DEGRADATION OF ORGANICS IN A GLOW DISCHARGE UNDER MARTIAN CONDITIONS. P.E. Hintze[1], C.R. Buhler[2], L.M. Calle[1], C.I. Calle[2], S. Trigwell[2], J.W. Starnes[2] and A.C. Schuerger[3]; [1]Corrosion Technology Laboratory, KT-E, NASA, Kennedy Space Center, FL 32899, Paul.E.Hintze@nasa.gov. [2]Electrostatics and Surface Physics Laboratory, KT-E, NASA Kennedy Space Center, FL 32899, Carlos.I.Calle@nasa.gov. [3]University of Florida, UF-1, Space Life Sciences Lab, Kennedy Space Center, FL 32899.

Introduction: The primary objective of this project is to understand the consequences of glow electrical discharges on the chemistry and biology of Mars. The possibility was raised some time ago that the absence of organic material and carbonaceous matter in the Martian soil samples studied by the Viking Landers might be due in part to an intrinsic atmospheric mechanism such as glow discharge. The high probability for dust interactions during Martian dust storms and dust devils, combined with the cold, dry climate of Mars most likely results in airborne dust that is highly charged. Such high electrostatic potentials generated during dust storms on Earth are not permitted in the low-pressure CO_2 environment on Mars; therefore electrostatic energy released in the form of glow discharges is a highly likely phenomenon. Since glow discharge methods are used for cleaning and sterilizing surfaces throughout industry, the idea that dust in the Martian atmosphere undergoes a cleaning action many times over geologic time scales appears to be a plausible one.

Although free radicals and UV light are present on Mars and available for reactions with organics,[1-3] a plasma introduces new and different reactive species. Chemistry in a plasma is driven by reactions due to the 'four horsemen' of the plasma: free ions, UV irradiation, free radicals and chemically reactive neutral species. This provides very different reactive conditions than would otherwise be found on Mars. Free ions would either be nonexistent or in very low concentrations. UV radiation created in the plasma is different than solar radiation and could exist in areas where UV solar radiation does not reach; for example, a dust storm would attenuate most solar radiation but discharges from the plasma would still provide light. Different free radicals would be expected in a plasma on Mars, than would be formed by other means. Finally, there are high energy neutral species in the plasma (excited states of N_2 for example), that would not otherwise be expected.

Procedure: Glow discharge (GD) experiments were performed in a vacuum chamber using a Mars gas mixture composed of 95.5% CO_2, 2.7% N_2, 1.6% Ar, 0.13% O_2 and 0.07% CO. The apparatus built to perform the GD experiments is shown in Fig. 1.

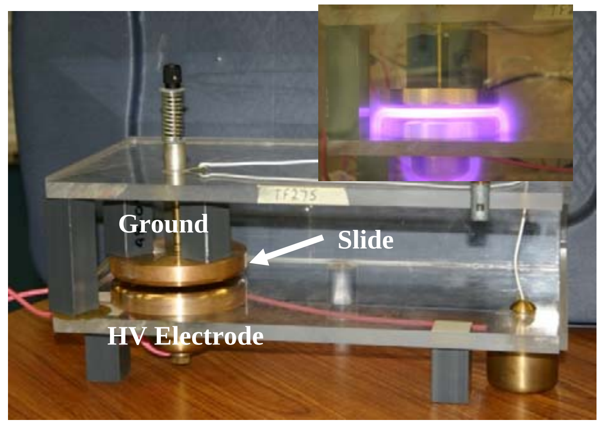

Fig. 1. Apparatus for creating a glow discharge. The inlay shows a low pressure plasma in air.

As a first step in understanding the reactions of organics in a GD plasma, thin films of organics were placed on glass slides and exposed to the GD plasma. The slides were placed between the two electrodes and exposed to the plasma for times up to 30 minutes. The products were analyzed using gas chromatography/mass spectrometry. The organic compounds remaining on the slide were derivatized using N,O-Bis-(trimethylslyl) Acetamide (BSA). BSA converts any alcoholic or carboxylic acid containing organic compounds to compounds more suitable for GC/MS detection. The reaction of benzyl alcohol with BSA is shown in Fig 2. We have exposed a number of organic molecules that have been found in meteorites[4, 5] to the plasma, including naphthalene, phenanthrene, benzyl ether and coronene.

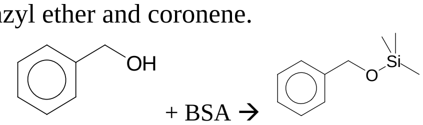

Fig. 2. The reaction of benzyl alcohol with BSA forming a trimethylsylyl ether product.

Results and Discussion: The emission spectrum from 200 to 500 nm of a glow discharge plasma is shown in Fig. 3. The emission is dominated by the CO_2^+ $A^2\Pi$ -- $X^2\Pi$ system. There are also lines from the N_2 $C^3\Pi_u$ -- $B^3\Pi_g$ and N_2^+ $B^2\Sigma_u$ -- $X^2\Sigma_g$ transitions. There is little evidence of emission from any NO bands, as has been seen in the nightglow on Mars.[6]

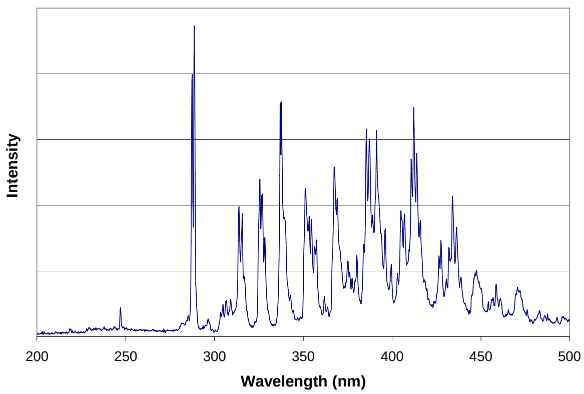

Fig. 3. The emission spectrum of the Mars gas glow discharge plasma.

After 30 minutes of exposure to the plasma, most of the organics had undergone some change in appearance. One showed a distinct brown color while another had changed from an oil to a wax-like appearance.

Initial GC/MS results indicate the formation of organic functional groups that are derivatized with BSA indicative of hydroxyl groups (R-OH). These functional groups are identified in the mass spectrum by their characteristic –$Si(CH_3)_3$ fragment at 73 mass to charge ratio (m/z). In the case of benzyl ether, a few different types of products were identified. There were multiple isomers for each type of product. Some products had the same main fragment as benzyl ether (91-92 m/z), while others appeared to undergo addition reactions. The mass spectrum of benzyl ether, BSA derivatized benzyl alcohol, and an unknown product are shown in Figs 4-6 respectively. All products had a longer retention time than the derivatized forms of benzoic acid and benzyl alcohol.

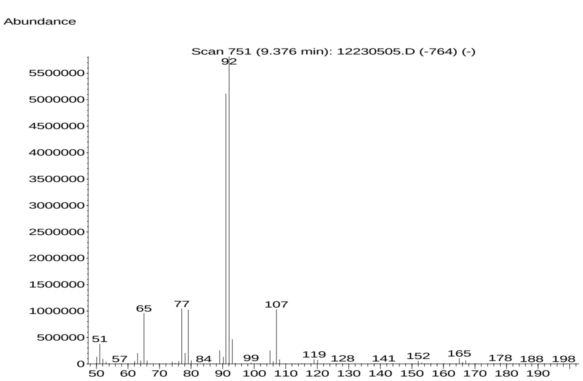

Fig. 4. The mass spectrum of benzyl ether.

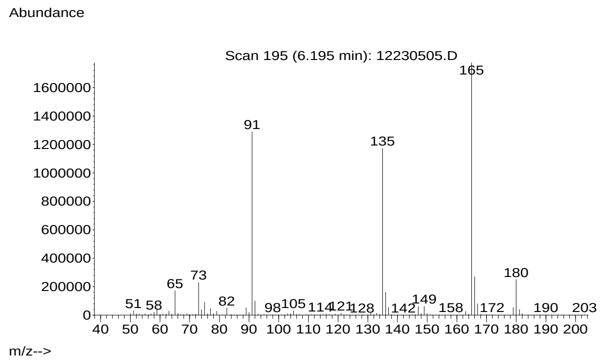

Fig. 5. The mass spectrum of derivatized benzyl alcohol. (The product in Fig. 2)

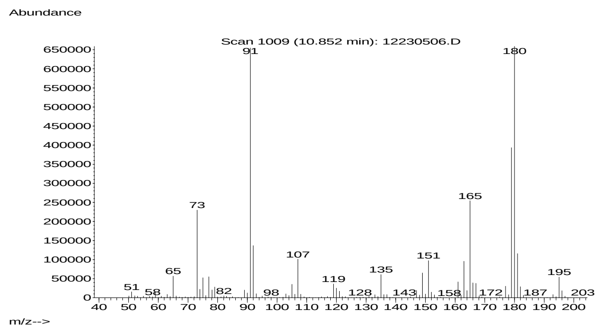

Fig. 6. The mass spectrum of an unknown product of the reaction of benzyl ether in the Mars gas GD plasma.

Benner *et al*.[1] suggested that, under Martian conditions, carboxylic acids would form during the degradation of organic material. This chemistry was based on the abstraction of hydrogen by a hydroxyl radical (HO•). The HO• radical is present on Mars due to photochemical reactions of water. Our results are consistent with this hypothesis, but also show additional chemistry. In the GD plasma, there are high energy ionized species not typically present. The high energy electrons and ionized CO_2^+ species may initiate chemistry that induces addition reactions or other mechanisms not typical of radical chemistry.

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