LLJs) are a nocturnal event, where concentrated high wind speeds flow together in the low levels of the atmosphere. They exist from a few hundred feet to five thousand feet above ground level. LLJs are formed by a difference in temperature and elevation between the West and East geographical locations in the United States.

This research provides a new perspective by focusing on the influence of LLJs on local temperature. LLJs drive the transportation of air from the Southeastern U.S. to the mid-Atlantic. With this research, temperature changes due to the LLJ that occurred the night before will become visualized through curtain plots and temperature time series.

In the work conducted, three different cities were chosen in the state of Maryland, during the day a LLJ occurred. The surface temperature and wind speeds of the LLJ was gathered through RADAR wind profiler data and the Automated Surface Observing System (ASOS) Network. With this data, subplots were created to highlight the effect of the wind speeds on the temperature at a given time.

All in all, it was found that the greater the magnitude of the wind speed was, the greater the temperature increased by. This is due to the warm, moist air that is traveling from up the Gulf Stream to the mid-Atlantic U.S.

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Explicit and reduced chemical mechanisms for indoor air quality models

Poster Presentation

Presented By: Roberto Sommariva, *University of Birmingham*

The air quality inside homes and workplaces is an important human health issue as most people spend the majority of their time indoors. The emissions, formation and removal of pollutants in indoor settings are significantly different than the equivalent processes in outdoor settings and require bespoke modelling tools to study and assess exposure and health impacts.

We present two chemical mechanisms, designed for use in indoor air quality models: 1) a highly detailed chemical mechanism which can be used in a flexible multi-box model (MBM-Flex) to study inter-room air quality variability, and 2) a reduced chemical mechanism derived from the Master Chemical Mechanism (MCM, Saunders et al., 2003; Jenkin et al., 2003) which can be used in a large eddy simulation model (Chem-LES) to investigate intra-room dynamics, ventilation effects and formation of pollutant hotspots within a room.

The two chemical mechanisms are compared to each other, to the INCHEM-Py indoor chemistry mechanism (Shaw & Carslaw, 2021), and to the MCM (used as reference standard) under a variety of chemical conditions and a range of indoor-outdoor exchange settings. We examine how well chemical mechanisms of different complexity are able to reproduce the concentrations of selected target species (e.g. O₃, NO_x, CO) within the timeframe of the simulations.

This work is part of the project "Indoor Air Quality Emissions & Modelling System (IAQ-EMS)", funded by the Met Office and UK Research and Innovation.

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Modeling the atmospheric fate of Per- and Polyfluoroalkyl Substances (PFAS)

Poster Presentation

Presented By: Emma D'Ambro, *US EPA, ORD*

Per- and polyfluoroalkyl substances (PFAS) are a class of human-made compounds that have received attention due to their presence in drinking water and resulting human exposure. More recently, air emissions, transport, and deposition have been identified as a likely pathway contributing to their water concentration. However, few studies have examined the air concentration and deposition of PFAS. One of the major impediments is the lack of emissions information since they are not a designated criteria or hazardous air pollutant and thus are not reported to regulatory agencies. Therefore, most modeling studies have focused on individual compounds and very few have investigated atmospheric chemical transformations. We present results from the Community Multiscale Air Quality (CMAQ) model applied to a case study of a fluoropolymer manufacturer in North Carolina. Emission rates of 53 speciated compounds were obtained for this point source, the most detailed emissions information from a point source to-date. Previously, we investigated the air concentrations and deposition extending up to ~150km from the facility. Here, we test the sensitivity of our previous results to different model inputs and find the level of chemical speciation is the most important factor for accurately predicting

transport and deposition. Future work will implement the suite of PFAS and their known atmospheric oxidation reactions into a box model framework to understand PFAS chemistry and partitioning.

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High time resolution ambient measurements of gas- and particle-phase perfluorocarboxylic acids (PFCAs): Implications for sources and fate

Poster Presentation

Presented By: Cora Young, York University

Per- and polyfluoroalkyl substances (PFAS) are widely used in numerous consumer and industrial products, including non-stick materials and firefighting foams. Perfluorocarboxylic acids (PFCAs) are a class of PFAS and are found ubiquitously in the environment, including in remote regions far from sources. While PFCAs can be directly emitted into the atmosphere through production and use of fluoropolymers, they can also be formed by atmospheric oxidation of volatile PFAS. A complete understanding of PFCA sources, fate, and transport requires atmospheric PFCA measurements. Current atmospheric sampling methods primarily rely on offline sampling techniques with timescales of several hours to days. Because atmospheric processes that drive production and fate of PFCAs occur on shorter timescales, faster measurement techniques are needed to provide insight into these processes. Here, we describe two new approaches to high time resolution atmospheric PFCA measurements, as well as their application to ambient measurements in Toronto, Canada. The ambient ion monitor-ion chromatograph-mass spectrometer (AIM-IC-MS) provides in situ hourly measurements of gas- and particle-phase PFCAs. The time-of-flight chemical ionization mass spectrometer (ToF-CIMS) measures in situ gaseous PFCAs at a timescale of 10 seconds. Data from the AIM-IC-MS and ToF-CIMS, along with co-located meteorological and air quality parameters will be used to describe new insights into PFCA sources, fate, and transport.

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Investigating the Chemistry of Isoprene Nitrates and Nitrooxyorganosulfates Under Polluted Urban Conditions

Poster Presentation

Presented By: Alfred Mayhew, *University of York*

Isoprene is the most emitted non-methane volatile organic compound, and the chemistry of isoprene in the atmosphere can have large impacts on air quality, climate, and public health. Isoprene nitrates and nitrooxyorganosulfates are important due to their potential to contribute to secondary organic aerosol (SOA).

This investigation involves a series of chamber experiments performed at the European PHOtoREactor (EUPHORE) designed to investigate the oxidation of isoprene, with a focus on oxidation by the nitrate radical (NO_3). Experiments were designed to reproduce and contrast conditions observed in Beijing in 2017 where high ozone concentrations resulted in low NO concentrations and in NO_3 playing a significant role in the formation of isoprene nitrates and nitrooxyorganosulfate aerosol in the late afternoon. All of the experiments were designed to reproduce a range of NO concentrations, photolysis conditions, and were performed both with and without seed aerosol in an effort to identify particle-specific reaction pathways.

A comparison of filter samples taken during the chamber experiments with ambient measurements made in Beijing and other cities, alongside box modelling of the experiments, allows for a detailed investigation into the formation pathways of isoprene nitrates and nitrooxyorganosulfates. The findings from this work will have implications for our understanding of the oxidation of isoprene under urban low- NO conditions similar to those observed in Beijing.

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Probing the DMS Oxidation Mechanism Through Measurements of the OH Radical

Poster Presentation

Presented By: Frank Winiberg, *Jet Propulsion Laboratory*

Dimethyl sulfide (DMS) is the largest contributor of natural sulfur to the atmosphere. The oxidation of DMS results in the formation of sulfate aerosols that can affect Earth's radiative balance by scattering solar radiation and serving as cloud condensation nuclei.

Hydroperoxymethyl thioformate (HPMTF), is a newly identified major oxidation product of DMS and could potentially have a major impact on the atmospheric budget of sulfur. In a recent study modeling study, we have shown that accounting for HPMTF chemistry results in a significant decrease in boundary layer levels of SO₂ and H₂SO₄ and increases in sulfate aerosol in the upper troposphere, with an associated 110% increase in sulfate aerosol nucleation rate.

We will present the preliminary results from the investigation of the formation kinetics of HPMTF by examining the hydroxyl radical (OH) co-product. The HPMTF formation rate coefficient will be studied using the Pulsed Laser Photolysis-Laser Induced Fluorescence apparatus from the chlorine-initiated oxidation of DMS under relevant temperature and pressure conditions for the troposphere. Analysis of the data will be completed by fitting the time dependent OH signals with a comprehensive chemical simulation model that will be developed as part of this work. The measured rate coefficients and atmospheric implications will be discussed.

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