

UV Photolysis of Mellitic Acid - A Possible Organic at the Mars Phoenix Landing Site

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Introduction: Despite the fact that each year an estimated 2.5×10^5 kg of organic material is delivered to the surface of Mars in the form of interplanetary dust and other particles smaller than 1mm [1], the Viking GC/MS instruments detected no organic molecules down to the parts per billion level [2]. This was interpreted to be the result of a Martian surface that was hostile to reduced carbon, with previous experimental results pointing to organic destruction via direct and oxidative photolysis [3,4]. However, recent work has shown that Viking may have missed certain Martian organics for two reasons: first, the pyrolysis temperature of the Viking instrument might have been too low to drive off some low-volatility organics [5]; second, the highly-oxidizing Martian surface could have combusted any organics present during pyrolysis, the result being that only CO_2 , and no organic fragments, would be evolved during analysis [6].

Most meteoritic organic matter is in the form of kerogen, a complex class of generic organic molecules which is fairly refractory (fairly refractory being defined as a molecule that is not driven off by pyrolysis below 500°C). Benner et al. show that when kerogens are oxidized, they form several decay products that they claim are stable to UV photolysis, and that an estimated 10% of the original meteoritic organic materia could accumulate as a metastable decay product, with mellitic acid (benzenehexacarboxylic acid, figure 1) being

identified as a prime candidate [7]. Importantly, mellitic acid is a fairly refractory organic molecule and might not have been driven off below 500°C , the peak temperature of the Viking ovens.

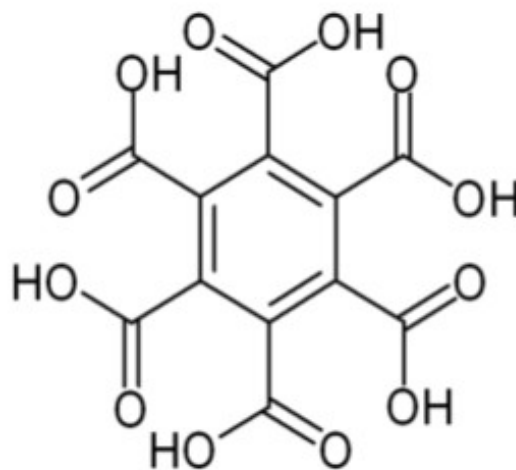


Figure 1 - Molecular Structure of Mellitic Acid

For the first time since Viking, the Mars Phoenix Lander carried an instrument capable of detecting organic material, the Thermal and Evolved Gas Analyzer (TEGA). TEGA discovered a low temperature release of CO_2 between $200\text{-}600^\circ\text{C}$ for several of the Phoenix soils. This low temperature release of CO_2 might be attributed to 1) desorption of adsorbed CO_2 , 2) thermal decomposition of Fe- and Mg-carbonates, and 3) combustion of organic molecules [8]. Another important TEGA finding was the release of a mass 32 fragment between $360\text{-}575^\circ\text{C}$ that is likely due to O_2 release during the thermal decomposition of a perchlorate salt [9].

Mellitic Acid and Mars: Though it has been posited that mellitic acid might accumulate on Mars as a metastable decay product of direct oxidation, its stability under Mars-like UV conditions has never been tested. This work is an attempt to understand the behavior of mellitic acid during photolysis and produce a residue that can be analyzed and identified.

After identification, the residue produced by UV photolysis can then be run through laboratory instruments that operate under TEGA-like conditions, giving us an idea of what a UV-degraded mellitic acid signature would have looked like on Mars. By comparing this data to the TEGA results, we will see whether or not the TEGA measurements are consistent with a mellitic acid-derived organic at the Phoenix landing site. If the laboratory results are inconsistent with TEGA data, our measurements will provide a quantitative constraint on the upper limit of mellitic acid present at the landing site. Preliminary thermal and evolved gas analysis on the effects of the thermal decomposition of perchlorate salts in the presence of untreated mellitic acid (i.e., not UV treated) indicate that O_2 released from perchlorate combusts mellitic acid and thereby releases CO_2 [8].

Methods: We irradiate mellitic acid with a 150 W UV-enhanced Xenon arc lamp, which is a good approximation of the solar spectrum (in shape, not exact intensity) from 190-400nm. The mellitic acid is placed in a solution of nano-pure water, pipetted onto a sample slide, and baked in an oven at $\sim 80^\circ C$ for 24hrs to drive off the water and create a relatively uniform film about $10\mu m$ thick. The sample slide is placed in the sample chamber and the system is brought to high vacuum. A fused silica window is used to pass through UV light down to around 190nm. After pumping and baking for another 24hrs, the UV light is turned on, with the destruction process being quantitatively investigated by monitoring the gaseous species in situ using a residual gas analyzer. The

destruction rate is calculated by monitoring the rate of pressure increase in the sample cell. The sample is illuminated for ~ 24 hrs—at which point the production rate of photolytic products is below background levels.



Figure 2 - Experimental Setup

Results: We have found that mellitic acid is not stable to photolysis under Martian UV conditions. Preliminary results indicate that primarily CO_2 and some CO are given off when mellitic acid is exposed to Mars-like UV light. Before photolysis, the mellitic acid has a white color and is very soluble in water. After photolysis, the residue is black and insoluble. The solubility of a putative organic is important because it is possible at the Phoenix landing site that there are occasionally thin films of liquid water [10] and a soluble organic could be processed differently than an insoluble organic.

References: [1] Flynn G. J. (1996) *Earth Moon Planets*, 72, 469-474. [2] Biemann K et al. (1977) *JGR*, 30, 4641-4648. [3] Klein H. P. (1979) *Origins of Life*, 9, 157-160. [4] Stoker C. R. and Bullock M. A. (1997) *JGR*, 102, 10881-10888. [5] Navarro-González . et al. (2003) *Science*, 302, 1018-1021. [6] Navarro-González R. et al. (2006) *PNAS*, 103, 16089-16094. [7] Benner S. A. et al. (2000) *PNAS*, 97, 2425-2430. [8] Ming D. W. et al. (2009) *LPSC XL*, this volume. [9] Hecht M. H. et al. (2009) *LPSC XL*, this volume. [10] Zent A. P. et al. (2009) *LPSC XL*, this volume.