

Example SURE Proposal: Chemistry

Over the past two years Dr. X's undergraduate research group has conducted multiple experiments in a large Teflon bag to figure out what conditions are needed for haze to form. The chemicals that have been used are found naturally as part of the complex mixtures present on haze in smoggy environments as found by John Seinfeld and his research group at Cal Tech. However, instead of working with the entire complex mixtures found in the environment, we select just a few of the chemicals. The reason that this is done is to simplify things so that the chemistry of particle formation can be determined.

While analyzing all the data that has been acquired over the past two years we have identified reactions occurring initially on the surface of the seed particle. We have observed new organic layers colonizing clean and organic-free seed particles in a way not previously thought to happen. What was previously thought is that there would be "chemically blind" condensation of multiple organics that have reached saturation in the gas phase. Instead, we saw on several occasions' condensation happening well before the predicted point of condensation, but only with certain combinations of gases and particles present. This has been seen with experiments done in our lab. One observation that we have made so far is that when you add aldehydes to an acidic environment condensation seems to occur before the predicted point. One example of this is seen when adding cinnamaldehyde or citral to an acidic system (such as seed particles made of tartaric acid). A possible reason that reactions may occur is that a layer of water exists on the outside of the seed particle. The more hygroscopic the particle material, the bigger this water layer is, even under dry conditions. A possible reaction mechanism is that the water layer provides a solvent layer in which reversible, acid-catalyzed reactions¹ can create the initial organic layer. Once the layer is started, other organics can mix into the organic layer at a higher rate, and therefore the overall rate of condensation will increase. We are interested in studying this set of reactions in which this summer. We are going to try and determine which if any of the proposed reaction mechanisms in Jangs paper¹ are occurring and if they are not we will try to determine the reaction mechanism causing the acid catalyzed condensation of aldehydes.

To test these theories of reaction mechanisms we are going to use Diffuse Reflectance Infrared Fourier-transform spectroscopy (DRIFTS). These DRIFTS are attachments that go on the chemistry department's new JASCO infrared spectrometers and allow the infrared spectra of rough surfaces to be recorded. The project that was proposed for last summer was unable to be completed in its entirety due to the fact that the delivery of the Diffuse Reflectance attachment for the Infrared Fourier-transform spectrometer was delayed. Instead, many experiments were done to determine the rates in which aldehydes and anhydrides are taken into water layers. These experiments were done using the FT-IRs both the single bounce and the double bounce attenuated total reflectance attachments. In using DRIFTS we hope to see the surface reaction of the organics with the seed particles. The seed particle surface will be simulated by grinding salts (or other particle materials) and placing them onto a small platform located in a chamber located in the sample compartment of the spectrometer. Gas-phase organics are then sent into the chamber through a quick release inlet while there is another line for venting of the gases in the system into the fume hood. The DRIFTS will take readings every couple of minutes to look for any differences in the infrared absorbance bands.

The way the bands are collected is that the infrared beam is guided by reflective optics onto the surface of the salt, and the diffuse reflectance is collected by large mirrors and guided to the

detector. All infrared-active compounds that are absorbed onto the surface can be detected. The DRIFTS are designed to have a small platform where the sample is located. The samples that are placed in the DRIFTS must be finely grained. The chemicals that are going to be used as the "seed particle" are going to be ground using an electric shaker; the chemical will be in a small vial with a small plastic ball that will crush the crystals making them much smaller.

To be able to fully simulate the chemistry of our Teflon bag experiments in the DRIFTS system, we have built a gas inlet system that controls the flow of the gaseous organics, humid air, and dry air into the infrared spectrometer to react with the solid. The new inlet system that was designed for the DRIFTS system is an exact replica of our large inlet system that has been used for the last two and half years to flow organics in to our large Teflon bag, except that the new system is much smaller.

When spectra are compared, Surface reaction products show up as growth in infrared absorbance, while disappearing reactants show up as negative bands in the spectra. While using this technique we will also be able to detect the loss of surface absorbed water. DRIFTS observations can thus show the reactions that are occurring on the surface of a solid.

Since sea salt spray is an important source of seed aerosol in San Diego and also globally, reactions involving these chemicals will also be studied using the DRIFTS. We will be using both sea salt from the ocean (collected from evaporated Sea water collected from around San Diego) and artificial sea salt (Instant Ocean™), which contains all the inorganic ions in seawater but none of the organic material, surfactants, or debris found in ocean water. We are interested in particles made from either of these two materials and how they may increase the rate of the formation of haze compared to other possible seed particle materials. We will evaporate these samples for use in the DRIFTS experiment.

We hope to determine the extent the presence of the Sea Salt particles have on the formation of haze in San Diego and other coastal communities.

1) Reaction schemes from Jang, M.; Czoschke, N. M.; Lee, S.; Kamens, R. M. *Science* 2002, 298, 814-817.