

ORGANIC ENVIRONMENTS IN THE OUTER SOLAR SYSTEM

Final Report

JPL Task 1006

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A. OBJECTIVES

The aims of the project were (a) to set up simulations of the production of Titan tholins as raw material for the exploration of analysis techniques and ultimately (in follow-on projects) to examine the chemistry of the aqueous alteration of Titan organics, (b) to examine impact crater environments in which liquid water might form and become admixed with chiral molecules (by computer simulation) and (c) to develop sensitive and novel approaches to the identification and characterization of chiral molecules in organic phases.

B. PROGRESS AND RESULTS

Major results include:

1. Detailed NMR and mass spectrometric data on synthetic products of Titan organic chemistry
2. Detailed numerical hydrodynamic models of the formation of craters on Titan, with the consequent mixing of organic molecules and liquid water
3. First quantitative application of piezoelectric and fluorescence detection techniques for determination of enantiomeric composition and chiral molecules.

Tholin production and initial analysis - Tholins, the complex organic precipitates originating from Titan's stratospheric aerosol layers, form the feedstock for any significant complex organic chemistry at the surface level. We have recently obtained detailed NMR and mass spectral data on the *nonvolatile* tholin fractions generated by plasma sources, that sheds new light on these polymer mixtures. The apparatus for plasma-generated tholins has been modified to allow minimal plasma processing of nascent tholin aerosols produced in the low-temperature gas mixtures. In particular, surface exposure to energetic particles and species capable of tholin processing or contaminant participation in tholin generation is carefully minimized. In addition, this apparatus has been constructed in a way that allows for comparative

photolytic tholin generation using the output of VUV resonance discharge lamps of high light throughput, and for general selection of average photon energy through lamp selection and thus variance of the active species expected in the gaseous polymerization processes.

Our results suggest that these mixtures are entirely aliphatic, contain little aromatic component, and are comprised of predominantly saturated aliphatic hydrocarbon polymer containing significant free amino, imino and nitrile functionality. Surprisingly simple and regular patterns in the molecular weight distribution of the mixtures are observed. The major components are observed to cover only narrow ranges of C/N ratio with the level of unsaturation scaling with degree of fixed nitrogen. The full range and scope of structural functionality of these mixtures, the dependence upon temperature, pressure and atmospheric composition, and preliminary results on key reaction pathways and product distributions as pertinent to Titan's surface are being explored now as the project draws to a close.

Computer simulations of formation of liquid water in impact cratering on Titan -

With collaborator N. Artemieva, we conducted three-dimensional hydrodynamical simulations of hypervelocity impacts into the crust of Titan to determine the fraction of liquid water generated, under the reasonable assumption that the crust is largely water ice, and to track the fate of the organic-rich layer that is thought to overlie the ice over much of the surface. Some of our results include: (i) impactors larger than a kilometer in diameter are only slightly affected by the atmosphere, while those well under that size are strongly decelerated and broken up before reaching the surface. (ii) impact of a 2 km diameter icy projectile into the crust at velocities of 7 km per second or higher, and angles of impact between 30° and 45°, generate about 2-5% melt by volume within the crater. (iii) while much of the organic surface layer is heavily shocked and ejected from the immediate region of the crater, a significant fraction located behind the oblique impact trajectory is only lightly shocked and is deposited in the liquid water at the crater base. Simple calculations suggest that the resulting aqueous organic phase may remain liquid for hundreds of years or longer, enough time for the synthesis of simple precursor molecules to the origin of life, such as amino acids. The results are in review in *Icarus*.

Chiral analysis techniques for evolved surface organic phases - Piezoelectric sensors:

The quartz crystal microbalance (QCM) is an extremely sensitive mass sensor, capable of measuring mass changes in the nanogram range. QCM's are piezoelectric devices, typically fabricated of a thin plate of quartz, with metal (usually gold) electrodes affixed to each side of the plate. When driven by a simple circuit, the crystal oscillates at a specific resonant frequency. The frequency of oscillation of the crystal is dependent on the mass undergoing oscillation. By attaching a foreign mass to the crystal, the change in frequency accompanying the attachment of mass can be measured. This property of the QCM can be exploited to make chemical sensors by coating the crystal with a layer that selectively adsorbs certain molecules. When the sensor is then exposed to these compounds, its mass increases in proportion to the amount of analyte adsorbed (Janata, 1989; Ali, 1999; Liang, 2002).

We have developed enantioselective coatings for QCMs based on derivatized self-assembled monolayers. Enantioselective QCMs have been reported before (Bodenhofer et al, 1997); however, these devices used bulk coatings, and their response times were on the order of minutes. The scheme for the synthesis of one of these monolayers is shown in Fig. 1. This

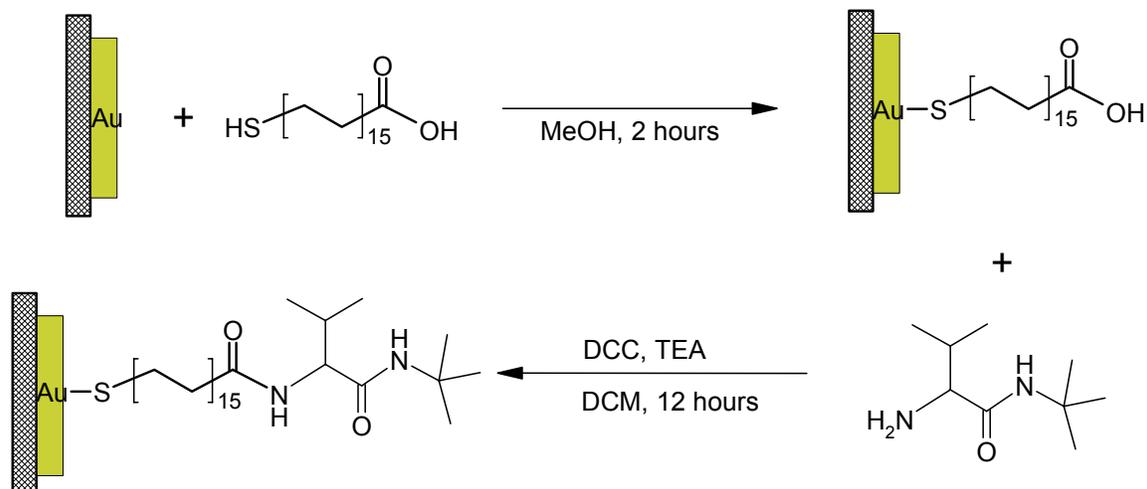


Figure 1. Synthesis of an L-valine t-butyl amide monolayer. L-valine t-butyl amide is coupled to a 16-mercaptohexadecanoic acid monolayer on gold to form a self-assembled monolayer (SAM)

monolayer is based on valine t-butyl amide as the chiral selector. This group has been used for years in chiral gas chromatography (as the Chirasil-Val stationary phase; Schreier, 1995), and has the ability to separate the enantiomers of a wide range of compounds. Fig. 2 shows the response of a crystal coated with this monolayer to the enantiomers of methyl lactate. Other experiments have developed monolayers from Boc-protected amino acids, and 3,5-dinitrobenzoyl- α -phenylglycine. The phenylglycine monolayer is expected to exhibit greater enantioselectivity than valine-based monolayers, and we are currently testing its response. Monolayer coatings show a fast response, good reversibility, and a clear enantioselectivity on exposure to analytes.

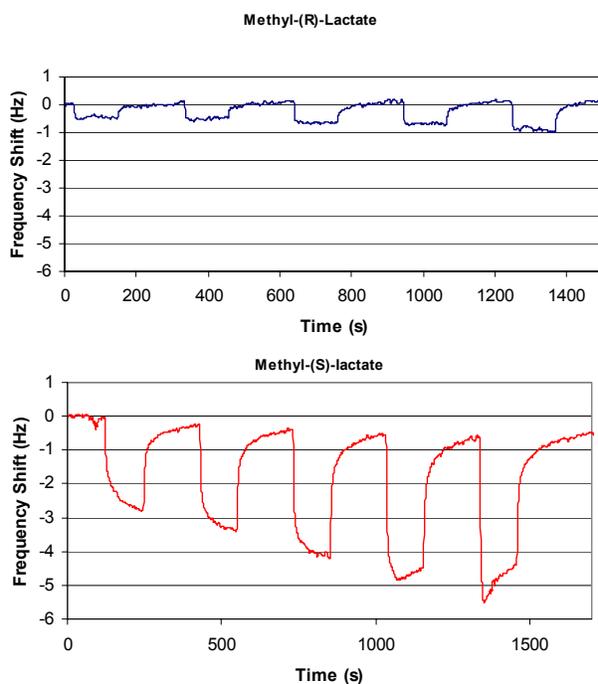


Figure 2. Response of a 15 MHz QCM to pulses of methyl lactate vapor. The sensor response to methyl-(S)-lactate is approximately 5 times greater than that of methyl-(R)-lactate. Concentrations are 16, 32, 64, 128, and 256 ppm for each.

In future work we intend to develop this technology for use as a gas chromatography detector capable of determining enantiomeric excess. The device in its final form would consist of two crystals with enantiomeric coatings. Monitoring the difference frequency between the crystals is then a measure of enantiomeric excess. Additional enantiomeric pairs would extend the range of the detector to a wider variety of analytes. We have already developed circuitry to extract the difference frequency and experimented with interfacing the QCMs to a gas chromatograph. Our initial results indicate that good temperature and gas flow control will be necessary to successfully develop a practical detection system.

We have also begun experiments with surface acoustic wave devices (SAW), piezoelectric mass sensors that operate on principles similar to QCMs. SAWs, however, operate at much higher frequencies, enabling much greater sensitivity, down to the picogram range (Levit, et al., 2002; Penza and Cassano, 2000). Our preliminary work confirms this degree of sensitivity. The enantioselective monolayers we have developed can also be applied to SAW devices, creating a more sensitive detector.

Fluorescence sensing: Our proposed fluorescence detection system was inspired by the work of Albert and Walt at Tufts University (Albert et al., 2001; Dickinson et al, 1999; Michael et al., 1998; White et al., 1996). The detector they describe is based on the differential adsorption of analyte vapors by porous, chemically-derivatized silica beads. A fluorescent, solvatochromic dye stains the beads. Solvatochromic dyes (Reichardt, 1994) undergo changes in fluorescence intensity as the polarity of their environment changes (as happens when analyte molecules are adsorbed). The beads are placed at the tip of an imaging optical fiber and excited with a Xe lamp. A CCD camera images the resulting fluorescence. By utilizing enantiomeric pairs of chirally derivatized beads, a gas-phase sensor for enantiomeric excess will be created. Such a system has a number of attractive features. The small bead size allows for a rapid response time, on the order of several hundred milliseconds. Each bead acts as an individual sensor, and imaging with a CCD allows the response of several hundred beads to be averaged, improving signal-to-noise.

Our initial work involved the synthesis of silica beads derivatized with chiral selectors, which we then stained with the solvatochromic dye Nile Red. These beads exhibited very large intensity shifts on exposure to solvent vapors. However, the beads tended to show diminishing responses after a few exposures to analytes, and did not exhibit significant selectivity with chiral analytes. Our next approach was to derivatize silica beads with a fluorescent, chiral valine selector (Fig. 3). Our approach differs from Walt's in that the fluorophore (in this case, the dansyl group (Haugland, 1998), an environmentally sensitive fluorophore) is covalently attached to the bead via the selector, instead of absorbed in the silica. We expect this to produce a more stable, robust sensor, and to increase the fluorescence response to analytes. The major difficulty with dansylated beads is that the excitation wavelength is in the UV, which causes some bleaching of the dye. We expect to overcome this difficulty with the use of longer wavelength UV from an LED. As well, we have experimented with simultaneously monitoring changes in fluorescence intensity and wavelength. Figure 4 shows changes in peak fluorescence wavelength as the beads are exposed to an analyte. By analyzing both intensity and wavelength changes, more specific responses to individual analytes are determined.

Chiral discrimination of gaseous analytes using optical transduction has been reported before, by a variety of techniques (Kieser et al., 2002; Bodenhofer et al., 1997). To our knowledge, chiral discrimination has not been reported using fluorescence sensing methodologies. We expect sensors based on this technique to be easier to implement in a space flight scenario, and more amenable to the creation of a sensory array comprising a range of different solvatochromic dyes.

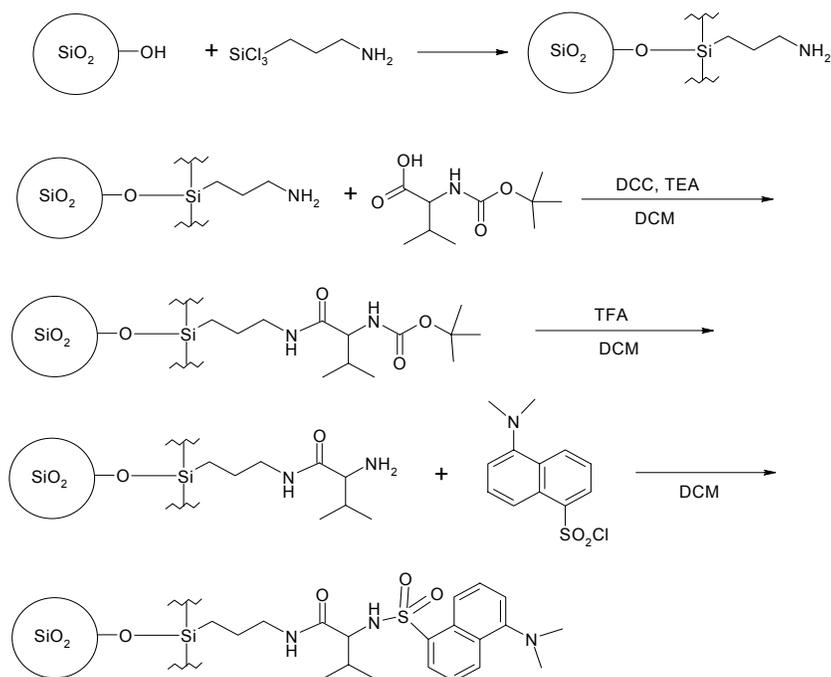


Figure 3. Derivatization of silica beads with a fluorescent chiral selector. The final step is the addition of the fluorescent dansyl

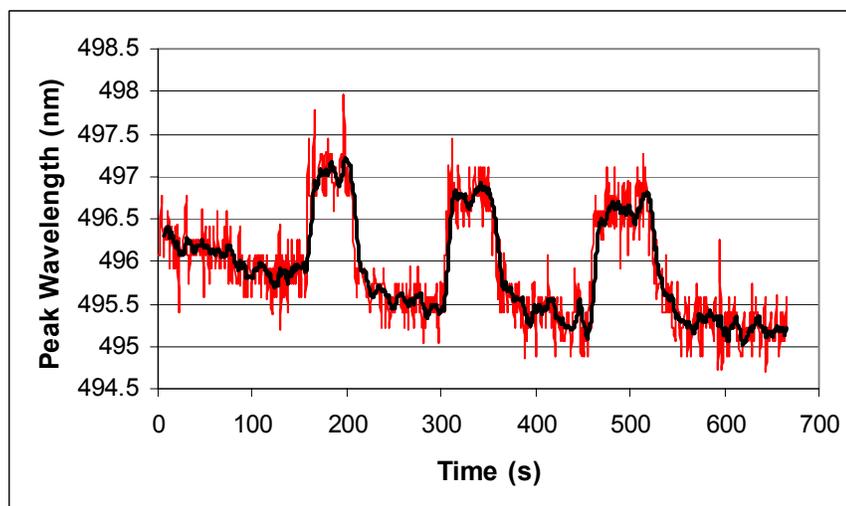


Figure 4. The response of dansyl valine-derivatized silica beads to methyl lactate vapor. The wavelength maximum of fluorescence shifts as the beads absorb methyl lactate. The black line is a 10 point running average.

C. SIGNIFICANCE OF RESULTS

The known organic environments in the solar system other than the Earth are located in the outer solar system. Those with astrobiological interest or potential are Europa, Titan and comets. Europa may contain organic compounds in a subcrustal liquid water environment, but this assumption will not be tested until after 2010. Titan is the focus of the present effort because (a) organic compounds are present on Titan's surface, protected from damaging particle and UV radiation by a thick atmosphere and (b) we should have a global spectroscopic inventory of organic molecules on the surface of Titan beginning in 2004 from Cassini-Huygens. Understanding the surface conditions of Titan from the view of chemical sources and continuing chemical dynamics is paramount to both analysis of forthcoming data from the Cassini mission and development of future probes to study extraterrestrial prebiological chemistry. The results obtained in this work are the first steps in understanding the chemistry of Titan's surface and in defining a set of instruments that could elucidate the chemical species present in a follow-on mission which would land on Titan.

D. FINANCIAL STATUS

The total funding for this task was \$200,000, all of which has been expended.

E. PERSONNEL

Chris Welch, Merck Corporation,
Francois Raulin, LISA/University

F. PUBLICATIONS

- (1) N. Artemieva and J. I. Lunine, "Cratering on Titan: Impact Melt, Ejecta, and the Fate of Surface Organics," *Icarus*, submitted 2002.
- (2) Ryan R. Julian, Robert Hodyss, Brian Kinnear, Martin F. Jarrold, and J.L. Beauchamp, "Nanocrystalline Aggregation of Serine Detected by Electrospray Ionization Mass Spectrometry: Origin of the Stable Homochiral Gas Phase Serine Octamer," *J. Phys. Chem. B*, **106**, 1219-1228 (2002).
- (3) Robert Hodyss and J. L. Beauchamp, "Quartz Crystal Microbalance Detector for Direct Enantiomeric Analysis of Chiral Molecules," *Anal. Chem.*, in preparation.
- (4) P. Beauchamp, J. I. Lunine, J. Beauchamp, D. Dougherty, C. Welch, M. Smith, "The Potential for Chemical Evolution on Titan," *CD-ROM Proceedings of the 2002 IEEE Aerospace Conference*, Big Sky, MT; March 9-16, 2002

Papers Presented

- (1) P. Beauchamp *et al*, "Detection and Characterization in Planetary Environments of Chemistry at the Threshold of Life," *Origins of Life Gordon Conference*, Ventura, CA 2002
- (2) P. Beauchamp, "From the Present to the Future of Mass Spectrometry in Space: Novel In Situ Measurements," *ASMS 17th Asilomar Conf. on Mass Spectrometry*, October 2001

- (3) J. L. Lunine, "Titan and the Origin of Life," *AGU*, Dec 02
- (4) J. L. Lunine, "Signs of Life," *COSPAR*, Houston Oct 02
- (5) J. L. Lunine, "Other Targets for Astrobiology: From Titan to Extrasolar Giant Planets," *AAS*, Wash. DC, Jan 02.
- (6) Mass Spectrometry: Solving Fundamental Problems in the Solar System, *ASMS*, Asilomar, Oct.01

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