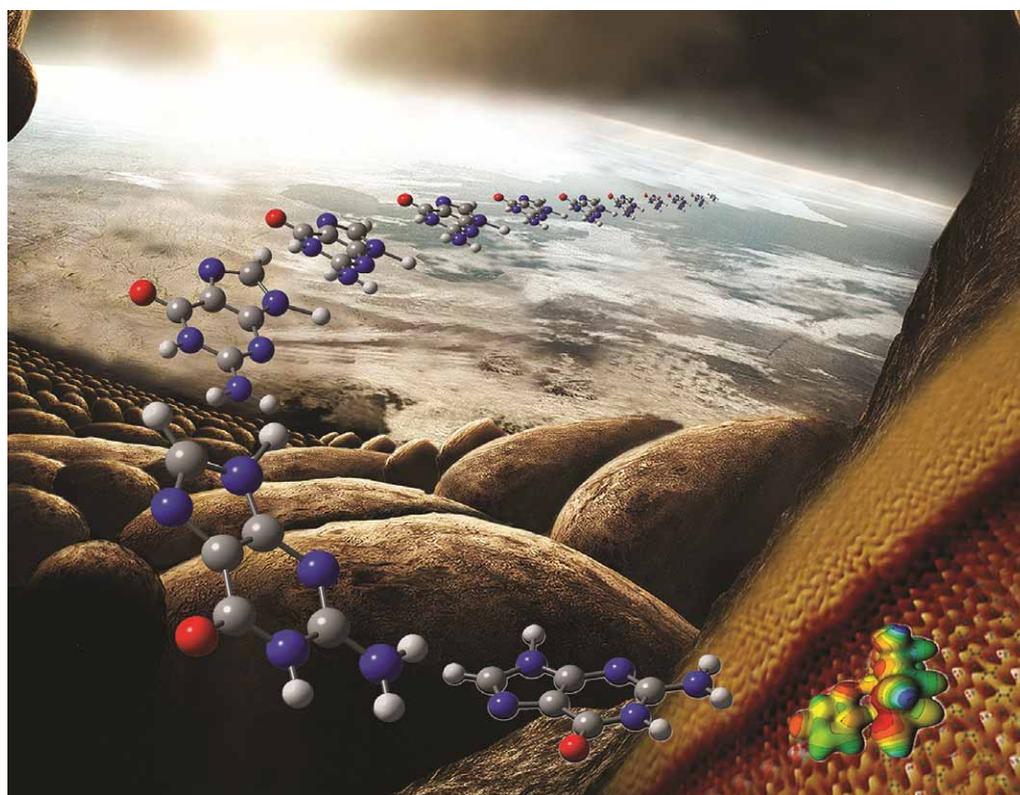


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TUTORIAL REVIEW

On the formation of polyacetylenes and cyanopolyacetylenes in Titan's atmosphere and their role in astrobiology†

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This tutorial review compiles recent experimental and theoretical studies on the formation of polyacetylenes ($\text{H}(\text{C}\equiv\text{C})_n\text{H}$) and cyanopolyacetylenes ($\text{H}(\text{C}\equiv\text{C})_n\text{CN}$) together with their methyl-substituted counterparts ($\text{CH}_3(\text{C}\equiv\text{C})_n\text{H}$, $\text{CH}_3(\text{C}\equiv\text{C})_n\text{CN}$) as probed under single collision conditions in crossed beam studies *via* the elementary reactions of ethynyl (CCH) and cyano radicals (CN) with unsaturated hydrocarbons. The role of these key reaction classes in the chemical evolution of Titan's orange-brownish haze layers is also discussed. We further comment on astrobiological implications of our findings with respect to proto-Earth and present a brief outlook on future research directions.

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1. Introduction

The arrival of the Cassini-Huygens probe at Saturn's moon Titan – the only Solar System body besides Earth and Venus with a solid surface and thick atmosphere – in 2004 opened up



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Ralf I. Kaiser received his PhD in Chemistry from the University of Münster (Germany) in 1994. He conducted postdoctoral work on the gas phase formation of astrochemical and combustion relevant molecules at UC Berkeley (Department of Chemistry). During 1997–2000 he received a fellowship from the German Research Council (DFG) to perform his Habilitation at the Department of Physics (University of Chemnitz, Germany) and Institute of Atomic and

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a new chapter in the history of Solar System exploration. Whereas *Pioneer* 10 & 11 and *Voyager* 1 & 2 merely ‘passed through’ the Saturnian system, the Huygens probe separated from the spacecraft and descended through Titan’s thick atmosphere, collecting unique data on the atmospheric and surface composition on line and *in situ*. With the *Cassini Extended Mission* in operation at least until 2017, particular attention has been drawn to the chemical processing of Titan’s atmosphere and to Titan’s most prominent optically visible features: the aerosol-based haze layers, which give Titan its orange-brownish color. Here, molecular nitrogen (N_2 ; 90–98%) and methane (CH_4 ; 1–6%) are the main atmospheric constituents followed by hydrogen (H_2), nitrogen-bearing molecules such as nitriles – organic molecules carrying the cyano (CN) group – and hydrocarbons as complex as benzene (C_6H_6) (Fig. 1).¹ Even though nitriles and hydrocarbon molecules like ethane (C_2H_6), diacetylene (C_4H_2), and benzene (C_6H_6) occur only in trace amounts, they are of particular importance because they are considered to be key ingredients and building blocks to form Titan’s organic, aerosol-particle based haze layers.^{2–5}

These haze layers are of basic significance to Titan’s chemistry and to hydrocarbon-rich atmospheres of planets in the outer Solar System in general.⁶ The organic aerosol particles absorb the destructive ultraviolet radiation to protect potential astrobiologically important molecules from being

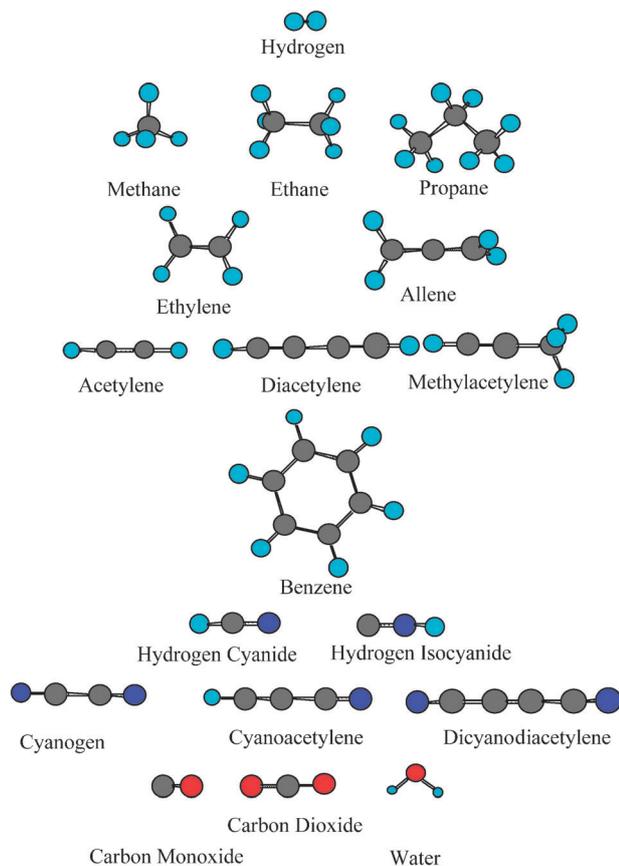


Fig. 1 Molecules identified in Titan’s atmosphere (in addition to the main constituent molecular nitrogen). The spectroscopic assignment of allene is currently being confirmed.

destroyed in the lower parts of the atmosphere and on Titan’s surface dubbing Titan’s haze as ‘prebiotic ozone’.⁷ 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 provides us with a unique prebiotic ‘atmospheric laboratory’ to study the chemical processes that may have been important to the history of our own planet. This affords the potential to reconstruct the scene of the primordial terrestrial atmosphere since Titan and proto-Earth are believed to have emerged with similar atmospheres from the Solar Nebula, although proto-Earth might have had a higher oxygen content than Titan.⁸ Further, the haze layer contains predominant ‘anti-greenhouse species’ which prevents Titan’s atmosphere from heating up.⁹ Therefore, hydrocarbon molecules play a crucial role in the radiation and temperature balance.¹⁰ Finally, Titan’s haze makes an important contribution to the dynamics of the atmosphere.¹¹ This leads to latitudinal and seasonal patterns of hydrocarbons in the atmosphere of Titan, which might provide nucleation sites for hydrocarbon snow and rain.^{12–14} Therefore, an understanding of the formation of the haze layers is also important to rationalize Titan’s meteorology.^{15,16}

However, the basic chemical processes, which initiate and control the formation of these haze layers, have been the least understood to date,¹⁷ and none of Titan’s photochemical models^{18–22} has been able to reproduce the atmospheric molecular mixing ratios obtained from the Cassini-Huygens observations.²³ The incapacity of models to match the observations reflects the lack of accurate data on the basic chemical reactions (products, low temperature rate constants). An understanding of these processes must start at the most fundamental, microscopic level and requires detailed chemical insights into the elementary chemical reactions of the simplest reactants, which initiate the hydrocarbon growth in Titan’s atmosphere.^{24–26} These considerations led to extensive laboratory studies aimed at mimicking Titan’s atmospheric chemistry by subjecting Titan-relevant gas mixtures to discharges, photolysis, and particle irradiation,^{27–32} yielding valuable information on the formation of tholins – a term coined by Sagan defining a mixture of organics observed after irradiating Titan-analogous gas mixtures.³³ Likewise, photolysis of atmospheric constituents like diacetylene^{34,35} and driven pathways to aromatics³⁶ provided important qualitative data on Titan’s chemistry. However, the products were formed under bulk conditions or in reaction flow tubes. Several limitations of these methods such as wall effects undermine their validity. With the reaction products often analyzed off-line and *ex situ*,^{37–40} the detailed chemical dynamics of the reaction – the role of radicals and intermediates – cannot always be obtained, and reaction mechanisms can at best be inferred qualitatively.

During the last few years, a different experimental approach – crossed molecular beams – has been utilized to investigate reactions of simple radicals in Titan’s atmosphere.^{41–44} Since the macroscopic alteration of Titan’s atmosphere consists of multiple elementary reactions that are a series of bimolecular encounters between radicals and molecules,^{45,46} a detailed understanding of the mechanisms initiating the haze formation at the microscopic level is crucial. These are experiments under

single collision conditions, in which particles of one supersonic beam collide only with particles of a second beam. Those *crossed molecular beam* studies extract the chemical dynamics of a reaction and suggest that the isoelectronic ethynyl ($C_2H(X^2\Sigma^+)$) and cyano ($CN(X^2\Sigma^+)$) radicals, which are generated in Titan by photolysis of acetylene (C_2H_2) and hydrogen cyanide (HCN) from solar ultraviolet photons, *i.e.* predominantly Lyman α radiation at 121 nm, must be considered as crucial open shell reactants to form upon reaction with unsaturated hydrocarbons two key classes of growth species leading to the complexation of Titan's haze layers: polyacetylenes and cyanopolyacetylenes, respectively. Polyacetylenes are hydrocarbon molecules described by the generic formula $H(C\equiv C)_nH$ and are derivatives of acetylene (C_2H_2) obtained by formally expanding the carbon chain stepwise by two carbon atoms. Cyanopolyacetylenes are related to polyacetylenes by replacing a hydrogen atom by the cyano group (CN; therefore, they also belong to the group of organic nitriles). Most importantly, recent kinetics experiments at temperatures as low as 13 K provided compelling evidence that ethynyl and cyano radical reactions with unsaturated hydrocarbons such as acetylene are fast ($10^{-10} \text{ cm}^3 \text{ s}^{-1}$) and proceed without entrance barriers.^{47–49} These results are also in line with a semiempirical criterion for a reaction between an unsaturated hydrocarbon with an open shell reactant such as ethynyl and cyano radicals to be barrier-less and fast at low temperatures as derived by Smith *et al.*⁵⁰ The authors suggested that if the difference of the ionization energy of the molecule (I.E.) and electron affinity of the open shell reactant (E.A.) is below 8.75 eV and the reaction rate constant at 298 K, k_{298} , is above $5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, the reaction is likely to accelerate to lower temperatures with rate coefficients approaching the collision-determined limit at very low temperatures. Both criteria are satisfied for the reaction of cyano and ethynyl radicals with unsaturated hydrocarbons. Considering Titan's low temperature of 94 K, the barrier-less and exoergic nature of these reactions presents crucial prerequisites. However, these kinetics experiments monitored only the decay kinetics of the ethynyl and cyano radicals, and reaction products could not be investigated. It should be noted that latest kinetics experiments at room temperature pioneered an isomeric-specific detection of reaction products utilizing time-resolved multiplexed photoionization mass spectrometry *via* synchrotron radiation.⁵¹ Under those experimental conditions, the reaction intermediates may undergo up to a few thousand collisions with the bath molecules so that three-body encounters cannot be eliminated, and true single collision conditions are not provided. On the other hand, in 'real' atmospheres, stabilizations due to collisions are important, and they can be only probed in collisional environments. Consequently, crossed beam experiments, studying the chemical dynamics of a reaction, and kinetics studies must be regarded as highly complementary.

Here, we review recent experimental and theoretical studies on the formation of polyacetylenes ($H(C\equiv C)_nH$) and cyanopolyacetylenes ($H(C\equiv C)_nCN$) together with their methyl-substituted counterparts ($CH_3(C\equiv C)_nH$; $CH_3(C\equiv C)_nCN$) as probed under single collision conditions in crossed beam studies *via* the elementary reactions of ethynyl (CCH) and

cyano radicals (CN) with unsaturated hydrocarbons. We also comment on astrobiological implications of our findings as well as connections to Titan's haze layers and present a brief outlook on further research directions.

2. The crossed molecular beam approach

The crossed molecular beam method with mass-spectrometric detection presents the most versatile technique to study elementary reactions with reaction products of *a priori unknown* spectroscopic properties, thus permitting the elucidation of the chemical dynamics and – in the case of polyatomic reactions – the primary products.⁵² The apparatus consists of two source chambers at a crossing angle of 90° , a stainless steel scattering chamber, and an ultra-high-vacuum tight, rotatable, differentially pumped quadrupole mass spectrometric (QMS) detector which can be pumped down to a vacuum in the high 10^{-13} torr range (Fig. 2 and 3). In the primary source, a *pulsed* beam of unstable (open shell) species is generated by laser ablation of graphite coupled with *in situ* reaction with molecular nitrogen and deuterium to form cyano (CN) and D1-ethynyl (C_2D) radicals.⁵³ The pulsed primary beam passed through a skimmer into the main chamber; a chopper wheel located after the skimmer and prior to the collision center selects a slice of beam pulse with well-defined velocity, which reaches the interaction region. This section of the beam intersects then a *pulsed* reactant beam released by a second pulsed valve under well-defined collision energies. The crossing geometry of both beams can be perpendicularly or – by placing the skimmer of the secondary source on a removable – at angles higher or lower than 90° . It is important to stress that *pulsed beams* allow that reactions with often expensive (partially) deuterated chemicals be carried out to extract additional information on the reaction dynamics, such as the position of the hydrogen and/or deuterium loss if multiple reaction pathways are involved. In addition, pulsed sources with high beam densities allow that the pumping speed and hence equipment costs for pumping systems be reduced drastically.

Which detection scheme is incorporated in our machine? Note that spectroscopic detection schemes like laser induced fluorescence (LIF) and Rydberg tagging⁵⁴ are restricted to hydrogen, deuterium, and oxygen atoms and to species such as hydroxyl radicals (OH), *i.e.* those with well-established spectroscopic fingerprints.^{55,56} Therefore, this approach is not suitable for the detection of distinct hydrocarbon species and nitriles, whose *a priori* spectroscopic properties are often unknown. To detect the product(s), the machine incorporates a triply differentially pumped, *universal* quadrupole mass spectrometric detector coupled to an electron impact ionizer. Here, any reactively scattered species from the collision center after a single collision event has taken place can be ionized in the electron impact ionizer, and – in principle – it is possible to determine the mass (and the molecular formula) of all the products of a bimolecular reaction by varying the mass-to-charge ratio, m/z , in the mass filter. Since the detector is rotatable within the plane defined by both beams, this detector makes it possible to map out the angular (LAB) and velocity distributions of the scattered products. Measuring the time-of-flight (TOF) of the products, *i.e.* selecting a constant mass-to-charge



Fig. 2 Image of the crossed molecular beam machine.

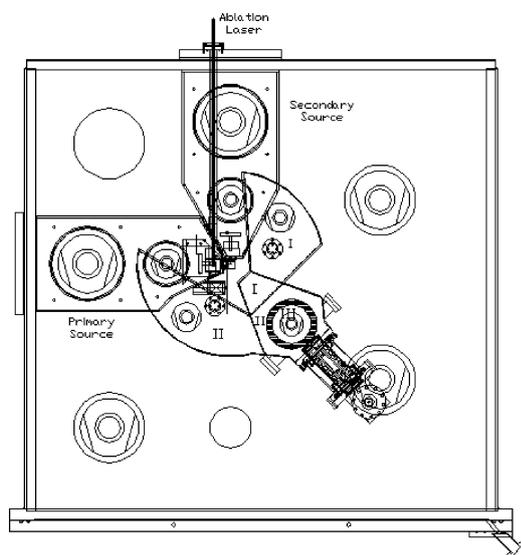


Fig. 3 Top view of the experimental setup with differentially pumped regions I–III, source chambers, chopper wheel, ablation source, and laser channel.

value in the controller and measuring the flight time of the ionized species, from the interaction region over a finite flight distance at different laboratory angles allows a determination of the product translational energy and angular distributions in the center-of-mass reference frame. This provides insight into the nature of the chemical reaction (direct vs. indirect), intermediates involved, the reaction product(s), their branching ratios, and in some cases the preferential rotational axis of the fragmenting complex(es) and the disposal of excess energy into the products' internal degrees of freedom as a function of scattering angle and collision energy. However, despite the triply differential pumping setup of the detector chambers, molecules desorbing from wall surfaces lying on a straight line

to the electron impact ionizer cannot be avoided. Their mean free path is of the order of 10^3 m compared to maximum dimensions of the detector chamber of about 1 m. 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 down to 4 K. In this way, the ionizer views a cooled surface which traps all species with the exception of hydrogen and helium.

What information can we obtain from these measurements? The observables contain some basic information. Every species can be ionized at the typical electron energy used in the ionizer and, therefore, it is possible to determine the mass and the molecular formula of all the possible species produced from the reactions by simply selecting different mass-to-charge (m/z) in the quadrupole mass spectrometer. Even though some problems such as dissociative ionization and background noise limit the method, the advantages with respect to spectroscopic techniques are obvious, since the applicability of the latter needs the knowledge of the optical properties of the products. Another important aspect is that, by measuring the product velocity distributions, we can extract the amount of the total energy available to the products and, therefore, the energy of reaction of the reactive collision. This is of great help when different structural isomers with different enthalpies of formation can be produced. For a more 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.⁵⁷ This approach initially assumed an angular distribution $T(\theta)$ and a translational energy distribution $P(E_T)$ in the center-of-mass reference frame (CM). TOF spectra and the laboratory angular distribution were then simulated from these center-of-mass functions. The essential output of this process is the generation of a product flux contour map, $I(\theta, u) = P(u) \times T(\theta)$, which essentially reports the flux of the reactively scattered products (I) as a function of the center-of-mass scattering angle (θ) and

product velocity (u). This function is defined as the reactive *differential cross section* and can be seen as the *image* of the chemical reaction containing *all* the information on the scattering process. Note that due to the universal electron impact ionization of the product with 80 eV electrons, *i.e.* at an energy at which the ionization cross sections of the organic molecules are at their maxima, even species with unknown spectroscopic properties like polyatomic, open shell hydrocarbon radicals can be detected. We have shown in our laboratory that this approach is well suited not only to monitor the atomic hydrogen and atomic deuterium loss channels, but also molecular hydrogen (H_2 , HD, D_2), atomic oxygen ($\text{O}(^3\text{P}_j)$),⁵⁸ and methyl radical (CH_3) loss pathways.⁵⁹ Our ionizer can also be operated *via soft* electron impact ionization as pioneered by Casavecchia *et al.*⁶⁰ This approach utilizes electrons with low, tunable energy (8–30 eV) to reduce strongly or even eliminate the problem of dissociative ionization from interfering species. However, soft ionization has one disadvantage: at electron energies of 8–30 eV, the ionization cross sections of the newly formed molecules are *at least* a factor of 20 lower than the electron impact ionization cross sections with 80 eV electrons. Therefore, in the case of pulsed crossed beam experiments with a lower duty cycle compared to continuous sources, soft ionization is impractical. Nevertheless, *soft electron impact ionization* can be utilized to characterize the reactant beams on axis and *in situ*. Finally, laser induced fluorescence (LIF) has been recently incorporated as a complementary detection scheme to characterize the rovibrational states of the reactants.⁶¹

3. Electronic structure calculations

Theoretical calculations are crucial to extend the experiments, which can be carried out only at discrete and hence limited collision energies (crossed beams) and temperatures/pressures (laboratory kinetics experiments). In the low density parts of Titan's atmosphere, single collision conditions simulated in the crossed beams studies prevail, while at lower altitudes and hence higher pressure, three-body processes become significant.⁶² The effect of these processes on the underlying chemistry can be tackled computationally. Here, potential energy surfaces (PESs) of the ethynyl and cyano radical reactions with hydrocarbons like acetylene and diacetylene were investigated by *ab initio* and density functional calculations. Within our theoretical approach, geometries of the reactants, products, intermediates, and transition states on these surfaces were optimized at the hybrid density functional B3LYP level^{63,64} with the 6-311G** basis set and vibrational frequencies were calculated using the same B3LYP/6-311G** method. Relative energies of various structures were then refined by employing the coupled cluster CCSD(T) method⁶⁵ with Dunning's correlation-consistent cc-pVTZ basis set.⁶⁶ Spin-restricted coupled cluster RCCSD(T) calculations were used for open-shell structures. All *ab initio* and density functional calculations were performed using the GAUSSIAN-98⁶⁷ and MOLPRO 2002⁶⁸ program packages. For the most important species, we carried out additional CCSD(T)/cc-pVDZ and CCSD(T)/cc-pVQZ calculations to extrapolate their CCSD(T) total energies to the complete basis set (CBS) limit

by fitting the following equation⁶⁹ $E_{\text{tot}}(x) = E_{\text{tot}}(\infty) + Be^{-Cx}$, where x is the cardinal number of the basis set (2, 3, and 4 for cc-pVDZ, cc-pVTZ, and cc-pVQZ, respectively) and $E_{\text{tot}}(\infty)$ is the CCSD(T)/CBS total energy. This three-point CBS extrapolation scheme has been tested earlier for the C_6H_3 PES,⁷⁰ where we performed additional CCSD(T)/cc-pV5Z calculations for selected critical structures and carried out the projection to the CBS limit more precisely, using four CCSD(T) total energies with the cc-pVDZ, cc-pVTZ, cc-pVQZ, and cc-pV5Z basis sets. We found that the relative energies obtained using CCSD(T)/CBS total energies from the three-point extrapolation normally do not deviate from those computed from the four-point extrapolation by more than 0.5 kJ mol^{-1} . We expect that our CCSD(T)/CBS + ZPE(B3LYP/6-311G**) relative energies should be accurate within ± 5 kJ mol^{-1} . A comparison of the CCSD(T) relative energies with the cc-pVTZ basis set and at the CBS limit shows that they normally agree within 3–5 kJ mol^{-1} or better. We also compare our CCSD(T) results with the earlier literature results obtained using the density functional B3LYP approach. In general, the coupled cluster CCSD(T) approach used here is considered to be the golden standard for *ab initio* calculations of molecules and radicals with wavefunctions of a small or moderate multireference character, and a reader can find details on this theoretical method in the recent reviews.^{71,72}

4. Results and discussion

4.1. Polyacetylenes

4.1.1. The acetylene–ethynyl radical system. The ethynyl radical, $\text{C}_2\text{H}(\text{X}^2\Sigma^+)$, can be formally derived from the acetylene molecule, $\text{C}_2\text{H}_2(\text{X}^1\Sigma_g^+)$, *via* homolytic bond rupture of the acetylenic carbon–hydrogen bond with the unpaired electron predominantly localized at the sp-hybridized carbon atom.⁷³ Upon collision with acetylene, the ethynyl radical adds without entrance barrier with its radical center to the acetylenic carbon atom to form a C_s symmetric doublet radical intermediate [1] (Fig. 4a). The latter is bound by about 247 kJ mol^{-1} with respect to the separated reactants and undergoes *cis–trans* isomerization to intermediate [2]. This intermediate was found to decompose *via* atomic hydrogen loss through a tight exit transition state located 28 kJ mol^{-1} above the separated products, forming the linear diacetylene molecule, $\text{HCCCCH}(\text{X}^1\Sigma_g^+)$. To a minor amount (15%), intermediate [2] can also isomerize *via* [1,2]-hydrogen shift to intermediate [3], which then loses a hydrogen atom, forming diacetylene. These complex-forming reaction dynamics involving an initial collision complex [1] were also verified experimentally based on the center-of-mass angular distribution, showing intensity over the complete angular range. The overall reaction was strongly exoergic by 118 kJ mol^{-1} (computed energetics) and 110 to 120 kJ mol^{-1} (experimental energetics). The ethynyl radical can also add with its radical center to the carbon–carbon triple bond of acetylene to form intermediate [4] without a barrier, but [4] would then easily isomerize to [2] *via* a transition state residing 133 kJ mol^{-1} below the reactants. It is also important to stress that computationally, an alternative addition pathway *via* the acetylenic CH group of

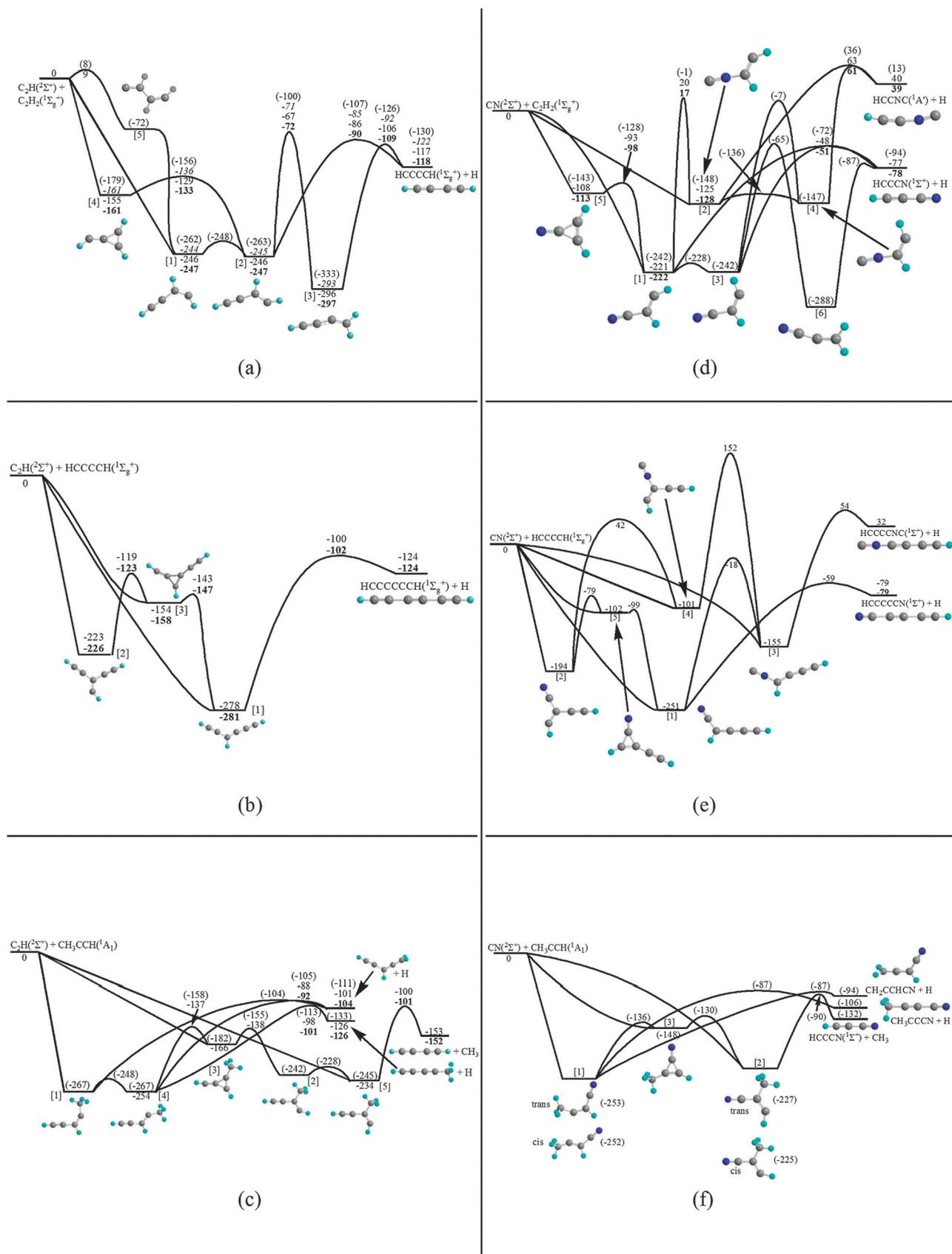


Fig. 4 Key reaction pathways involved in the reaction of ethynyl radicals (left column) and cyano radicals (right column) with acetylene (top), diacetylene (center), and methylacetylene (bottom). Relative energies in kJ mol^{-1} are calculated at various levels of theory: in parentheses – literature data at the B3LYP level; plain numbers – CCSD(T)/cc-pVTZ; numbers in bold – CCSD(T)/CBS; numbers in italic – literature data at the G2M(MP2) level.

ethynyl to the acetylene molecule was investigated as well. This addition has a significant entrance barrier of about 9 kJ mol^{-1} , which would be formally equivalent to about 800 K. However, the existence of the intermediate [5] formed as a result of such addition appears to be an artifact of density functional B3LYP calculations; at higher levels of theory, [5] is not a stationary point on the PES and it undergoes a spontaneous 1,2-H shift to form [1]. Moreover, the entrance barrier cannot be overcome under conditions as present in Titan's atmosphere. To summarize, our studies conclude that the diacetylene molecule can be formed *via* a single collision event between a neutral radical (ethynyl) and a closed shell molecule (acetylene) without entrance barrier in an overall exoergic reaction with indirect scattering dynamics.

4.1.2. The diacetylene–ethynyl radical system. As in the reaction of ethynyl with acetylene, the reaction of ethyl with diacetylene is initiated by a barrierless addition of the ethynyl radical with its radical center to the acetylenic carbon atom of diacetylene, *i.e.* the C1 and/or C2 positions, or to the $\text{C1} \equiv \text{C2}$ bond at the diacetylene molecule, yielding intermediates [1], [2], and [3], respectively (Fig. 4b).^{70,74} These doublet radicals are bound by 281, 226, and 158 kJ mol^{-1} with respect to the separated reactants. Structure [3] connects [1] and [2] *via* a ethynyl group shift from the diacetylenic C2 to the C1 carbon atom. Intermediate [1] ultimately ejects a hydrogen atom involving a tight exit transition state located 22 kJ mol^{-1} above the separated products to yield the triacetylene molecule. The overall reaction was found to be exoergic by 125 kJ mol^{-1} (experimental energetics) and 124 kJ mol^{-1} (computed energetics). Similar to the acetylene–ethynyl system, the addition of the ethynyl radical with its CH group is expected to be prohibited in Titan's atmosphere and also to rapidly lead to the same intermediates [1] and [2] *via* facile 1,2-H shifts in the initial adducts occurring without or with a very low barrier. Therefore, all reactive collisions are anticipated to ultimately yield the triacetylene product plus atomic hydrogen.

4.1.3. The methylacetylene–ethynyl radical system. Compared to the acetylene–ethynyl system, the reaction of ethynyl with methylacetylene (CH_3CCH) is more complicated since the hydrogen atoms at the methyl and acetylenic groups are chemically not equivalent (Fig. 4c).⁷⁵ To pin down the chemical dynamics and the mass-to-charge ratios of the ionized products, reactions with partially isotopically substituted reactants are invaluable. These are the reactions of D1-ethynyl (C_2D) with methylacetylene (CH_3CCH), D3-methylacetylene (CD_3CCH), and D1-methylacetylene (CH_3CCD). The chemical dynamics of these reactions were found to be indirect and once again dictated by addition of the ethynyl radical with its radical center to the carbon–carbon triple bond of methylacetylene. Since the C1 and C2 carbon atoms of the triple bond are chemically non-equivalent, this can lead to two distinct collision complexes [1] and [2]. The reduced cone of acceptance of the carbon atom holding the methyl group favors a carbon–carbon bond formation at the carbon atom adjacent to the acetylenic hydrogen atom (C1 atom). Note that both collision complexes are interconnected *via* the cyclic intermediate [3]; also, both [1] and [2] can undergo a facile *cis*–*trans* isomerization, yielding intermediates [4] and [5], respectively. Detailed studies with partially

deuterated methylacetylenes demonstrated explicitly the position of the atomic hydrogen losses. Here, two reaction channels were identified with intermediate [4] decomposing predominantly to methylacetylene (CH_3CCCH) and to a lesser extent to ethynylallene ($\text{H}_2\text{CCCHC}_2\text{H}$). Both processes involve hydrogen atom losses, tight exit transition states, and overall exoergic reactions in the range of 104 – 126 kJ mol^{-1} . Since the reaction has no entrance barriers, is exoergic, and all transition states are located well below the energy of the separated reactants, the assignment of the ethynyl *versus* hydrogen atom exchange suggests the formation of both isomers under single collision conditions in Titan's atmosphere. According to statistical RRKM calculations of product branching ratios, they appear to be sensitive with respect to the initial collision complex. If ethynyl adds to the C1 carbon to form [1], the hydrogen atom loss channels dominate with the computed branching ratios being around 55% and 20% for methylacetylene and ethynylallene, respectively, and 25% for the methyl loss channel from [5], producing diacetylene with the overall exoergic of 152 kJ mol^{-1} . Alternatively, ethynyl addition to C2 leading to the collision complex [2] makes the diacetylene plus methyl radical product channel more important ($\sim 55\%$), whereas the calculated relative yields of methylacetylene and ethynylallene decrease to 32% and 12%, respectively. Noteworthily, the three products, $\text{CH}_3\text{CCCH} + \text{H}$, $\text{C}_4\text{H}_2 + \text{CH}_3$, and $\text{H}_2\text{CCCHC}_2\text{H} + \text{H}$, were also observed in the slow flow reactor experiments at 4 Torr and 293 K by Goulay *et al.*⁷³ Finally, it shall be stressed that once again, the addition of the ethynyl radical with its CH group to the acetylenic bond is expected to have substantial entrance barrier and to lead to the same collision complexes [1] or [2] after a spontaneous 1,2-H shift.

4.2. Cyanopolyacetylenes

4.2.1. The acetylene–cyano radical system. The reactions of the isoelectronic ethynyl ($\text{C}_2\text{H}(\text{X}^2\Sigma^+)$) and cyano ($\text{CN}(\text{X}^2\Sigma^+)$) radicals hold striking similarities, but also important differences. In contrast to the ethynyl radical, which can only add barrierlessly with its radical center to the acetylenic triple bond, the cyano radical can add both with its radical center at the carbon atom and with the nitrogen atom to the acetylenic carbon atom without barrier, yielding doublet nitrile- and isonitrile-like collision complexes [1] and [2], respectively, in their *cis* form (Fig. 4d).⁷⁶ Note that the absence of a barrier for the cyano radical addition to a triple C–C bond by the N end might be an artifact of B3LYP calculations and requires further verification at higher levels of theory. The complexes [1] and [2] rearrange rapidly to their corresponding *trans* isomers [3] and [4], respectively. Rather than decomposing *via* hydrogen loss to form the isocyanacetylene isomer in an endoergic reaction ($+39 \text{ kJ mol}^{-1}$), the isonitrile intermediates isomerize to their more stable nitrile counterparts [1] and [3] or dissociate back to the reactants. The former can decompose *via* hydrogen loss through a tight exit transition state located about 27 kJ mol^{-1} above the separated reactants to cyanoacetylene (HCCCN). The overall reaction was determined to be exoergic by 78 kJ mol^{-1} (theory) and 80 to 100 kJ mol^{-1} (experimental). It should be noted that statistical calculations predicted that intermediate [3] can also undergo a [2,1]-hydrogen shift, yielding intermediate [6],

which then decomposes through a tight transition state forming hydrogen plus cyanoacetylene (HCCCN).

4.2.2. The diacetylene–cyano radical system. The combined experimental and computational study of the cyano–diacetylene system suggests that the linear cyanodiacetylene molecule (HCCCCCN) presents the sole reaction product (Fig. 4e).⁷⁷ Cyanoacetylene (HCCCN) speculated to be synthesized *via* the exchange of the ethynyl by the cyano group, and the 1,3-butadiynyl radical (HCCCC) thought to be formed *via* hydrogen abstraction could be clearly ruled out. Similar to the reaction of the cyano radical with acetylene, the cyano radical can add with its carbon or nitrogen atom to the acetylenic bond. Since there are two non-equivalent carbon atoms in diacetylene (C1/C2), this process can lead to a total of four initial collision complexes [1] to [4]; none of these pathways has an entrance barrier, at least at the B3LYP level of theory. Note that both isocyano-type intermediates [3] and [4] can isomerize to yield ultimately the doublet [1] intermediate or dissociate back to the reactants; likewise [2] can rearrange *via* a bicyclic structure [5] to [1]. Therefore, intermediate [1] can be classified as the central decomposing complex ejecting a hydrogen atom to ultimately yield cyanodiacetylene (HCCCCCN) in an overall exoergic reaction (-79 kJ mol^{-1}). With the exception of the barrier-less addition of the cyano radical with its nitrogen atom *versus* the inherent barrier when ethynyl radical adds with its CH group to the carbon–carbon triple bond, the reaction dynamics of the cyano and ethynyl radicals with diacetylene are quite similar and both involve indirect scattering dynamics through bound reaction intermediates, which ultimately decompose *via* atomic hydrogen emission.

4.2.3. The methylacetylene–cyano radical system. Similar to the ethynyl–methylacetylene system, the reaction of the cyano radical with methylacetylene is more complicated compared to the cyano–acetylene system, since the hydrogen atoms in methylacetylene are chemically non-equivalent (Fig. 4f).⁷⁸ Consequently, to elucidate the chemical dynamics, reactions with partially isotopically substituted methylacetylenes (D3-methylacetylene (CD_3CCH), D1-methylacetylene (CH_3CCD)) were carried out. Here, the C1 and C2 carbon atoms of the carbon–carbon triple bond are chemically non-equivalent; this results in four distinct collision complexes with the cyano radical adding with its carbon or nitrogen atom to the C1 and C2 carbon atom of the methylacetylene reactant forming *cis* and *trans* conformations of intermediates [1] and [2] and their isocyano analogs. The *cis* and *trans* conformations can rapidly rearrange to one another *via* very low barriers.⁷⁶ As for the cyano–acetylene and cyano–diacetylene systems, the isocyano-like radical intermediates can ultimately isomerize, leading to intermediates [1] and [2]. Further, intermediate [2] can undergo a cyano group migration *via* a cyclic structure to [1]. Consequently, isomer [1] must be classified as a central decomposing complex. As suggested by detailed experiments with partially deuterated methylacetylenes, intermediate [1] fragments *via* two pathways: a hydrogen loss from the methyl and acetylenic carbon atom resulting in the formation of cyanoallene (H_2CCCHCN) and cyanomethylacetylene (CH_3CCCN), respectively. Both pathways involve tight exit transition states and

overall exoergic reactions in the range of $100\text{--}110 \text{ kJ mol}^{-1}$. Alternatively, [2] can lose the methyl group, yielding the cyanoacetylene product exoergic by 132 kJ mol^{-1} .

5. Astrobiological implications

The formation of organic cyanides in the bimolecular reactions of cyano radicals with unsaturated hydrocarbons has important astrobiological implications. Even though the nitriles occur only in trace amounts of a few parts per billion at most, they are of particular importance because they are thought to be the key intermediates to form biologically relevant molecules. Here, nitriles can be hydrolyzed and react *via* multistep synthesis ultimately to amino acids, thus providing one of the basic “ingredients” for life. In strong contrast to Earth, however, the surface temperature of Titan is about 94 K – too cold for liquid water to exist. As a consequence, the chemical evolution has remained frozen at an early stage and no biochemistry as we know it could have developed. Therefore, the study of the chemistry of Titan’s atmosphere and of the nitriles in particular offers the unique opportunity to reconstruct the scene of the primordial terrestrial atmosphere and to unveil key concepts about how biologically active molecules and their nitrile precursors could have been synthesized on proto-Earth.

6. Summary

The reactions of the cyano radicals with acetylene, diacetylene, and methylacetylene display striking similarities, but also important differences to the reactions of the isoelectronic ethynyl radical. First, both the cyano and ethynyl radical react *via* indirect scattering dynamics through complex formation by adding to the carbon–carbon triple bond. With the cyano radical adding barrierlessly with its carbon or nitrogen atom, only the carbon atom holding the radical center reacts without barrier in the case of ethynyl radical reactions; reactions with the CH end of the ethynyl radical adding to the carbon–carbon triple bond are predicted to have a significant barrier of at least 8 kJ mol^{-1} . Ultimately, the isocyano-type intermediates isomerize to the thermodynamically more stable cyano-type intermediates or decompose back to the reactants. All collision complexes, formed by addition of the ethynyl and cyano radicals with their radical centers, are doublet radicals and stabilized by 240 to 295 kJ mol^{-1} with respect to the separated reactants and exist in their *cis* and corresponding *trans* forms. The predominant reaction pathways of these radical intermediates follow unimolecular decomposition *via* emission of hydrogen atoms through tight exit transition states located about 8 to 25 kJ mol^{-1} above the separated products, which are formed in overall exoergic reactions (-80 to -130 kJ mol^{-1}). The exoergicity of the reactions together with the finding that all barriers involved are located below the energies of the separated reactants are two crucial prerequisites so that these reactions are relevant to Titan’s atmospheric chemistry. Due to Titan’s low temperature, any entrance barrier would effectively block a reaction from happening; these are reactions in which the ethynyl radical adds with its CH-group to the carbon–carbon triple bond, but also hydrogen abstraction

pathways by ethynyl and cyano radicals leading to acetylene and hydrogen cyanide, respectively.

Note that besides the systems presented here, copious additional reactions of cyano and ethynyl radicals with unsaturated hydrocarbons relevant to the chemical processing of Titan's atmosphere have been studied both theoretically and experimentally in our labs.⁷⁹ These processes were found to yield two

important classes of organic molecules: highly unsaturated nitriles and hydrogen-deficient hydrocarbons (Fig. 5). We also inferred the existence of multiple reaction intermediates on the doublet potential energy surfaces. Under single collision conditions as present in the crossed beam experiments, the reaction intermediates cannot be stabilized; however, in Titan's atmosphere, a stabilization might occur *via* a three

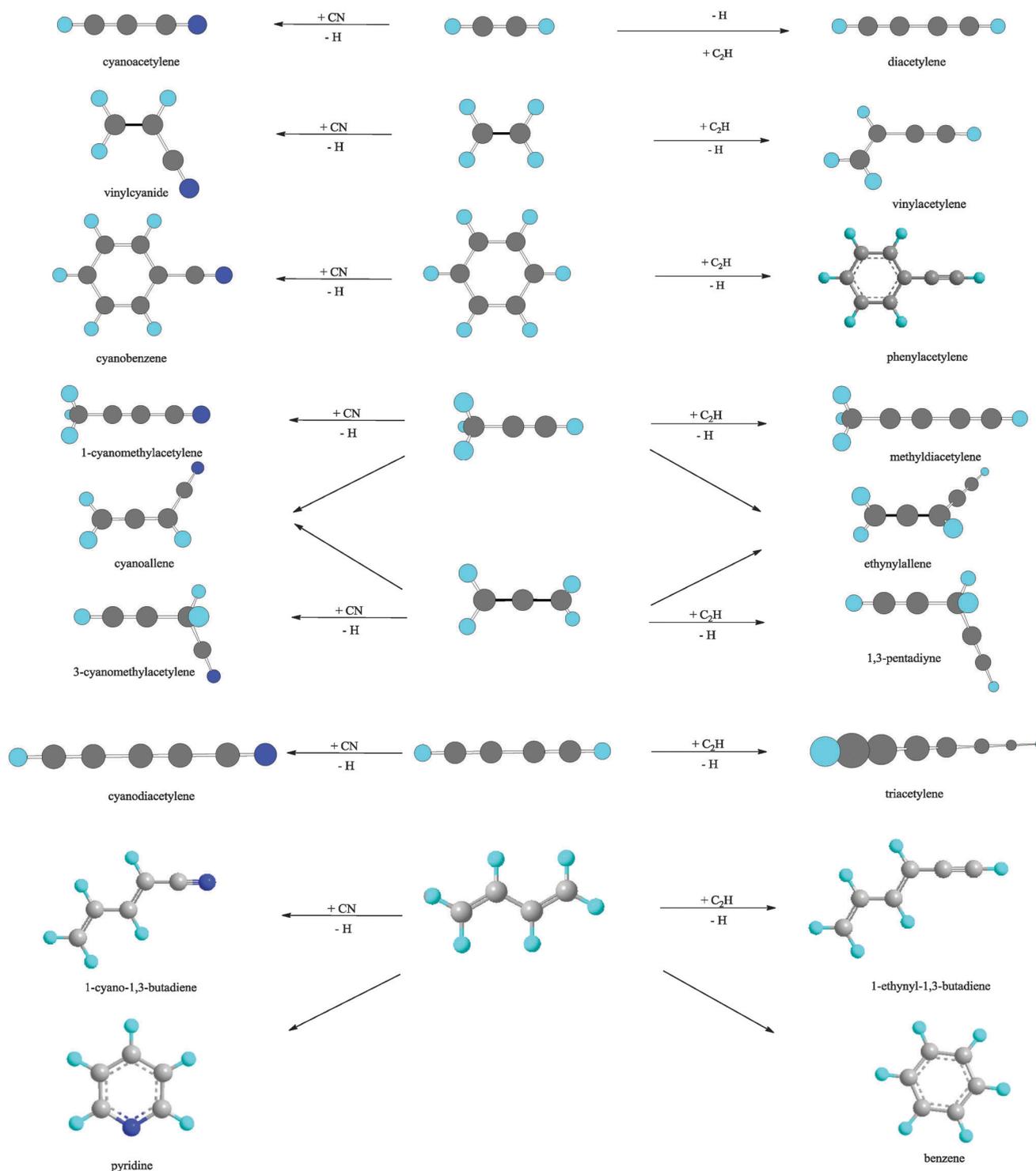


Fig. 5 Products synthesized in the reactions of ethynyl and cyano radicals with unsaturated hydrocarbon molecules under single collision conditions *via* hydrogen atom loss pathways. Pyridine is formed only at levels of one percent at most.

body collision if the life time of the intermediate is longer than the time scale of collision of the intermediate with a bath molecule, *i.e.* predominantly molecular nitrogen.

7. Outlook

Our combined experimental and theoretical studies present a concise picture of how elementary reactions of ethynyl (CCH) and cyano (CN) radicals with unsaturated hydrocarbons can lead to two key classes of organic molecules contributing to the complexation of Titan's aerosol layers: polyacetylenes ($\text{H}(\text{C}\equiv\text{C})_n\text{H}$) and cyanopolyacetylenes ($\text{H}(\text{C}\equiv\text{C})_n\text{CN}$). Which laboratory and computational studies lie ahead? Incorporating uncertainties of rate constants together with a systematic error and sensitivity analysis into Titan's atmospheric models, Hebrard *et al.* disseminated that the modeled depth-dependent mole fractions even for the simplest hydrocarbons (C1–C4) like methane (CH_4) and ethane (C_2H_6) cannot be predicted accurately and vary by at least a factor of five.^{80,81} Therefore, although we unraveled the underlying mechanisms how two key classes of complex molecules contributing to Titan's organic haze layers such as polyacetylenes and cyanopolyacetylenes can be formed under collision-less conditions, Hebrard *et al.* concluded that current state-of-the-art models of Titan's atmosphere – as a matter of fact of any hydrocarbon-rich atmosphere – do not deliver quantitative atmospheric models. A vital result from these models was that in order to develop predictive atmospheric models of Titan's chemistry, it is imperative to understand the energetics, dynamics, and kinetics of the chemical reactions, which *initiate* and control the synthesis of the very first low-molecular weight hydrocarbons, from the 'bottom up'.⁸² These are reactions of the simplest hydrocarbon radical, methylidyne ($\text{CH}(\text{X}^2\text{II})$), formed *via* photodissociation of methane, with key small hydrocarbon molecules in Titan's stratosphere (C1–C4) [~ 700 km] and ion–molecule reactions in the ionosphere [~ 1000 km].^{83–87} Whereas a coherent picture of the Titan's ion chemistry has begun to emerge recently, a systematic understanding of the neutral chemistry and of the energetics and dynamics of methylidyne radical reactions with simple C1–C4 hydrocarbons is still in its infancy.^{88,89} This is due to the insurmountable difficulties in preparing a supersonic molecular beam of methylidyne radicals of a sufficient high intensity to detect the final reaction products. Therefore, to fully understand the basic elementary processes, which initiate the formation of low-molecular weight hydrocarbon molecules in Titan's atmosphere, a concerted and systematic experimental and theoretical study of the energetics, dynamics, and kinetics of methylidyne radical reactions with small hydrocarbons from the 'bottom up' combined with atmospheric modeling is essential. Only this concerted attack can unravel the very first chemical reactions leading ultimately to Titan's organic haze layer.

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