

PROJECT STATEMENT

High Energy Chemistry: Atmospheric Chemistry Above the Boreal Forest

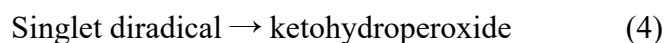
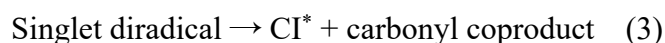
- *Project Overview*

This project seeks to address an important question in atmospheric chemistry and extend the applicant's expertise in unraveling chemical reaction dynamics. This project taps expertise at a Norwegian Centre of Excellence for computational study. The project will be of value scientifically and will aid in understanding of important tropospheric chemistry above boreal forests, an important biome in Norway.

Boreal forests represent about 1/3 of the global forest cover and are a key resource in Scandinavia. Volatile organic compounds and monoterpenes in particular are concentrated above these forests [1]. The reaction of monoterpenes, e.g. pinene emitted above northern boreal forests, with ozone (ozonolysis) is a source of aerosol and reactive OH radical [1B, 2]. OH radical is a key oxidative ingredient in the troposphere involved in breaking down trace atmospheric species and thus "cleansing" the atmosphere.

The ozonolysis of atmospheric unsaturated hydrocarbons has received substantial recent experimental and theoretical study. The formed primary ozonide is highly vibrationally excited and can form excited Criegee intermediate (CI*) which can either promptly undergo unimolecular dissociation or collisionally stabilized Criegee intermediate (CI). Unimolecular dissociation is ultimately a source of OH radical, and collisional stabilization can lead to aerosol formation [3]. This proposed project seeks to extend knowledge on the formation and reactivity of smaller CI to larger biogenic species such as those above Scandinavian boreal forests.

Experimental studies to date have examined the reactivity of CIs produced by a separate light activated (photolytic) pathway with a diiodoalkane (CH₂I₂) precursor in the presence of oxygen. These experimental studies are limited to select smaller Criegee intermediates, such as CH₂OO, in the laboratory. This approach has yielded key insights based on this model system which can be extrapolated to the atmospheric setting. In one elegant study Fourier transform microwave spectroscopy was used to characterize the simplest CI directly from ozonolysis of ethylene yielding similar product ratios and confirming the validity of early experiments producing this simple CI indirectly [4]. These experiments on smaller CIs, however, do not include key biogenic species. The overall processes can be summarized in the following chemical equations:



Biogenic terpenes such as pinene and their ozonolysis, a subject of the proposed project, have been the subject of recent experimental studies with these studies revealing important differences in reactivity [5]. A recent study used trapping to detect a Criegee intermediate resulting from α -pinene ozonolysis using mass spectrometry [5B].

Computational study of CI have utilized *ab initio* quantum chemical calculations to examine the energetics of reactants, intermediates, and reaction transition states. One question is both the distribution of products and their energy as this determines the ultimate atmospheric impact of this chemistry. In some cases calculations and statistical theories can be used to predict the distribution but in many cases the statistical approach falls short and more elaborate sampling techniques are needed to get at the atmospheric process and its impact. In addressing this question, calculations can be coupled with statistical theories and a master equation approach to include a distribution of reactant energies and allow competition between reaction and collisional stabilization to compute relative reaction rates and product distributions [6]. The primary ozonide is formed with substantial vibrational energy amounting to ~ 50 kcal/mole in $C_2H_4 + O_3$ [7]. This highly vibrationally excited species likely samples a large range of the molecular potential energy surface and thus may not lend itself to statistical transition state approaches as found by Klippenstein, Hase and coworkers [7].

In this proposed project by studying the reactions using direct dynamics and product disposition as a function of initial energy distribution computationally, a link can be formed between experimental results and more realistic molecular reaction dynamics and atmospheric conditions.

- *Objectives and Methodology*

The basic project idea is to consider the products of the most energetic steps in the formation of Criegee intermediates. The terpenes from northern forests are prime targets for ozonolysis. In collaboration with colleagues at the Hylleraas Centre I plan to refine the application of direct dynamics to map product and energy disposition of the ozonolysis of increasingly complex alkenes. This work will build on an early collaboration with Prof. Michele Cascella, a principal investigator in the Centre, to carry out coupled cluster molecular dynamics on small molecules.

The chemistry of these energized molecular species can be studied and sampled using computer molecular dynamics simulation. These dynamics will map out the sampling of energetic species and their transformation to atmospheric species. These dynamic simulations will be repeated 100-1000 times to gain statistically significant counts and energetic distributions of product channels. Given that these species sample parts of the potential energy surface far from equilibrium and often well above transition states they are not amenable to traditional calculations. Quantum *ab initio* based direct dynamics simulations provide an *a priori* approach to sampling trajectories on these potential energy surfaces. I am currently applying these methodologies to study the product state distribution of an energized pyrazine molecule formed following internal conversion from an electronically excited state. I have found an 11% yield of energized acetylene and HCN fragments, in close agreement with our experiments. I am also currently developing new tools and associated algorithms which use the potential energy points computed in initial *ab initio* direct dynamics as a training set for machine learning development of a potential energy surface which can be used for further molecular dynamics and other calculations. This involves an adaptation of the PES Learn code developed by the Schaefer group [8]. This novel approach has now been applied to gaseous formic acid and its dimer with a

surface capable of produced a Hessian resulting in good quality agreement with published vibrational frequencies. Pinene and related terpenes are substantially larger molecular species with 26 atoms but I have success in applying less expensive DFTB molecular dynamics using the CP2K package and the above machine learning algorithms.

The proposed project is highly feasible in the host country of Norway. The proposed research is ideally suited to carry out in conjunction with the Hylleraas Centre for Quantum Molecular Sciences at the University of Oslo. An academic year (9 month) time frame will permit time to learn the local computational environment, develop code and script to process calculations, establish collaborations, and to benchmark early computations. Substantial high performance computing (HPC) and workstation resources are available through the Hylleraas center as a Norwegian Centre of Excellence.

- *Professional Experience Relevant to Proposed Project*

I am currently Associate Professor of Chemistry at Temple University, where my expertise is in computational modeling and spectroscopy of reaction dynamics. I welcome the unique opportunity to apply these skills as a Fulbright Scholar in Norway. I am excited to apply my computational modelling skills and my deep scientific knowledge of complex systems to investigating tropospheric chemistry above boreal forests and contributing to an area of significant interest in atmospheric chemistry.

There are two compelling aspects to my background. First, I am an established scientist with fundamental understanding of dynamics at the molecular level including detailed studies of atmospheric chemistry. These studies include reactions of translationally hot hydrogen atoms with SO₂ and CO₂. Secondly, I am skilled at developing, coding, and applying new algorithms which have extended computational chemistry modeling to new studies.

I contribute a strong scientific track record. By way of overview, my research examines chemical reaction dynamics of highly vibrationally excited species such as those created from atmospheric photolysis and in combustion using computational chemistry and spectroscopy. These highly excited species sample parts of the potential energy surface far from equilibrium and often well above transition states and thus not amenable to traditional model calculations. Direct dynamics trajectories provide an a priori approach to sampling molecular properties and reactions on these potential energy surfaces. Time resolved infrared emission spectroscopy provides the identities and energetics of the reactive species and is well correlated with the computations. I have shown that at high energy or in collisions between a high energy collider and molecules, energized long-lived intermediates are formed (Journal of the American Chemical Society 2014, 136 (5), 1682- 1685). Most recently I have demonstrated that this combined experimental and computational approach can be used to unravel a photolytic mechanism which can explain the anomalous ratio of HNC to HCN found in the interstellar medium and comets (The Astrophysical Journal 2017, 849 (1), 15).

My research has been disseminated in thirty peer reviewed papers, including high impact articles in the Journal of the American Chemical Society, Physical Review A Communication, and the Journal of Physical Chemistry Letters. I have a solid record of receiving grant support for his research and broader multi-disciplinary efforts. I have sought and received external funding from the National Science Foundation (NSF), American Chemical Society petroleum research fund (ACS-PRF), Camille and Henry Dreyfus Foundation, Howard Hughes Medical Institute (HHMI), and Merck-American Association for the Advancement of Science (AAAS). My

computational modeling work was deepened during a sabbatical visit at the University of Minnesota with Professors of computational chemistry, Donald Truhlar and Chris Cramer. My spectroscopic work grows out of his PhD work and postdoctoral work at Yale and MIT. I am also a founding and continuing member of the Midwest Undergraduate Computational Chemistry Consortium which serves as a NSF supported high performance computing (HPC) cluster and hub for supporting computational research.

My computational skills have been honed through direct and hands-on development of code and algorithms. These codes range from novel implementation of new models using primarily FORTRAN code to Python and shell scripting to extract and process computed data on a LINUX platform. I also have significant skills in working with HPC resources from building a cluster to using large cluster resources at the University of Minnesota and Temple.

- *Scientific and Professional Significance of Proposed Project*

The proposed project is both scientifically and professionally significant. The outcomes of this project will contribute to the discipline, to my professional development, and to Norway.

Scientifically, the project contributes to the understanding of the kinetics of biogenic alkene ozonolysis. This project brings improved understanding of the role of terpenes and their ozonolysis above boreal forests in producing OH radicals and other product channels, all of which will have a strong effect on local tropospheric concentrations of trace species. Further, the project makes a methodological contribution through the further application of *ab initio* direct dynamics to the study of vibrationally highly excited species and their unique reactivity and product state and energetic distribution.

Professionally, I expect my research as a Fulbright scholar in Norway to enable me to return to Temple University with broadened computational capabilities, new global collaborations, and a heightened sense of Scandinavian culture. This project is an excellent opportunity to develop a new collaboration that leverages the host institutions' expertise and my own skills in this area applied to a scientifically novel and important question.

This project is also inherently of interest to Norway, where the boreal forest plays a prominent ecological and economic role.

- *Appropriateness of Norway as Host Country for Proposed Project*

Norway is an outstanding host country for this research for several reasons. The project will leverage the expertise and deep research resources at a Norwegian Centre of Excellence, the Hylleraas Centre for Quantum Molecular Sciences. Additionally, the Norwegian Institute for Air Research (NILU) has a significant atmospheric monitoring program with several field sites and active atmospheric scientists centered in Oslo. This should also serve as a resource through outreach and potential collaboration. I will be well-situated for access to Norwegian atmospheric data. Furthermore, the atmospheric chemistry has deep relevance to Norway given the prevalence and importance of the boreal forest ecosystem.

- *Outcomes and Contributions*

The results of the proposed research will be disseminated in the U.S. and internationally. In particular, I expect to present early results in the local Norwegian scientific community, with presentation at European scientific meetings during the Fulbright visit (Winter/Spring 2020). I would hope to have and share initial findings and the scientific concept to Norwegians in a broader public forum given the interest in the chemistry above the forests. I anticipate presenting

results at the American Chemical Society (ACS) annual meeting at the end of summer. I expect to prepare and submit 1-3 manuscripts in collaboration with my Norwegian coauthors, with the goal of publication in top scientific journals. As well, this research will form the basis for future ongoing collaboration.