

## Annual Project Progress Report for PRF # 58962-UNI4

### “Fragmentation and functionalization: characterizing condensed phase autoxidation of hydrocarbons”

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#### **1) Summary of Project Objectives**

The primary goal of this project is to determine the autoxidation products formed in low volatility alkanes with a comparison between thin films vs. bulk samples. This will improve our understanding of the aging behavior of longer chain alkanes found in both lubricating oil and in aerosol particles. The comparison between bulk and thin films has implications for both industrial applications in terms of lubricant oil aging in vehicles as well as the characterization of laboratory platforms for aerosol particle aging. Depending on the volatility of the products formed, thin films may undergo different aging processes as bulk samples can be diffusion limited.

Long chain alkanes will include both straight alkanes as well as functionalized alkanes including squalane and squalene. In the condensed phase, autoxidation is a process where radicals are formed and an oxygen adds to the molecule forming an alkylperoxy radical. The products formed from this alkylperoxy radical include carbonyls, peroxides, and alcohols. Hydrogen shifts can also occur, leading to the production of peroxy radicals and potentially further oxidation down that pathway. The dominant products formed and the kinetics for these processes may vary depending on the radical initiation pathway, the structure of the alkane, and as mentioned above, the limits of diffusion in bulk vs. thin films.

Characterization of this process is being carried out using a range of different mass spectrometry techniques in order to probe the optimum analytical method. These methods include gas chromatography/mass spectrometry (GC/MS) as well as offline-Aerosol Mass spectrometry (offline-AMS). GC/MS can provide separation and characterization of the products formed at discrete time points while off-line AMS provides a comprehensive view of the ensemble properties of the mixture as a whole. With offline-AMS, higher time resolution is enabled and components which may form that are too low volatility to pass through the GC/MS will still be measured. While it is not a primary focus of this project, the development of offline-AMS for the work here will enable the rapid characterization of composition and aging for very low volatility hydrocarbons, an important class of molecules in petroleum studies. Specific tasks to be carried out are: (1) characterization of initiation steps for radical formation, (2) development of GC/MS and offline-AMS characterization platforms for time resolved studies, (3) analysis of the kinetics and product distribution formed for both thin film and bulk alkanes, (4) comparison of these rates and products between different alkane structures, (5) compilation, interpretation, and dissemination of results.

#### **2) Accomplishments in Year 1 of the project + career impacts**

Work over the first year centered on developing a platform to initiate the chemistry and testing out both characterization methods (GC/MS and offline-AMS). In addition, we have worked on further developing the offline-AMS method to have continuous solvent with the removal of un-evaporated solvent via a denuder. One of challenges to atomizing materials like lubricant oils or even asphaltene is the fact that these more viscous materials can clog capillaries, especially after they have oxidized. As a postdoc, the PI helped develop and characterize an ultrasonic nebulizer that can atomize very small volumes of sample. Here, we are extending that work to enable the atomization of viscous, non-water soluble material via dissolution in organic solvents and continuous introduction into the nebulizer.

In our initial experiments, we have found that hexanes work very well as a solvent for the squalane system. Figure 1 shows example mass spectra for the two types of samples. Here, iododecane is used as a radical initiator as it can be easily photolyzed with UV light at ~ 350 nm. The photolysis process creates a solution with a purple tint, making it easy for undergraduates to see the completion of the reaction. Aliquots of this mixture were mixed into hexanes (10  $\mu$ L of squalane + iododecane into 1 mL hexanes) and were atomized into the AMS. Figure 1a shows the mass spectra for both samples. Here, the hexanes produced a little signal of their own. The mass spectra for the hexanes alone was collected after these runs and subtracted from the total mass spectrum. The data shown here is after ~ 30 min of reaction and while very small shifts in the mass spectra are observed, very little additional oxygen was observed in the system. The challenge here may be one of several options: (1) the reaction is slower than expected

at room temperature or (2) the iododecane is forming a radical but is not abstracting a hydrogen from squalane to initiate autoxidation (i.e. there is no bimolecular chemistry occurring). To probe these questions, we will be testing out squalene, which should have weaker C-H bonds due to the double bonds along the backbone. We are also interested in probing alkanes with other oxidized functional groups as these groups can also weaken the C-H bond making hydrogen abstraction, and the formation of the first alkylperoxy radical more likely. We will also try initiating the

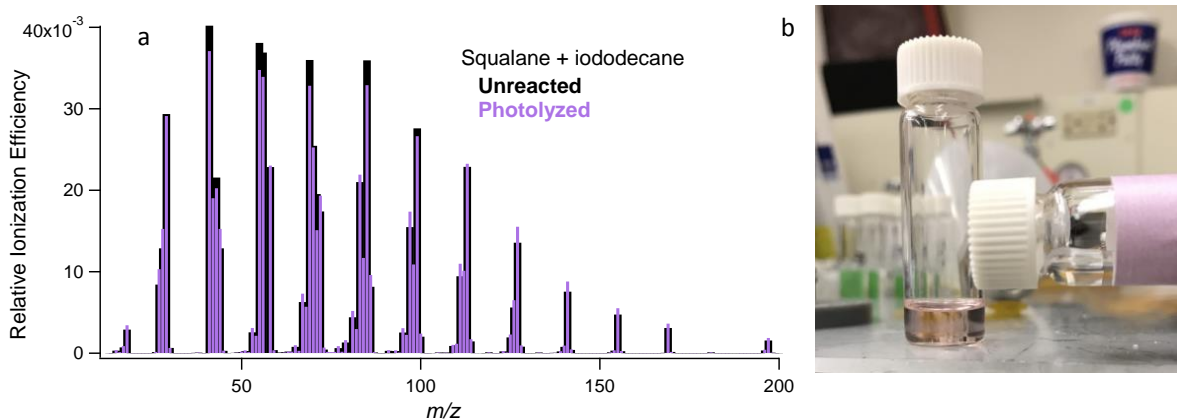


Figure 1. (a) Offline AMS mass spectra of the mixture of iododecane + squalane. The unreacted sample is shown in black and the sample that has had the iododecane photolyzed to produce the radical is shown in purple. (b) photo of the reacted (left vial) and unreacted (right vial, held sideways) mixtures showing the purple color that appears when the radical is formed. These initial data sets show small shifts in the mass spectra after the reaction is initiated, but very little increase in oxygen content.

chemistry with OH radicals in the gas-phase. To produce these radicals, we will use volatilized hydrogen peroxide and a mercury xenon arc lamp available in the laboratory. The use of gas-phase OH radicals is also beneficial as limits the organic system to one component.

Additional work has been carried out using GC/MS. Here, full separation of the two components was achieved and some trace oxidized molecules were observed for decane. None of the expected products for squalane oxidation chemistry were found. This supports the conclusions of the above experiments, that the radical is being formed on the decane but there is no bimolecular radical abstraction is occurring. The additional experiments mentioned above, alternative radical abstraction methods and alkanes with more labile hydrogens, will also be analyzed with GC/MS.

On the side of analytical developments, we have also worked to add a denuder on-line between the nebulizer and the AMS. This denuder removes the solvent signal, making it much easier to correctly measure the elemental ratios for the chemicals in the sample. We are also working to add an internal standard to the solvents to enable quantification of the material as it reacts. Ammonium iodide has been found to be a good internal standard for acetonitrile solutions, this and other inorganic salts will also be tested with hexanes. Finally, we have developed an atomizer to enable the formation of thin films by collecting aerosolized droplets onto Teflon filters. For irradiation, we will use the recently developed photolysis box which is a polycarbonate box with the front cover cut-out and replaced with a thin Teflon film. Filters can be placed in this box and the box can be irradiated with the arc lamp. This experimental platform will be used for both tests: the gas-phase OH radical experiments as well the tests with squalene etc.

The funding for this project has impacted my career by supporting the development of multiple different experimental and analytical platforms in my laboratory at William & Mary. It has provided a means for me to explore the reactivity of bimolecular systems and has enabled a research experience for an undergraduate. The undergraduate had the opportunity to travel to NASA to be trained on the AMS and has now gained experience with the mercury xenon arc lamp, and the UV/VIS. I plan to expand the project to involve a larger group of undergraduates next summer, once we have the experimental methodology fully developed. The current undergraduate and one masters student are working with me on that this semester.