

Laboratory Chemical Dynamics in Hydrocarbon Rich Atmospheres of Outer Planets

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Investigating the formation of organic molecules in hydrocarbon rich atmospheres of planets and their moons is of paramount importance to understand the chemical composition, mixing ratios, and the future evolution of carbon bearing species in Solar System environments. The diacetylene molecule (C_4H_2) as detected in the stratosphere of Saturn and its moon Titan is the largest polyatomic organic species observed so far in the outer Solar System. In addition the methyl radical (CH_3) together with methane (CH_4), acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), methylacetylene (CH_3CCH), propane (C_3H_8) and the CN bearing species hydrogen cyanide (HCN), dicyan (NCCN), methylcyanide (CH_3CN), cyanoacetylene (HCCCN), and presumably solid state dicyanoacetylene (NCCCN) were detected as well. Photochemical models of Jupiter, Saturn, Uranus, Neptune, Pluto and their satellites Titan and Triton predict further the presence of even more complex hydrocarbons up to triacetylene (C_6H_2) and tetraacetylene (C_8H_2). Previous experiments attempting to unravel the formation of these molecules in planetary environments employed and open reactors subjecting gas mixtures to high energy discharges or electron bombardments; often products were analyzed via gas chromatography coupled to a mass spectrometer (GS-MS). This approach can match the existence of major trace constituents. However, no information on radical intermediates could be supplied; further, possible open shell products and extremely labile products cannot be identified; hence involved reaction mechanism can only be guessed. However, the explicit identification of reaction intermediates, ALL reaction products, and the mechanism are a top priority to give a systematic picture on the chemistry in hydrocarbon rich atmospheres and to predict the formation of hitherto unobserved molecules.

Therefore, a new experimental approach is desirable. First, experiments must be conducted under single collision conditions. This means that in a binary reaction proceeding via a complex, $A + BC \rightarrow [ABC]^* \rightarrow AB + C$, one species A reacts only with one species BC without collisional stabilization or successive reaction of the initially formed $[ABC]^*$ complex (exclusion of three body reactions). This requirement guarantees that the nascent reaction product undergoes no secondary reaction. Second, highly unstable and reactive radicals must be prepared under well-defined conditions (internal states, velocity, velocity spread) and reaction products with often unknown spectroscopic properties have

to be probed. Hence, the majority of interesting unsaturated nitriles cannot be sampled via optical detection schemes such as laser induced fluorescence (LIF) and resonance enhanced multi photon ionization (REMPI), and a “universal” detector is crucial. Finally, we have to take into consideration that a variety of structural isomers can contribute to the reaction product. Here, the knowledge of detailed chemical dynamics of a reaction can be employed to elucidate the product isomer(s). Our experiments were designed to investigate for the first time systematically and completely the formation of nitriles (species carrying a CN group), polyynes (molecules with triple bonds), and allene derivatives (species with a C=C=C unit) in these planetary environments. The prime directives are (1) an identification of the reaction products, (2) an elucidation of involved reaction intermediates (these are often radicals which can undergo a subsequent reaction in dense planetary environments), and (3) setting up detailed mechanism to predict the presence of unobserved molecules. These objectives are tackled investigating the chemical dynamics of cyano radicals ($\text{CN}(^2\Sigma^+)$) and ethynyl radicals ($\text{C}_2\text{H}(^2\Sigma^+)$) reacting with unsaturated hydrocarbons acetylene, ethylene, methylacetylene, allene, and benzene as a possible source to carbon bearing species in planetary environments on the most fundamental, molecular level employing the crossed molecular beam technique. In Saturn’s moon Titan, for example, short wavelength photons ($\lambda < 200 \text{ nm}$) can penetrate to the stratosphere and dissociate acetylene to atomic hydrogen plus an ethynyl radical or hydrogen cyanide to the cyano radical plus an H atom. Upon reaction with our target molecules the formation of complex hydrocarbons is strongly anticipated.

All experiments were performed employing the crossed molecular beam method (Lee 1987). The 266 nm output of a solid state Nd:YAG laser is focused onto a carbon rod, and ablated carbon species are seeded into neat nitrogen or deuterium which acts as a reactant gas as well (Kaiser et al. 1999). The resulting supersonic beam of *in situ* generated cyano radicals $\text{CN}(X^2\Sigma^+)$ or ethynyl radicals $\text{C}_2\text{D}(X^2\Sigma^+)$ is chopped and crosses a second, pulsed hydrocarbon beam perpendicular in the interaction region. Time-of-flight (TOF) spectra and angular distributions of reactively scattered products are monitored using a quadrupole mass spectrometer coupled with an electron-impact ionizer. Information on the chemical dynamics and reaction products are gained by transforming our data from the laboratory to the center-of-mass (CM) coordinate system (Kaiser et al. 1998). The final outcome of the experiment is the CM product flux contour map, where the differential cross section is reported as a function of product CM scattering angle and velocity. This map holds all the information of the reactive scattering process.

A detailed analysis shows that all reactions are initiated by addition of the radical reactant to the double or triple bond of the unsaturated hydrocarbon molecule forming a complex. These reactions have no barrier – an important finding since the temperature in the atmospheres of planets and moons is $< 200 \text{ K}$ and reactions should have no entrance barriers and must be exothermic (Balucani et al. 2000a). The initial collision complex either loses an H atom to form the reaction product(s) or undergoes isomerization (cis/trans, H atom migration) prior to decomposition. The overall reactions to form the nitriles, (substituted) diacetylenes, and allenes are all exothermic (Fig. 1); most important, no isonitriles were identified, and competing H abstraction channels are

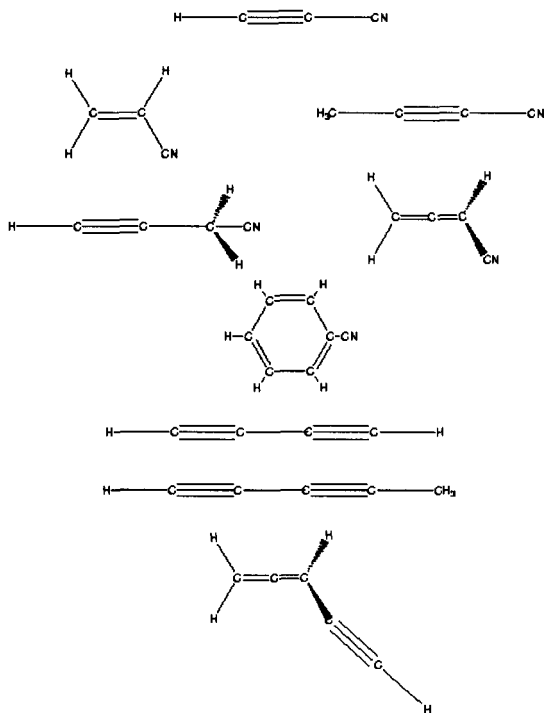


Figure 1. Structures of reaction products as identified in our crossed beam reactions. From top to the bottom: cyanoacetylene (CN/C₂H₂) (Huang, Lee & Kaiser 1999), vinylcyanide (CN/C₂H₄) (Balucani et al. 2000b), 1-methyl-2-cyanoacetylene (CN/CH₃CCH) (Huang et al. 1999), 1-methyl-1-cyanoacetylene (CN/allene) (Balucani et al. 2000a), cyanoallene (CN/allene and CN/CH₃CCH), cyanobenzene (CN/C₆H₆) (Balucani et al. 1999), diacetylene (C₂H/C₂H₂) (Kaiser et al. in preparation), methyldiacetylene (C₂H/CH₃CCH) (Kaiser et al. submitted 2000), and ethynylallene (C₂H/CH₃CCH).

found to be only of minor importance. Our crossed beam studies provided for the very first time unprecedented comprehensive insights in the chemical dynamics on the reaction of cyanides, allenes, and polyynes in hydrocarbon rich planetary atmospheres. We have assigned ten reaction products; two molecules cyanoacetylene and diacetylene have been observed in the outer Solar System and the remaining species are strongly expected to be identified in the framework of the Cassini-Huygens mission to Titan. In addition, the involved potential energy surfaces exhibit no entrance barriers, all reactions are exothermic, and transition states are below the energy of the reactant molecules; therefore, all neutral-neutral elementary reactions as studied in our crossed beam experiments present an efficient pathway to produce nitriles and (substituted) diacetylene molecules in planetary atmosphere in those regions where density profiles of cyano and ethynyl radicals and hydrocarbon molecules overlap. We

identified further at least thirty radical intermediates. Under our experimental single collision conditions the lifetime of these complexes which are formed with extremely high internal excitation is in the order of a few picoseconds. Hence these intermediates fragment before they can be detected. However, in denser atmospheres of Titan and Saturn, three body collisions have a profound impact on the atmospheric chemistry and can divert the internal energy thus stabilize these intermediates. Most important, these free radicals can undergo subsequent reactions with distinct trace gases C_2H_2 , C_2H , or C_4H_2 to form even more complex molecules such as C_6H_5 , C_6H_4 , C_6H_3 , C_8H_5 , and C_8H_4 isomers extremely unstable species which have been only partly included into chemical reaction networks of these Solar System environments. Based on our versatile concept of an initial addition of the ethynyl radical to the unsaturated double or triple bond we can predict that upon reaction of C_2H with ethylene, allene, and benzene the hydrocarbons butenine ($C_2H_3C_2H$), ethynylallene, $H_2CCH(C_2H)$, ethynylmethylacetylene, $HCCCH_2(C_2H)$, and phenylacetylene ($C_6H_5C_2H$) will be formed and must be observable in Titan's atmosphere. Their identification will be a unique task of the Cassini-Huygens mission to Titan which is scheduled to arrive in 2004.

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