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Laboratory Investigations of the Production of Negative Ions in Titan's Atmosphere

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Abstract

Negative ions can be produced by electron and photon stimulated processes and can be used to probe dissociative electron attachment resonances, transient negative ions, dipolar dissociation and desorption channels from organic adsorbants. Ices of increasingly higher N/C ratios have been used as surrogates to provide fundamental information regarding prebiotic chemistry and large negative ion formation. Laboratory experiments have been performed to determine cross-sections, kinetic reaction rates, and product distributions of nonthermal irradiation chemistry on N-rich organic ices and tholin aerosols, which can be incorporated into atmospheric models of Titan and possibly the interstellar medium. We seek to determine how nonthermal irradiation of N-rich organic ices contributes to the formation of large negative ions and subsequently prebiotic molecules.

1. Introduction

Solar irradiation initiates various types of reactions in gas-phase molecules in the Titan environment. Despite being in the gas phase, large aerosol particles can provide ideal catalytic surface sites for chemical reactions. The Cassini Plasma Spectrometer (CAPS) spacecraft's instrument onboard Cassini unexpectedly discovered large negative ions in Titan's atmosphere.[1] These negatively charged species can precipitate down to the surface to catalyze reactions and possibly become molecular hydrogen sinks.[2] This is due to the low energy (5-20 eV) dissociative electron attachment resonance of H- that liberates H, producing molecules that are highly unsaturated.[5, 6]

2. Electron Attachment

Time-of-flight spectra of molecular negative ions from multilaver N-rich ices have recently been obtained by electron induced desorption. In Figure 1, a plot of the total integrated yields versus the incident electron energies have been plotted. The H resonance from dissociative attachment of HCN is centered at 20 eV. The association product NCN is the primary molecular anion with CN-, CH-, C₄H-, and C₃N⁻ appearing as minor channels. The electron affinities (EA) from gas phase molecules containing high N/C ratios, are in decreasing order of EA: C₃N⁻ $> CN^- > NCN^-$. Also, C_4H^- and C_6H^- anions have EAs comparable to CN⁻. These data indicate that the stable anion precursor neutrals are polymerized dimer and trimer HCN molecules with possible trace amounts of tetramer HCN.

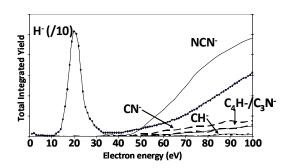


Figure 1: Dissociative electron attachment of H and dipolar dissociation of molecular anions from HCN ice at 120 K.

Schleyer and coworkers in 2007 performed calculation indicating that in solution trace amounts of H₂O can lower the activation energy for the polymerization of HCN to form the very important nucleobase adenine.[4] Experiments are underway to determine the effects of trace amounts of oxygen and water in irradiated CN ices.

These data can provide insight into the mechanism and activation energies for the formation of prebiotic molecules in the Titan environment.

Summary and Conclusions

Although the temperatures are too cold for most thermal initiated reactions to occur efficiently, nonthermal irradiation processes are producing large complex organic molecules in Titan's dense atmosphere. Observations made by the Cassini orbiter provide evidence of surprisingly massive negative ions. The formation of these large negative ions and their relevance to astrobiology is still under debate. Many of the processes that lead to the formation of these complex organic species are still unknown. Recent studies have shown that chemical synthesis yields in solid films can be attributed to the formation of shape resonances decaying into dissociative electron attachment (DEA) channels.[3, 5] Our results on the association of HCN derived anions suggest that these electron attachment channels may contribute significantly to the synthesis of large organic species.

Acknowledgements

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