CHEM 690 Seminar Course-Fall 2007
Seminar #5 (October 18, 2007)
Title: "Research at the FBI"
Speakers: Rena Merrill and Brian Eckenrode
Affiliation: Counterterrorism and Forensic Science Reserach Unit F B I
Location: Robinson Hall, B-224

       The research and development branch of the FBI has a purpose of supporting analyst divisions, helping solve technology and scientific issues when they arise. Currently, these include things such as human nuclear and mtDNA analysis, antropoligy studies, chemical development, and volatile organic compounds.

       Human nuclear and mtDNA analysis deals with identification of people. They are trying to see what information the Y-chromosome provides and how to look at children's prints. There is also a DNA testing process that is backlogged over 3 million and waiting.

       Antropoligy studies deals with rebuilding a face with just bone fractures.

       Chemical development includes modifying pepper spray to be clear, with a pigment that reacts when tested. Also testing for common crime drugs, like date rape drugs and poisons.

       Of particular interest is the volatile organic compounds that are emitted from the body and how to detect them. It is known that dogs have a keen scent ability that helps them find human remains, but the ultimate goal is to make a low cost field detector that will replace dogs. The volatile organic compounds are the result of autolysis, or the self digestation of the body.

       Unfortunately, there are numerous variables that can affect the organics, such as temperature, pressure, water, acidity/alkalinity, and availability of oxygen. In the last ten years, it was determined that common burial parameters for victims are in shallow graves of less than 2.5 feet deep and usually near water or a poorly traveled road.

       What makes dogs so impressive when detecting in these parameters is their ability to differentiate between human and nonhuman remains. The burial can be up to 100 years before. Further, the dogs are not only sensitive, but also selective.

       In attempting to mimic the decomposition, pipes are run under and over the bodies of decomposing bodies. Air samples were taken and about 478 chemicals were given off. One chemical of note was the dicholodoflouromethanes. Most likely due to the florinated water we drink.

       The key now is to determine which chemical the dogs are able to sent, and then create a field gc to detect that compound. The first idea was to make a heated coil in a tube that would ionize the air samples, attached to a field gc unit. The current problem is getting a high air flow and accurate detection. While direct analysis in real time is possible for some compounds, like testing the presence of helium, the technology is not quite to the level to make this process possible.

CHEM 690 Seminar Course-Fall 2007
Seminar #6 (October 25, 2007)
Title: "Modifying Fatty Acid Ester Composition and Structure of soybean oil-based biodeisel spereation and catalytic conversion"
Speakers: Dr. Kesete Ghebreyessus
Affiliation: Department of Chemistry, Hampton University
Location: Robinson Hall, B-224

There are two parts to the process, partial separation of the polyunsaturates and a reation in the the converter.

First, Ag+ is usd to attack the unsatureated double bonds in the glicerides. Once done, the trigyleride is reacted with NaOH to create glycerol and biodiesel. The problem is there are mix of saturations, with some having poor cold flow and others having poor oxidation stability. Five fatty acids are the most common.

By changing the structure of the fatty acids, the oxidation stability changes, but as a result, the reduced double bonds reduces the melting temperature, causing a lack of performance in colder conditions.

The current methods used are to separate the various oxidation states are low temperature crystallization and urea adduct fractionation. Both have problems with purity and effectcivity, so fractional distatlation is preferred. Yet fractional distlataion can cause the double bonds to break as a result of the heating.

Instead, they used AgNo3/SiO2 as an adsorbent for the extraction process. They found five key fatty acids, with 18:3 regarded as the highest oxidizer, and therefore the most desirous to remove. When testing 5g sample the separation was 35-65%, but 2 gram sample sepearated at 65-35% ratios.

It was proposed that the high number of double bonds would cause a higher selectivity for the unsaturated, yet adding the results did not reflect that. Neither did adding more absorbent effect the results. Perhaps the silica was covered and layered, rather than creating more surface area to react.

AfPFo/[BMIM]BF4 was also tested as an abosrbant, but the resilts were similar. The major difference was the length of time require to complete the separation.

The catalycitc conversions deals with reacting the unsaturated bonds to form various other compounds. Hybrization of methyl undecenate went to 92% baranated. Immeriation of hydrobaration of methyl oleate resulted in only 45% conversion. Brown suggests this may be the result of reatrangment. Also, trace amounts of water will cause hydrolysis, kicking off the torate.

Dihydroxylatoin of methyl oleate under metal and solvent free medium is also possible. The process is environmentally friendly, but always results with some left over. Because the catalyst is large, it is easily filterable, and easy to separate.

CHEM 690 Seminar Course-Fall 2007
Seminar #7 (November 1, 2007)
Title: " Health Effects of Airborne Particulate Matter, Volume One: Detection of Protein-Metabolite Adducts"
Speakers: Dr. Paula Mazzer
Affiliation: Department of Chemistry, Old Dominion University
Location: Robinson Hall, B-224

The presentation was made in two parts. First, the partial separation of polyunsaturated FAME in biodiesel. Second, the reaction in a converter.

First, Ag+ is used to weaken double bonds of H3C(H2C)7-C=C-(CH2)7CH2Me. The purpose of doing this is to reduce the fatty acid with an 18:3 ratio because it is the most oxidation sensitive out of the products of biofuel from trigycerides.

When triglyceride is catalyzed by NaOH, three biodiesel fuel molecules and glycerol are produced. But he mixture has various saturations, some of which cause poor cold flow due and others which have oxidative stability issues. Most vegetable oils have 5 key fatty acids, but different ratios of the total number of each. With allylic position where oxidation can occur, the more double bones results in faster oxidation. Oxidation then ruins the fuel by contaminating it.

By changing the structure of the fatty acid, it is expected that the oxidation stability can be increased. Of course, that means the melting temperature decreases, but that is the inherent trade off.

Three methods are discussed to change the structure: low temperature crystallizations, urea adduct fractionation, and fraction distillation. Fraction distillation is most favored, but heating breaks some of the double bonds.

AgNO3/SiO2 adsorbent was used for the extraction process. It was interesting that 5 sample- 35g adsorbent ratio went 65%, but 2-65g ratio only went 35%. It is likely the adsorbent covers the AgNO3, coving the reation areas so the addition provides no benefit.

Then extraction with 10% AgPF6/[BMIM]PF6 was used. It appeared to selectively remove 18:3 fatty acid. Again, 10% worked better than 20%. The results were much better, but the separation is much slower.

Finally, the catalytic conversion converts the H3C(H2C)7-C=C-(CH2)7CH2Me to various products. Hydroboration of methyl undecenoate goes to 92% borated. Isomerization of hydroboration of methyl oleate goes to 45%. Brown suggested the Borats attach, but then rearrange. Trace amounts of water likely cause hydrolysis that kicks off the borates.

The borat version of separation is more environmentally friendly and it is easily filterable. Unfortunately, there is always some left over.

CHEM 690 Seminar Course-Fall 2007
Seminar #8 (November 8, 2007)
Title: "Electron transport through molecules"
Speakers: Dr. Daniel Kosov
Affiliation: Department of Chemistry, University of Maryland, College Park
Location: Robinson Hall, B-224

Started in Germany to calculate the electron transport through molecules using quantum theory. While expected to be simple, but turned out to be much more complex.

The single molecule circuit is two macroscopic electrode continuums attached by a single molecule, which results in discrete energy levels interacting electrons. These systems are used as radiation sources.

The theoretical question is having one reservoir that transports energy across a molecule to another reservoir: $eV = \mu_L - \mu_R$. No one knows how to describe this effectively.

In experimentally, because metals want to reduce the conduction gap when a molecule is attached. So if the potential of one electrode is higher than the other, the system will want to equalize.

By finding a wave-function for the whole system, then we can calculate the electric current. But the wave-function for infinitely large non-equilibrium is hard to calculate. To resolve this, scattering theory is applied, where only the local molecule system is examined. Three states are possible, (1) the initial where the molecule is not connected, (2) connected, and (3) connected at an infinite time period.

This can then be used to find electric current, where $I = <psi|J|psi> = \lim..$

2 years of work resulted in a formula that was simplified. Current through molecule is equal to the integration between L and R scattering function times a transmission coefficient T(e). But this has issues when looking at non-equilibrium electron density. But to calculate, we need Green's function. It becomes a circular argument.

Using this theory, it was calculated that certain molecules will be more effective, which supported physical molecules. Also, can use self assembly for molecules.

So best calculation so far is with amine anchored junctions. Calculating benzenedithiolate v benzenediamine results almost identical results. Yet the law results do not support the calculations. So then the connection sites were determined and it appears the amine (one adsorption range) does not bind as well as the thilate (thee possible adsorptions ranges). So three different transmission spectra can be calculated, one of which has a broader range of compounds.

4 problems occur. (1) Accurate first principles <u>always over estimates</u> experimental current by 6-10%. All programs agree with each other, but not with experimental results. (2) Electron transport with "post Hartree-Fack" e-e calculation. No one knows how to solve e-e correlations. (3) Molecular junction geometry and it evolution during the transport. Currently assumed, but not determined effectively. (4) Is there life after the Landauer theory. Experimentally we know current, but in theory we use voltage. Needed to figure out how to deal with the time variable, but recently determined using constrained current and dissipation.