NEW PATHWAYS FOR THE FORMATION OF COMPLEX ORGANICS AND PREBIOTIC SYNTHESIS IN THE GAS PHASE. M. Samy El-Shall, Department of Chemistry, Virginia Commonwealth University, Richmond, VA 23284-2006, mselshal@vcu.edu

To understand how life can begin on a habitable planet such as the Earth, it is essential to know what organic compounds were likely to have been available. Our research addresses two major questions: (1) how are simple organic compounds assembled into more complex molecular systems? and (2) what are the essential processes and pathways by which complex systems can develop those basic properties that are critical to life's origins?

Well over one hundred organic molecules, including acetylene, benzene and water are present in interstellar clouds, molecular clouds, solar nebulae, and in envelopes expelled by evolved stars. Acetylene molecules and ions are also likely to be present in the hydrocarbon-containing ionospheres of Jovian planets, Titan, and in interstellar clouds. The wide range of temperature and pressure conditions in outer space environments allows diverse and unique chemistry to take place. These processes can lead to complex organics, clustering, and polymerization that produce nucleation centers for the formation of grains.

We studied the reactions of the acetylene radical cation ($C_2H_2^{+\bullet}$) with H_2O, using ion mobility mass spectrometry. We found the primary products to be the $C_2H_3O^+$ and $C_2H_4O^{+\bullet}$ ions, produced with an overall rate coefficient k (300 K) = 2(±0.6) × 10^{-11} cm^3 s^{-1} that increases with decreasing temperature. In the $C_2H_4O^{+\bullet}$ adduct channel, the reactivity and energetics suggest that the adduct is the $H_2C{=}CHOH^{+\bullet}$ (vinyl alcohol) ion. The reactivity, combined with energetics, suggests that the protonated ketene CH_2COH^+ is the most likely observed $C_2H_3O^+$ ion probably with some contribution from the cyclic *c*-CH_2CHO^+ ion.

Very recently, we discovered new reactions of the benzene radical cation with acetylene over a wide temperature range from 120 K to 680 K, showing that acetylene undergoes sequential additions onto the benzene cation with two different mechanisms operating at low and high temperatures.

At low temperatures (123 K) clustering of several acetylene molecules onto the benzene cation is observed leading to the generation of $(C_2H_2)_n^{+\bullet}$ ions with n≥6 to n = 10. This can be explained by Associative Charge Transfer (ACT) reactions where acetylene molecules bind non-covalently to $C_6D_6^{\bullet+}$ and partial charge transfer from the ion activates an acetylene molecule for addition polymerization with other associated acetylene molecules. The ACT process can generate the benzene cation from the associated acetylene molecules.

At high temperatures the barrier of the covalent addition of acetylene to the benzene cation to form a styrene-type ion is measured as 3.5 kcal/mol. The addition of the second acetylene followed by H elimination to form a naphthalene-type ion is calculated to be highly exothermic and without a barrier. These reactions can explain the formation of complex organics by gas phase ion-molecule reactions under a wide range of temperatures and pressures in astrochemical environments.