ANALYSIS OF MIXED ARYL/ALKYL ESTERS BY PYROLYSIS GAS CHROMATOGRAPHY-MASS SPECTROMETRY IN THE PRESENCE OF PERCHLORATE. A. S. Burton[1*], D. R. Locke[2], and E. K. Lewis[3], [1]Astromaterials Research and Exploration Science Division, NASA Johnson Space Center, Houston, TX 77058 (*aaron.burton@nasa.gov), [2]HX5 – Jacobs JETS Contract, NASA Johnson Space Center, Houston, TX 77058, [3]NASA Postdoctoral Program administered by USRA, NASA Johnson Space Center, Houston, TX 77058.

Introduction: Mars is an important target for Astrobiology. A key goal of the MSL mission was to determine whether Mars was habitable in the past, a question that has now been definitely determined to be yes. Another key goal for Mars exploration is to understand the origin and distribution of organic material on Mars; this question is being addressed by the SAM instrument on MSL, and will also be informed by two upcoming Mars exploration missions, ExoMars and Mars 2020. These latter two missions have instrumentation capable of detecting and characterize organic molecules. Over the next decade, these missions will analyze organics in surface, near-surface and sub-surface samples. Each mission has the capability to analyze organics by different methods (pyrolysis gas chromatography-mass spectrometry [py-GC-MS]; laser desorption and thermal volatilization GC-MS; and Raman spectroscopy).

Plausibly extraterrestrial organics were recently discovered by the Mars Science Laboratory (MSL), providing an important first step towards understanding the organic inventory on Mars [1]. The compounds detected were chlorobenzenes and chloroalkanes, but it was argued that chlorination of these compounds occurred during pyrolysis of samples containing unchlorinated organics in the presence of perchlorate. A recent report analyzed a suite of aromatic (benzene, toluene, benzoic acid, phthalic acid, and mellitic acid) and aliphatic (acetic acid, propane, propanol, and hexane) by pyrolysis under SAM-like conditions in the presence of perchlorate to attempt to constrain possible precursor molecules for the organic molecules detected on Mars. For aromatic compounds, the aromatic acids all readily produced SAM-relevant chlorobenzes, whereas benzene and toluene did not. This observation suggests that the chlorobenzene detected on Mars could have derived from compounds like mellitic acid, consistent with the previous hypothesis by Benner et al. [3]. Among the aliphatic molecules, it was shown that pyrolysis of alkanes and alcohols in the presence of perchlorates produced polychlorine containing chloroalkanes similar to what was observed on Mars. Surprisingly, however, similar treatment of acetic acid produced chloroketones, instead, and no chloroalkanes were reported. This suggests that the chloroalkanes detected in the Sheepbed mudstone were not derived from aliphatic carboxylic acids, but instead were from more reduced alcohols or even alkanes, or perhaps were degradation products of more complicated organic material.

Because organics analyses on mars will rely heavily on py-GC-MS of perchlorate-containing samples over the next decade, it is important to understand the fate of organic molecules of biotic and abiotic origin under such conditions. In this work we begin a series of experiments to improve our understanding of products generated during py-GC-MS of increasingly complex organic molecules (esters, amides, peptides, nucleic acids, fatty acids) in the presence of perchlorate.

Samples and Analytical Techniques: A sample of San Carlos olivine was ground and sieved to -100 mesh to serve as a Mars regolith analog. The prepared olivine sand was heated to 500 ºC for eight hours to destroy any organic compounds. The pyrolysis sample was prepared in a glass capillary by adding 10 mg of olivine sand with 1 wt% calcium perchlorate in water and 50ng each of six different phthalate esters in methanol (Restek calibration mix 606).

Py-GC-MS analysis was run using a CDS 5250 pyroprobe coupled to a Thermo Trace-Ultra GC and Thermo DSQ II mass spectrometer. Samples were pyrolyzed from 50-750 ºC, at a rate of 35 ºC min^{-1}, in He gas at a flow rate of 35 ml min^{-1}. The pyrolzate was collected on a Tenax TA trap at 40 ºC. Following the pyrolysis experiment the compounds on the trap were rapidly desorbed at 350 ºC and transferred to the GC inlet for analysis. The GC was equipped with a Restek Rxi-5ms column (30m length, 0.25mm ID, 0.25 µm film thickness). The GC was programmed to hold at 35 ºC for five minutes then ramp to 300 ºC at a rate of 10 ºC min^{-1} and hold at the final temperature for 8.5 minutes. He gas flow through the GC column was 1.5 ml min^{-1} at a split ratio of 10:1. The DSQ II mass spectrometer was operated in the electron impact (EI) mode at 70 eV and scanned between m/z 10-535.

Results and Discussion: Preliminary analysis of the phthalate ester mix in the presence of perchlorate by py-GC-MS revealed a suite of chlorinated products, including chloroalkanes, benzylchlorine and chlorobenzene. Additional experiments are in progress.

Acknowledgements: E. K. Lewis is supported by a NASA Postdoctoral Program Fellowship administered by the United States Research Association.

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