THE ROLE OF CYANO (CN) AND ETHYNYL (C_2H) RADICALS IN ASTROBIOLOGY AND IMPLICATIONS TO THE ORIGIN OF LIFE ON EARTH

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ABSTRACT

Crossed beam experiments of cyano $CN(X^2\Sigma^+)$ and ethynyl $C_2H(X^2\Sigma^+)$ radicals with unsaturated hydrocarbons acetylene, ethylene, methylacetylene, and benzene have been performed to investigate synthetic routes to form nitriles, polyynes, and substituted allenes in hydrocarbon-rich atmospheres of planets and their moons. All radical reactions proceed without entrance barrier, have exit barriers well below the energy of the reactant molecules, and are strongly exothermic. The predominant identification of the radical versus atomic hydrogen exchange channel makes these reactions compelling candidates to form complex organic chemicals – precursors to biologically important amino acids - in solar system environments.

INTRODUCTION

Understanding the complex organic chemistry of the atmosphere of Saturn's moon Titan is of crucial importance to unravel the origin and chemical evolution of biologically important molecules in our solar system. Titan's chemistry is strongly related to astrobiological problems and serves as a model for the prebiotic chemistry and origins of life on Earth (Clarke and Ferris, 1995; Raulin et al., 1999). Analogous to proto Earth, Titan's atmosphere is dense (1.6 atm) and consists mainly of molecular nitrogen (N_2) and trace amounts of hydrocarbons methane (CH_4), acetylene (C_2H_2), ethylene (C_2H_4), ethane (C_2H_6), methylacetylene (CH_3CCH), propane (C_3H_8), diacetylene (HCCCCH), nitriles - molecules containing a cyano (-CN) group - hydrogen cyanide (HCN), cyanomethane (CH_3CN), dicyan (NCCN), cyanoacetylene (HCCCN), and presumably solid phase dicyanoacetylene (NCCCCN) as well as two oxygen-bearing species carbon monoxide (CO) together with carbon dioxide (CO_2) (Letourneur and Coustenis, 1993; Clarke and Ferris, 1997; Raulin et al., 1990; Hidayat et al, 1998; Hidayat et al., 1997; Tanguy et al., 1990; Raulin et al., 1998; Lara et al.,1991; Clarke and Ferris, 1998; Griffith et al., 1998; Thompson, 1991; Karkoschka, 1994; Lunine et al., 1998). Photochemical models proposed pathways to even larger, more complex species such as triacetylene (C_6H_2) and tetraacetylene (C_8H_2) (Yung et al., 1984). Even though the nitriles occur only in trace amounts of a few parts per billion, these species are thought to be ***the*** key intermediates to form biologically relevant molecules in solar system environments. In fact, nitriles can be hydrolyzed and react via multi-step synthesis leading ultimately to amino acids and thus providing one of the basic 'ingredients' for life (Brack 1998). As opposed to Earth, however, the surface temperature of Titan is about 94 K - too cold for liquid water to exist - and the chemical evolution has remained frozen at an early stage. As a consequence, Titan's chemistry offers us the unique opportunity to reconstruct the scene of the primordial terrestrial atmosphere aeons ago and to unveil key concepts on how biologically active molecules and their nitrile precursors were synthesized on proto-Earth.

To untangle the prebiotic chemistry in Titan's and Earth's atmosphere comprehensively, we have to break down the question how distinct solar system environments evolved from the astrobiological viewpoint into two parts. First, we have to investigate how are nitriles - the precursors to amino acids – formed in the reducing atmospheres of Titan and proto Earth, and – possibly – in the cold interstellar medium where averaged temperatures of 10 K prevail. Secondly, it is crucial to investigate how these precursors could have been protected in the atmospheres of Titan and proto Earth from the destructive, solar ultraviolet radiation field. This brings us to the hitherto unanswered question how diacetylene (HCCCCH) is formed in these environments. We like to recall that this molecule is thought to play a key role in atmospheric chemistry since diacetylene likely serves as an ultraviolet radiation shield in planets and their moons. In analogy to ozone protecting Earth from ultraviolet photons today, diacetylene could have absorbed the destructive range of the cosmic ray spectrum in Titan and proto Earth to preserve their lower atmospheric layers and surfaces (Zwier et al., 1996).

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The basic questions to be solved are if and how the nitrile and polyyne chemistry can be initiated in those low temperature environments. We have to take into consideration that the atmospheres of Titan and proto Earth have been constantly bombarded with high-energy photons and cosmic ray particles for the last 4.5 billion years. In the upper atmospheric layers, the energy deposition is mainly from strongly ionizing high-energy electrons from planetary magnetospheres and short wavelength solar ultraviolet photons ($\lambda <$ 155 nm). Hence, ion – molecule reactions dominate in these regions (Fox and Yelle, 1997; Ewan et al, 1998; Ip 1990; Nagy and Cravens, 1998; Keller et al. 1990). However, longer wavelength photons penetrate the stratosphere and photodissociate HCN as well as C_2H_2 to yield cyano, $CN(X^2\Sigma^+)$, and ethynyl $C_2H(X^2\Sigma^+)$ radicals, respectively. Since the ethynyl and cyano radical concentration profiles overlap with atmospheric regions containing unsaturated hydrocarbons such as acetylene, it has been speculated that these radicals react with unsaturated hydrocarbons via neutral – neutral reactions to produce unsaturated nitriles and polyynes through the generalized schemes (1) and (2) (Seki et al., 1996; Lorenz et al., 1997; Yung et al., 1984):

$$(1) \quad CN(X^2\Sigma^+) + C_nH_m \rightarrow C_nH_{m-1}CN + H(^2S_{1/2}),$$
$$(2) \quad C_2H(X^2\Sigma^+) + C_nH_m \rightarrow C_nH_{m-1}CCH + H(^2S_{1/2}).$$

However, to judge the importance of these reactions in solar system environments, it is necessary to investigate experimentally i) if these reactions can take place at low temperatures (chemical kinetics), ii) if nitriles and polyynes are the reaction products (chemical reaction dynamics), and iii) what the underlying reaction mechanisms are (chemical reaction dynamics).

Recent laboratory studies on $CN(X^2\Sigma^+)$ and $C_2H(X^2\Sigma^+)$ radical reactions with unsaturated hydrocarbons down to temperatures as low as 13 K suggest indeed that these reactions are very fast and hold rate constants in the order of gas kinetics of about 10^{-10} cm^3s^{-1} (Rowe and Parent, 1995; Smith et al., 1997; Chastaing et al. 1998). In all those experiments slightly negative temperature dependencies, i.e. acceleration at decreasing temperatures, were recorded. These fast rates suggest further the absence of any entrance barrier. Unfortunately, missing information about the reaction products of such kinetic experiments is a major drawback. This limitation clearly indicates the urgency of novel and systematic laboratory studies to identify the primary reaction products of these important neutral-neutral encounters. The present paper fills this gap and compiles recent accomplishments on reactions of cyano and ethynyl radicals with unsaturated hydrocarbons disclosing ultimately the intermediates involved and the primary reaction products. This paper is organized as follows. Section 2 outlines the experimental approach, i.e. crossed molecular beam experiments, and the information which can be obtained from these studies. Section 3 focuses on the experimental results on reactions of cyano and ethynyl radicals with acetylene, ethylene, methylacetylene, allene, and benzene. All these molecules except allene have already been identified in hydrocarbon-rich atmospheres of planets and partly in their moons; recent data of the European Infrared Satellite Observatory (ISO) derived upper limits of allene of about 5×10^{-9}. The final chapter gives a short summary and outlook.

THE CROSSED BEAM APPROACH
THE PRINCIPLES

Our goal was to set up a research program to investigate the formation of nitriles, polyynes, and allene derivatives in planetary environments such as Titan systematically. The prime directives were the identification of the (different) reaction products and the reaction intermediates, furthermore the elucidation of the reaction mechanisms. The crossed molecular beam setup is a powerful experimental method to acquire these information. The complex network of chemical processes occurring in each planetary or satellite atmosphere consist of a series of elementary reactions, most of which are bimolecular collisions between a radical or atom and a closed shell species. Hence a detailed experimental knowledge of the elementary processes involved at a most fundamental, microscopic level is imperative. Experiments under single collision conditions are essential to achieve this goal. This means that in a binary reaction proceeding via a complex $[RHC_2H]^*$, for example the reaction of a C_2H radical with an unsaturated hydrocarbon molecule RH, one radical reacts only with one hydrocarbon molecule without collisional stabilization or successive reaction of the initially formed complex (exclusion of three body reactions). Only this requirement guarantees that the real reaction products are identified. This scenario holds especially in cold molecular clouds where the low number densities of 10^2 – 10^4 cm^{-3} supports only binary reactions; a collision of the $[RHC_2H]^*$ with another species does not take place considering time scale of ternary (three body) reactions larger than the life-time of cold molecular clouds of about 10^9 years. However in dense planetary atmospheres, three body collisions may occur, and the reaction intermediate $[RHC_2H]^*$ might be stabilized or, since these transient species are often radicals, react leading to more complex molecules. Therefore, is necessary to obtain two kinds of information to get a global picture on the involved processing of planetary and satellite atmospheres: i) the identity of the reaction product(s) and ii) the assignment of the intermediate(s) involved.

Finally, the crossed beams technique allows to prepare even highly unstable and extremely reactive reactants under well-defined conditions (internal states, velocity, velocity spread; in addition, reaction products with often unknown spectroscopic properties have to be probed. Hence, the majority of interesting unsaturated nitriles cannot be scrutinized by optical detection schemes, such as laser induced fluorescence (LIF) or resonance enhanced multi photon ionization (REMPI), and a "universal detector" is crucial.

THE EXPERIMENTAL SETUP

All experiments were conducted with the 35" crossed molecular beam machine (Balucani et al., 2000a). This setup consists of two source chambers fixed at 90^0 crossing angle, a stainless steel scattering chamber, and an ultra high vacuum tight, rotatable triply differentially pumped quadrupole mass spectrometric detector ($<8\times10^{-13}$ mbar) (Figure 1). In the primary source, a pulsed supersonic cyano or ethynyl radical beams are generated *in situ* by laser ablation of graphite and subsequent seeding of the liberated species in molecular nitrogen and hydrogen, respectively, which also serve as reactants. A Nd:YAG laser operates at 30 Hz repetition rate at 266 nm. The output power was limited to a maximum of 30 mJ per pulse to avoid generation of vibrationally excited radicals which might show different reaction dynamics compared to those in their vibrational ground state (Kaiser and Suits, 1995; Kaiser et al., 1999). The ablated carbon species were seeded into the carrier gas released by a pulsed valve. These *in situ* generated radicals pass though a skimmer into the main chamber of the machine. A four-slot chopper wheel is located after the skimmer and selects a slice of well-defined velocity and speed ratio from the pulsed beam which reaches the interaction region. Here, the radicals collide with the second pulsed beam of the hydrocarbon at distinct collision energies between 21 and 35 $kJmol^{-1}$.

Reactively scattered species are registered at different mass to charge ratios (m/e) by a triply differentially pumped detector consisting of a liquid nitrogen cooled electron impact ionizer followed by a quadrupole mass detector, and a Daly type detector. This setup is rotatable in the scattering plane as defined by both beams. An electric signal of the ionized and mass selected species is fed into the multi channel scaler which records the time-of-flight (TOF) spectra of the arriving ions. Despite the triply differential pumping setup, molecules desorbing from wall surfaces lying on a straight line to the electron impact ionizer cannot be avoided. To reduce this background, a copper plate attached to a two stage closed cycle helium refrigerator is placed right before the collision center and cooled to 4.5 K: the ionizer views a cooled surface which traps all species except H_2 and He.

For a detailed physical interpretation of the reaction mechanism it is necessary to transform the laboratory (LAB) data into the center-of-mass (CM) system using a forward-convolution routine. This procedure initially assumes trial angular, $T(\theta)$, and translational energy, $P(E_T)$, distributions in the CM reference frame. Laboratory TOF spectra and angular distributions are then calculated from $T(\theta)$ and $P(E_T)$ averaging over the apparatus and beam functions. The procedure is repeated until a satisfying fit of the LAB distributions is achieved; the CM functions so determined are called "the best-fit CM functions". The ultimate output data of the experiments is the generation of a product flux contour map which reports the differential cross section (the intensity of the reactively scattered products), $I(\theta,u) \sim P(u) \times T(\theta)$, as the intensity as a function of angle θ and product center-of-mass velocity u. This map serves as an image of the reaction and contains all the information of the scattering process. The $I(\theta,u)$ plot is crucial to determine the intermediates involved and the reaction products, especially structural isomers - molecules with the same chemical formula but different connectivities of the atoms such as cyanoacetylene (HCCCN) and isocyanoacetylene (HCCNC). If complex, multi atomic system are studied, it is often very useful to combine these crossed beam experiments with electronic structure calculations.

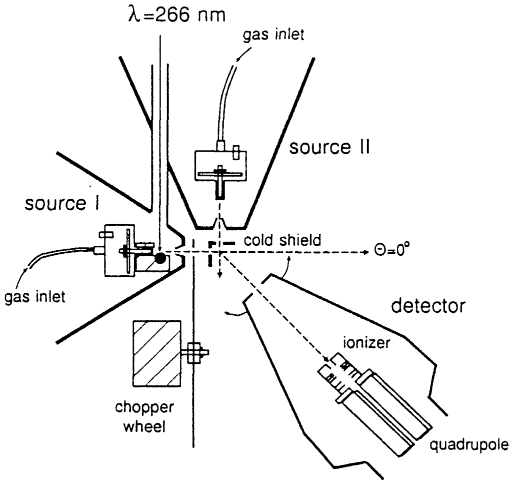

Figure 1: Schematic crossed beam setup

RESULTS

In this section experimental findings for the eight reactions of cyano and ethynyl radicals with unsaturated hydrocarbons listed in the Introduction are reported. The reactions with C_2H_2 and C_2H_4 are prototype reactions with radicals plus the simplest alkyne and alkene, respectively, and thus are expected to reveal key concepts for reactions with the higher members of the same series. The reactions with methylacetylene were selected to observe the effect of the H-substitution with one methyl group. Binary collisions with allene, when compared to the reaction with its isomer methylacetylene, are expected to reveal how distinct isomers react. Finally, the reaction with benzene is the prototype for the series of reactions of radicals with aromatic hydrocarbons. To demonstrate the unique power of the crossed beam approach, details on the experimental results are given here explicitly for the reaction of cyano radicals with acetylene. Hereafter, the experimental findings of the other reactions are compiled.

In the experiments we detected the $CN(X^2\Sigma^+)$ radical versus $H(^2S_{1/2})$ atom exchange to form HC_3N; reactive scattering signal was observed at mass to charge ratios m/e = 51 and 50 (HC_3N^+ and C_3N^+, respectively), cf. Figure 2. Time-of-flight spectra of both ions show identical patterns and could be fit with the same center-of-mass functions, strongly indicating that the parent cracks to m/e = 50 in the electron impact ionizer. This result alone is the first experimental proof that HC_3N isomers can be formed in this radical – neutral reaction. Although no radiative association to a H_2C_3N adduct (m/e = 52) was found under our single collision conditions, denser extraterrestrial environments such as Titan's atmosphere can supply a three body reaction to stabilize the H_2C_3N intermediate(s) thus making the involved chemistry more complex than in lower density molecular clouds.

We now unravel these involved reaction intermediate(s) and identify the HC_3N product isomer(s). To get a picture on the energetics, a closer look at the center-of-mass velocity u of the products is necessary (Figure 3). Here, all the information we gain from u translates to information on the translational energy and $P(E_T)$. To elucidate the chemical reaction dynamics, the maximum translation energy E_{max} can be used to identify the nature of the products. Here, E_{max} is simply the sum of the reaction exothermicity obtained either from electronic structure calculations or literature and the collision energy in our experiments. Therefore, if we subtract the collision energy from the experimentally determined E_{max} we simply get the exothermicity of the reaction. The ab initio calculations reveal that the formation of cyanoacetylene, HCCCN (Figure 4), is exothermic by 94 $kJmol^{-1}$. An inspection of the product flux contour maps allows a direct comparison of the theoretically predicted reaction exothermicity with the maximum product velocity. The derived reaction exothermicity is in the range 80 – 110 $kJmol^{-1}$ and therefore in excellent agreement with our ab initio calculations. We like to stress that formation of another isomer, isocyanoacetylene, HCCNC, is endothermic by 20 $kJmol^{-1}$, and hence its formation is inhibited in cold environments of Titan. Secondly, the flux velocity contour maps of the HC_3N product are slightly asymmetric with respect $\theta=90^0$ and reveal a higher intensity at a $\theta = 0^0$ ('forward') compared to $\theta = 180^0$ ('backward'). This feature depends on the collision energy, and as the latter rises, the flux in the 'forward' direction gains intensity at the expense of the 'backward' hemisphere. These findings suggest that the reaction proceeds through indirect scattering dynamics via a H_2C_3N complex and that the lifetime of the intermediate, which fragments to HC_3N, is comparable to the rotational period of the collision complex.

Based on these considerations, the chemical dynamics of the reaction can be discussed. The CN radical attacks the π-orbital of the C_2H_2 molecule without an entrance barrier to form a cis and/or trans 2-cyanovinyl radical complex (Figure 4). Both complexes are stabilized in a potential well by 242 $kJmol^{-1}$ with respect to the separated reactants and can isomerize via a barrier of 14 $kJmol^{-1}$ through TS1. Both intermediates can decompose via hydrogen atom emission through TS3 yielding cyanoacetylene, HCCCN $(X^1\Sigma^+)$. In addition, a hydrogen shift can transform the trans 2-cyanovinyl radical into the 1-cyanovinyl radical. This isomer is energetically favored by 57 $kJmol^{-1}$ compared to the former isomer and is the global minimum of the doublet H_2C_3N potential energy surface. The 1-cyanovinyl radical can lose a hydrogen atom through TS4 to form cyanoacetylene. About 80 % of the cyanoacetylene is formed via fragmentation of the 2-cyanovinyl radical, whereas a hydrogen migration via TS2 prior to decomposition of 1-cyanovinylradical accounts for 20 % of the cyanoacetylene formation.

These investigations provided detailed insights in the formation of cyanoacetylene, $HCCCN(X^1\Sigma^+)$, in Titan's atmosphere. We have identified cyanoacetylene as the sole product in the reaction of cyano radicals, $CN(X^2\Sigma^+)$, with acetylene, $C_2H_2(X^1\Sigma_g^+)$ under single collision conditions. This neutral – neutral elementary reaction presents an efficient pathway to HCCCN production and therefore should be contemplated as the central pathway to cyanoacetylene in those extraterrestrial environments where density profiles of cyano radicals and acetylene molecules overlap. The potential energy surface of the reaction exhibits no entrance barrier, the reaction is exothermic, and all transition states involved are below the energy of the reactant molecules. This means a synthesis of HCCCN even in the coldest molecular clouds and in Titan on a planetary scale is clearly feasible. This is the first experimental proof to a long-standing problem in astrophysics and planetary sciences, i.e. the formation of cyanoacetylene in interstellar space and hydrocarbon rich planetary atmospheres. We identified further three stable cyanovinyl radical intermediates. Under our single collision conditions the lifetime of the H_2C_3N intermediates which are formed with extremely high internal excitation is in the order of 0.8 – 1.2 ps and hence the complexes fragment before the adduct can reach the detector. Therefore, in cold molecular clouds these intermediates cannot be stabilized by a three-body reaction. In Titan's denser atmosphere however ternary collisions may have a profound impact on the atmospheric chemistry and can lead to a stabilization and/or successive reaction of the intermediate(s). These free radicals might undergo subsequent reaction with other unsaturated trace gases to form even more complex nitriles and/or stabilization in denser environments

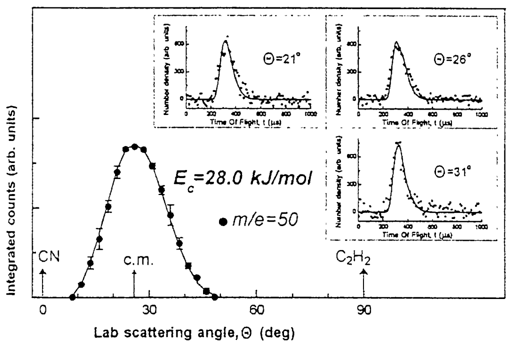

Figure 2: Selected laboratory data at m/e = 50 of the reaction of cyano radicals with acetylene.

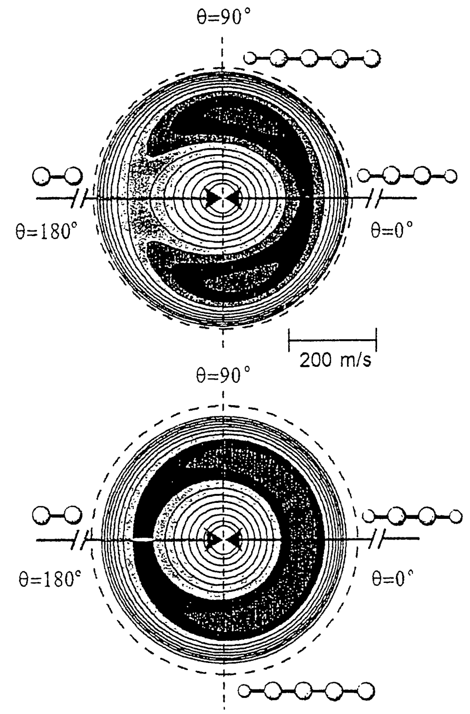

Figure 3: Flux contour plots of the cyanoacetylene product of the reaction of cyano radicals with acetylene at two selected collision energies.

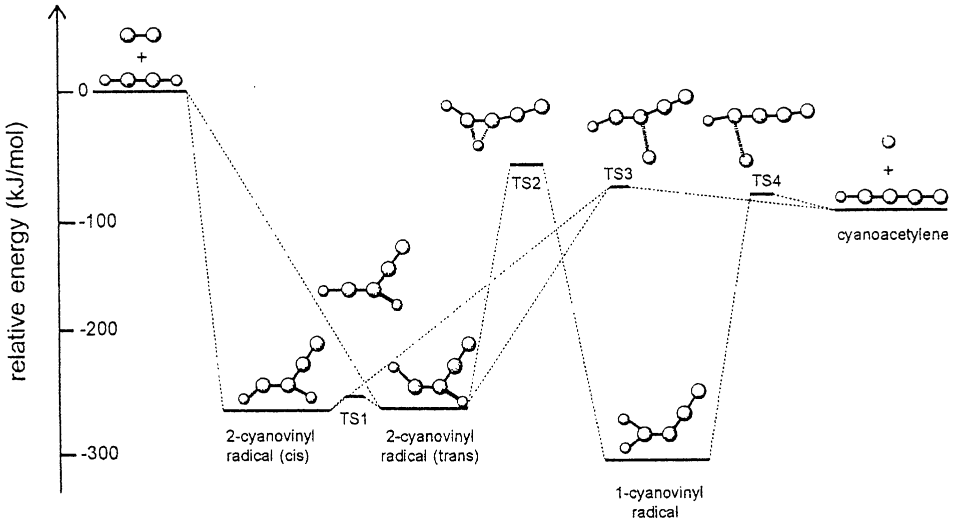

Figure 3: Schematic potential energy surface of the reaction of the cyano radical with acetylene.

We now compile briefly the underlying dynamics of the remaining reactions studied; for a detailed description, the original literature is referred to (Balucani et al., 2000b; Huang et al., 2000; Huang et al., 1999; Balucani et al., 1999a; Balucani et al., 2001; Balucani et al., 1999b; Balucani et al., 2000c;Kaiser et al., 2001; Stahl et al., 2001). The reactions of CN and C_2H radicals with close shell unsaturated hydrocarbons are initiated by addition of the radical reactant to the double or triple bond of the hydrocarbon molecule forming a complex (Baluchani et al., 2000a). These reactions have no entrance barrier. The initial collision complex(es) either loses an H atom to form the reaction product(s) or undergoes isomerization (cis/trans, H atom migration) prior to decomposition; all transition states involved are below the energy of the reactant molecules. The overall reactions to form nitriles, (substituted) diacetylenes, and allenes are all exothermic (Figure 5); no isonitriles were identified, and competing H abstraction channels are found to be only of minor importance. In the case of the C_2H/C_2H_2 system, we identified an additional H_2 elimination pathway to form the butadiynyl radical (HCCCC). Under the experimental single collision conditions the lifetime of all complexes which are formed with extremely high internal excitation is in the order of a few picoseconds. Hence these intermediates fragment before it can be detected. However, in denser atmospheres of Titan, three body collisions have a profound impact on the atmospheric chemistry and can divert the internal energy thus stabilize these intermediates.

SUMMARY AND CONCLUSIONS

The crossed molecular beam experiments have been proven an elegant method to unravel the chemical reaction dynamics, complexes involved, and product isomers of neutral - neutral reactions of cyano, $CN(X^2\Sigma^+)$, and ethynyl, $C_2H(X^2\Sigma^+)$, radicals with unsaturated hydrocarbon molecules acetylene (C_2H_2), ethylene (C_2H_4), methylacetylene (CH_3CCH), allene (H_2CCCH_2), and benzene (C_6H_6). First, we inferred information on the feasibility of these reactions in extraterrestrial environments. Here, the reactions have no entrance barriers and are all exothermic. Since the transition states involved range well below the energy of the separated reactants, these reactive collisions can occur even in low temperature environments such as in cold molecular clouds and in the atmospheres of planets and their moons. We identified further the underlying reaction mechanism. All reactions proceed via an initial addition of the radical to alkenes, alkynes, and aromatic species. This is followed either by a hydrogen emission and - in the case of the C_2H_2 and C_2H_4 reactions - by a hydrogen migration prior to an H atom loss. The versatile reaction mechanism of a radical addition followed by a H atom can be even utilized to predict the reactivity of hitherto not investigated reactions of cyano and ethynyl radicals. The C_2H/C_2H_2 system deserves particular attention as a molecular hydrogen elimination was observed as well.

Secondly, we identified 11 reaction products, among them nitriles, polyynes, substituted allenes, and radicals (Figure 5). The reaction of cyano and ethynyl radicals with acetylene form cyanoacetylene (HCCCN) and diacetylene (HCCCCH), respectively, which have been both observed in the interstellar medium and in Titan's atmosphere. Further, the formation of the butadiynyl radical (HCCCC) was unraveled. The explicit assignment of this reaction pathway is unique to crossed beam experiments. As radicals are extremely reactive, bulk experiments subjecting gas mixtures to discharges and coupling this setup to a gas-chromatography-mass spectrometer (GC-MS) cannot identify open shell reaction products. Thus important information can be lost, and detailed crossed beam experiments are clearly desired. Further, reactions of $CN(X^2\Sigma^+)$ with ethylene and benzene yield vinylcyanide (C_2H_3CN) and cyanobenzene (C_6H_5CN) which have not yet been detected in Titan's atmosphere so far. However, vinylcyanide was observed toward hot molecular cores and cold clouds. Most important, our investigations yielded data on distinct reactivities of structural isomers. Here, the reactions of cyano and ethynyl radicals with methylacetylene and allene gave three distinct isomers each: CH_3CCCN, $H_2CCCH(CN)$, and $HCCCH_2(CN)$ (CN systems) as well as CH_3CCCCH, $H_2CCCH(C_2H)$, and $HCCCH_2(C_2H)$ (C_2H system). These isomers have different spectroscopic properties, photochemical activities, and distinct chemical reactivities. Among them, only CH_3CCCN and CH_3CCCCH have been detected in cold molecular clouds. The explicit experimental identification of unsaturated nitriles, polyynes, and allenes hitherto unobserved in Titan makes these molecules a unique target for the NASA-ESA Cassini-Huygens mission to Titan. The spacecraft Huygens will carry an IR mapping spectrometer as well as a quadrupole mass spectrometer capable of identifying closed shell isomers in Titan's atmosphere.

Thirdly, the crossed beam method is unique in identifying unstable reaction intermediates. Here, more than 100 species have been assigned (see original literature for details). All intermediates are doublet radicals, rovibrationally excited, and hence highly reactive in planetary atmospheres. Although under the experimental single collision conditions the lifetime of these radicals is too short for a three-body reaction, these processes are relevant in Titan's dense environment. However, the collision induced stabilization of the intermediate(s) strongly depends on the temperature as well as density profile of Titan's atmosphere, and hence on the mean collision frequency of the complexes with the bath molecules. Further, these free radicals have unknown spectroscopic properties and could make them responsible for the orange color of the upper atmospheric layers.

The present work is the very first step towards a comprehensive and systematic understanding of the fundamental elementary processes involved in the chemistry of hydrocarbon-rich planetary atmospheres. Our experiments exposed explicitly synthetic routes to nitriles – precursor molecules to aminoacids – and polyacetylene – often dubbed as 'prebiotic ozone'. The experimental data can be employed to set up a systematic database of reaction products and can predict the formation of hitherto unobserved gas phase molecules in Titan and in the framework of the Cassini-Huygens mission. These applications of the crossed beam method to planetary chemistry problems have just begun to scratch the surface. Many interesting problems remain to be studied. In the coming century, laboratory experiments of the kind we have presented here combined with planetary space mission data will undoubtedly unravel the complex chemical processes prevailing in planetary atmospheres of our solar system. This is if crucial importance as the planetary modeling community and the correct outcome of their (photo)chemical reaction networks of planetary and satellite atmospheres depend heavily on input data into these models (rate constants, reaction products, isomers, intermediates). Sophisticated, cutting edge laboratory experiments are crucial to provide these data.

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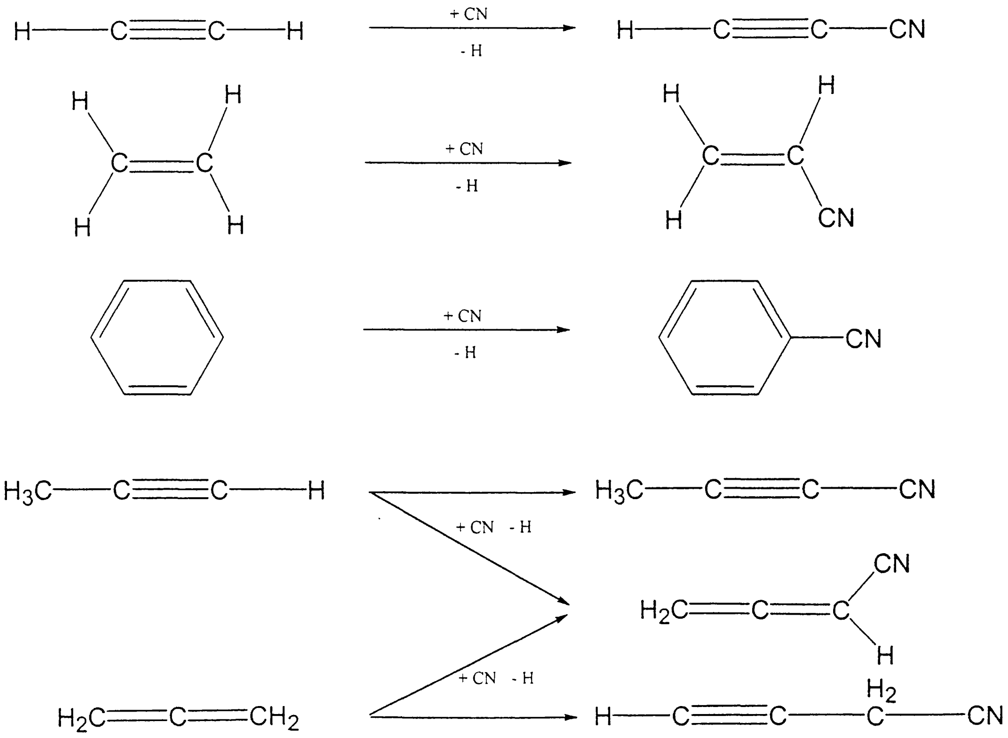

Figure 5: Reactants and reaction products of cyano and ethynyl radical reactions.

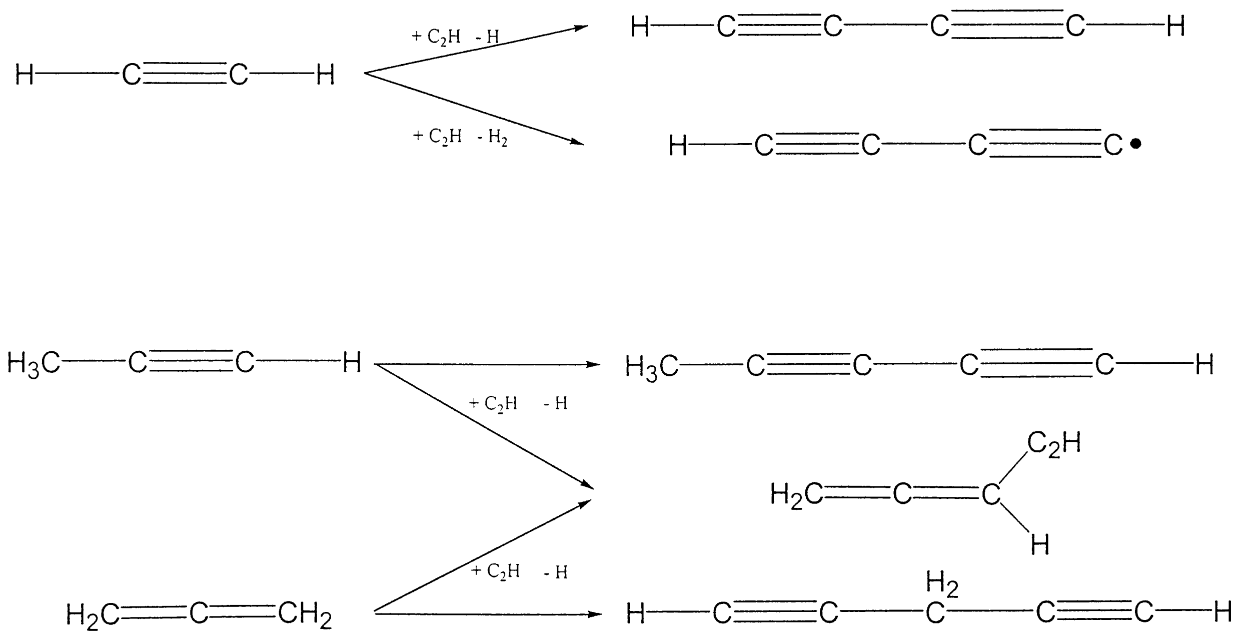

Figure 5 (continued): Reactants and reaction products of cyano and ethynyl radical reactions.

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