



# Reactions of ethynyl radicals as a source of C<sub>4</sub> and C<sub>5</sub> hydrocarbons in Titan's atmosphere

F. Stahl<sup>a,b</sup>, P.v.R. Schleyer<sup>a,b</sup>, H.F. Schaefer III<sup>b</sup>, R.I. Kaiser<sup>c,\*</sup>

<sup>a</sup>*Institut für Organische Chemie der Universität Erlangen-Nürnberg, 91054 Erlangen, Germany*

<sup>b</sup>*Center for Computational Quantum Chemistry, The University of Georgia, Athens, GA, 30602, USA*

<sup>c</sup>*Department of Chemistry, University of York, York YO10 5DD, UK*

## Abstract

Crossed molecular beam experiments augmented by electronic structure computations of neutral–neutral reactions of the ethynyl radical (C<sub>2</sub>H, X<sup>2</sup>Σ<sup>+</sup>) with the unsaturated hydrocarbons acetylene (C<sub>2</sub>H<sub>2</sub>), methylacetylene (CH<sub>3</sub>CCH), and allene (H<sub>2</sub>CCCH<sub>2</sub>) are reviewed briefly. All reactions are characterized by a C<sub>2</sub>H versus H atom exchange and in the case of the C<sub>2</sub>H/C<sub>2</sub>H<sub>2</sub> system by an additional molecular hydrogen (H<sub>2</sub>) elimination pathway. The attack of the ethynyl radical onto the π-electron density of the unsaturated hydrocarbons has no entrance barrier and initializes each reaction. Consecutive hydrogen atom migrations may precede the exit channels. Diacetylene (HCCCCH), the butadiynyl radical (HCCCC), methylacetylene (CH<sub>3</sub>CCCCH), ethynylallene (H<sub>2</sub>CCH(C<sub>2</sub>H)), and penta-4-diyne (HCC(CH<sub>2</sub>)C<sub>2</sub>H) were identified as products of which only diacetylene has yet been observed in Titan's atmosphere. Our results, however, strongly suggest the presence of all these species on Titan, and the Cassini–Huygens mission is likely to detect these upon arrival in the Saturnian system in 2004. © 2002 Published by Elsevier Science Ltd.

## 1. Introduction

The active and evolving organic chemistry on Saturn's moon Titan, the second largest satellite in the solar system, serves in many aspects as a model for the prebiotic chemistry on Earth (Clarke and Ferris, 1997; Raulin et al., 1999). Analogous to proto Earth, Titan's atmosphere is dense (1.6 atm) and consists mainly of molecular nitrogen (N<sub>2</sub>). "Greenhouse gases" (methane and molecular hydrogen on Titan, water and carbon dioxide on Earth), as well as anti-greenhouse species (hazes and clouds on Titan and aerosols and clouds on Earth) are present. Furthermore, both planetary systems exhibit similar vertical temperature profiles with tropospheric and stratospheric layers, but the temperatures deviate significantly: 94 K on Titan's surface versus 273 to < 373 K on proto Earth. The ambitious NASA-ESA "Cassini–Huygens" mission (Huygens-Science, 1997) is currently on its way to Saturn and is scheduled to arrive in 2004. While the Cassini spacecraft will become an orbiter around Saturn, the Huygens

probe will enter Titan's atmosphere to carry out a detailed analysis of its chemical diversity.

The present knowledge of the chemistry on Titan is grounded on observations from Earth-based telescopes, spacecraft instruments, bulk laboratory experiments, as well as on photochemical models (Hanel et al., 1981; Kunde et al., 1981; Lara et al., 1996; Toubanc et al., 1995; Yung et al., 1984). The latter use reaction pathway parameters such as rate coefficients, branching ratios, photolysis frequencies, and absorption spectra (IR, UV) for which laboratory data at low temperatures often are not available or have large uncertainties. All species observed thus far provide a fundament with further chemical and exobiological implications in Titan's atmosphere: diacetylene (**1**, Fig. 1) is the largest linear polyatomic molecule identified in the outer solar system. The hydrocarbons methane (**2**), acetylene (**3**), ethylene (**4**), ethane (**5**), methylacetylene (**6**), propane (**7**), and the cyano-hydrocarbons hydrogen cyanide (**8**), cyanogen (**9**), acetonitrile (**10**), cyanoacetylene (**11**), and presumably solid state dicyanoacetylene (**12**) also were detected (Bandy et al., 1992). The proposed pathways to larger, more complex species are suggested to proceed via polyynes and cyanopolyynes (Yung et al., 1984). Photochemical models predict further the presence of triacetylene

\* Corresponding author.

E-mail addresses: franks@uga.edu (F. Stahl), schleyer@chem.uga.edu (P.v.R. Schleyer), hfsiii@arches.uga.edu (H.F. Schaefer III), rik1@york.ac.uk (R.I. Kaiser).

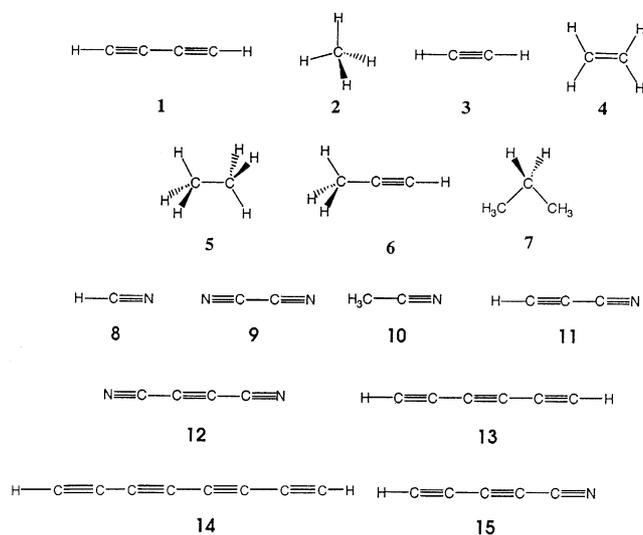


Fig. 1. Hydrocarbons and cyano-hydrocarbons that already have been detected or are proposed to be present in the atmosphere of Titan.

(13), tetraacetylene (14), and cyanodiacetylene (15) (Bandy et al., 1992; Zwier and Allen, 1996).

To simulate the chemical processing of Titan's atmosphere, the overwhelming diversity of all processes has to be broken down into binary reactions of a reactant A with a second collision partner BC which have to be studied individually. Hence, precise insight into a single reactive encounter is the most fundamental piece to assemble the complete puzzle accurately. Therefore, all experiments must be performed under single collision conditions. This means that the initial reaction complex ( $[ABC]^*$ , Eq. (1)) formed by a binary reaction is not stabilized by further collisions (exclusion of three body reactions):



Further, highly unstable and reactive reactants 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 scrutinized by optical detection schemes, such as laser induced fluorescence (LIF) or resonance-enhanced multi-photon ionization (REMPI). Therefore, a universal, mass spectrometric detector operated in the time-of-flight (TOF) mode is crucial. Finally, different structural isomers of a reaction product might be formed and need to be distinguished. The latter can be accomplished by studying the distinct chemical dynamics of a reaction.

## 2. A combined experimental and theoretical approach

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

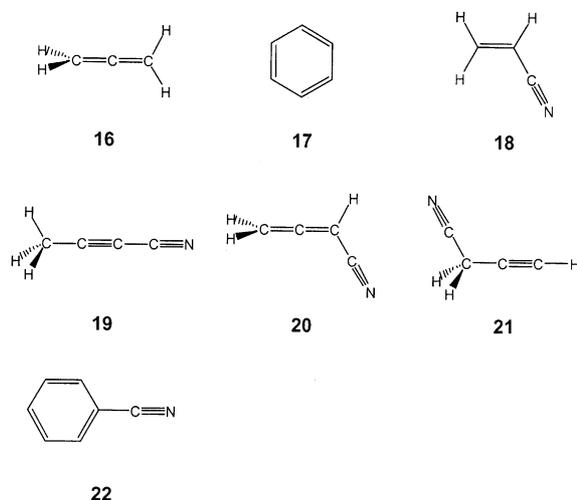


Fig. 2. Molecules that have been used as reactants or were detected as reaction products in our crossed molecular beam experiments.

prime directives were the identification of the (different) reaction products and the reaction intermediates, furthermore the elucidation of the reaction mechanisms. We realized this aspiring project by a combination of crossed molecular beam experiments (Fig. 2) linked to a TOF mass spectrometer and high level *ab-initio* computations. Using this complementary approach we studied the reactions of the isoelectronic radicals CN ( $^2\Sigma^+$ ) and C<sub>2</sub>H ( $^2\Sigma^+$ ) with the unsaturated hydrocarbons acetylene (3), ethylene (4), methylacetylene (6), allene (16), and benzene (17) on the most fundamental molecular level. Short wavelength photons ( $\lambda < 200$  nm) can penetrate into the stratosphere of planetary atmospheres such as that of Titan and dissociate acetylene (3) or hydrogen cyanide (8) into atomic hydrogen and an ethynyl radical (C<sub>2</sub>H) or atomic hydrogen and a cyano radical (CN), respectively (Raulin et al., 1999). The formation of more complex systems from consecutive reactions of these highly reactive radicals with abundant species is strongly anticipated and is modeled in our experiments and computations.

The formation of nitriles in Titan's atmosphere and their role as a precursor for amino acids on proto Earth is now well understood. The highly reactive and unstable nitriles cyanoacetylene (11) (Huang et al., 2000, 1999a), vinylcyanide (18) (Balucani et al., 2000b), 1-cyanopropyne (19) (Huang et al., 1999b), cyanoallene (20), 3-cyanopropyne (21), and cyanobenzene (22) (Balucani et al., 1999) were detected as products of the reaction of the cyano radical with acetylene (3), ethylene (4), methylacetylene (6), allene (16), and benzene (17) (Balucani et al., 2000a, c). Despite this progress, it is still uncertain how these molecules were shielded from destructive ultraviolet (UV) radiation. Diacetylene (1) acts, analogous to ozone for Earth today, as an efficient UV radiation shield (Bandy et al., 1992; Flasar, 1998; Kunde et al., 1981) in the stratosphere of several solar system planets and moons, e.g. Titan. Due to the lack of oxygen, no ozone layer could have been formed in the

early stages of Earth. Hence, Zwier and Allen (1996) suggested that diacetylene (**1**) and complex polyynes also protected proto Earth in the early stages of evolution. Despite this crucial role for various planetary systems and probably even for the prebiotic history of our own planet, the mechanism(s) for the formation of **1** remain speculative.

Current chemical models assume the production of **1** primarily via Eq. (2) and furthermore **1** as the sole product of this reaction (Pedersen et al., 1993; Yung et al., 1984)



Alternate pathways are based on the decomposition of species such as dimethylacetylene which are built up via **1** and, hence, are not initial formation processes. Photochemical models predict also larger mixing ratios of **1** and other molecules than are actually observed. Hence, either alternative reaction products of the reaction of the ethynyl radical  $\text{C}_2\text{H}$  with acetylene (**3**) are involved or the abundance of **1** is reduced by additional consecutive reactions such as electronically excited diacetylene molecules (Zwier and Allen, 1996).

### 3. Study of reactions of the ethynyl radical ( $\text{C}_2\text{H}$ ) with unsaturated hydrocarbons

Recent laboratory experiments demonstrate the ability of  $\text{C}_2\text{H}$  ( $X^2\Sigma^+$ ) to react with unsaturated hydrocarbons at temperatures as low as 15 K. Chastaing et al. (1998) reported reaction rate constants for the reaction of ethynyl radicals with acetylene (**3**) and ethylene (**4**) ( $2.2\text{--}2.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  at 15 K). Hoobler and Leone (1999) studied the reactions of  $\text{C}_2\text{H}$  with methylacetylene (**6**) and allene (**16**) in the 155–298 K temperature range ( $k_{\text{CH}_3\text{CCH}} = 1.9 \pm 0.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ ,  $k_{\text{CH}_2\text{CCH}_2} = 1.7 \pm 0.3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  at 298 K). In all those experiments slightly negative temperature dependencies, i.e. acceleration at decreasing temperatures, were recorded. This in turn implies an initially associative process which results in a negative term for the entropy ( $\Delta S$ ) and therefore benefits from low temperatures. Furthermore, the fast rates suggest the absence of an entrance barrier for these reactions. Unfortunately, missing information about the reaction products of such kinetic experiments is a major drawback.

We studied the reactions of the  $\text{C}_2\text{H}$  radical with acetylene (**3**) and methylacetylene (**6**) using the combination of crossed molecular beam experiments and electronic structure calculations employed in our earlier work (Kaiser et al., 2000; Stahl et al., 2000). These reactions are prototypes of ubiquitous stratospheric ethynyl radicals reacting with the unsaturated hydrocarbons, acetylene and methylacetylene, both of which are present on Titan and on proto Earth. After briefly outlining our experimental set up and the theoretical methods used, we then summarize our results for the reactions of  $\text{C}_2\text{H}$  with acetylene (**3**) and methylacetylene (**6**). Finally, we comment on the reaction of  $\text{C}_2\text{H}$  with allene investigated computationally.

### 4. Experimental and theoretical approach

The experiments were carried out under single collision conditions coupling a novel ethynyl,  $\text{C}_2\text{D}(X^2\Sigma^+)$ , source with a universal crossed molecular beams machine (Kaiser et al., 1999; Lee, 1987). Note that the experiments were performed with  $\text{C}_2\text{D}$ , not  $\text{C}_2\text{H}$ , since a mass-to-charge signal of 45 can be caused by  $^{12}\text{C}^{13}\text{C}$  or  $^{12}\text{C}^{12}\text{C}^1\text{H}$  but when using  $\text{C}_2\text{D}$  a signal from  $^{13}\text{C}^{13}\text{C}$  at 46 is unlikely. The differences in the reaction energies compared to  $\text{C}_2\text{H}$  are only  $1\text{--}2 \text{ kJ mol}^{-1}$  due to the different zero-point-vibrational energies (ZPVE) and such isotopic effects were considered in our complementary computations. The 266 nm output of a neodymium–yttrium–aluminum–garnet laser is focused onto a rotating carbon rod and ablated species are seeded into deuterium which acts as a reactant gas as well. The supersonic beam of in situ generated ground state ethynyl radicals is chopped and crosses a second, pulsed acetylene/methylacetylene beam perpendicular in the interaction region at a collision energy of  $26.1/39.8 \text{ kJ mol}^{-1}$ . TOF spectra are monitored at different laboratory angles using a quadrupole mass spectrometer coupled with an electron-impact ionizer under ultrahigh vacuum conditions ( $< 8 \times 10^{-13} \text{ Torr}$ ). Information on the chemical dynamics and reaction products are extracted by transforming our data from the laboratory to the center-of-mass (CM) coordinate system to yield a CM product flux contour map. The plot reports the differential cross section,  $I(\theta, u)$ , as a function of product CM scattering angle  $\theta$  and velocity  $u$ . This map is an image of the reaction and holds all the information of the reactive scattering process.

We chose density functional theory (DFT) (Gill, 1998; Koch and Holthausen, 2000; Kohn et al., 1996; Parr and Yang, 1989) to study the reactions reported here theoretically. This method is particularly suitable to describe reactions involving radicals since it is less prone to suffer from spin contamination which is often a problem with Hartree–Fock, second-order perturbation theory (MP2) or other post-Hartree–Fock methods (Davidson, 1998; Hehre et al., 1986; Wong and Radom, 1998). In all computations, we employed the most widely used B3LYP, Hartree–Fock/DFT hybrid functional (Becke, 1993; Lee et al., 1988) and the Pople-style 6-311+G\*\* basis set as implemented in the GAUSSIAN 98 quantum chemistry program package (Frisch et al., 1999). This basis set includes polarization functions for carbon and nitrogen (d-orbitals) as well as for hydrogen (p-orbitals) and a set of diffuse (sp) functions which adds desirable flexibility, especially in describing the unpaired electron of radical species which is not necessarily bound tightly. We optimized the geometries of all species and computed the corresponding harmonic vibrational frequencies subsequently. While reactants, intermediates, and products only show real frequencies, transition states are characterized by one imaginary frequency. To confirm which two minima are connected by a transition state, we ran intrinsic reaction coordinate (IRC) calculations

for most cases. Those computations follow the forces that result from the imaginary frequency of the transition state in both directions, hence, geometry optimizations are performed along the reaction coordinate that eventually reveal the two corresponding minima. The zero-point vibrational energies (ZPVE), as generated by our frequency computations, were used unscaled to correct the B3LYP/6-311+G\*\* energies.

### 5. The reaction of C<sub>2</sub>H (23) with acetylene (3)

The experiments were performed at a well-defined collision energy of 26.1 kJ mol<sup>-1</sup>. Experiment and theory agree that the ethynyl radical (C<sub>2</sub>H, <sup>2</sup>Σ<sup>+</sup>, **23**), attacks the π-electron density of the acetylene molecule (**3**) without a barrier to form intermediate **24** (Fig. 3). This initial reaction intermediate can undergo *cis/trans* isomerization to **25** which involves only a small barrier or generate species **26** by a 1,2-hydrogen shift which has a high barrier. Intermediate **25** can decompose via C–H bond rupture to give diacetylene (HCCCCH, X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>, **1**) and a hydrogen atom. Analysis of the experimental data suggests that **1** is the main product formed via a product-like exit transition state under emission of a hydrogen atom parallel to the total angular momentum vector. Our computations reproduce these findings for the transition state connecting **25** and **1**. Hence,

the most direct channel, the reaction path from the initial intermediate **24** via *cis/trans* isomerization to **25** and successive H-atom emission to **1**, dominates the reaction. The formation of diacetylene (**1**) is computed to be exothermic by 129 kJ mol<sup>-1</sup> with respect to C<sub>2</sub>H and acetylene, in good agreement with experiment (110–120 kJ mol<sup>-1</sup>). Even the energetically highest lying transition state involved in this reaction path is still 106 kJ mol<sup>-1</sup> more stable than the separated reactants. Alternatively, diacetylene may result from **26**. This path, however, involves the high barrier for the formation of **26** from **24**. In the corresponding exit transition state, the H atom is not emitted parallel to the total angular momentum vector; hence, this reaction path is only of minor importance. Although the barrier for the rearrangement of **24–26** is high, note that it is still well below the totally available energy of the reaction. The presence of **26** as an intermediate during the experiments is supported by the observation of an additional, minor reaction channel for which **26** is the only conceivable precursor molecule: the formation of the butadiynyl radical (HCCCC, <sup>2</sup>Σ<sup>+</sup>, **27**) and molecular hydrogen H<sub>2</sub>. This reaction channel is computed to be 4 kJ mol<sup>-1</sup> endothermic and is found to be thermoneutral in the experiments. The observation of such H<sub>2</sub> loss under single collision conditions is remarkable. The theoretical description of such processes is not trivial. The electronic ground state of **27** has the unpaired electron bound in a σ-orbital, <sup>2</sup>Σ<sup>+</sup>, but in the first excited state,

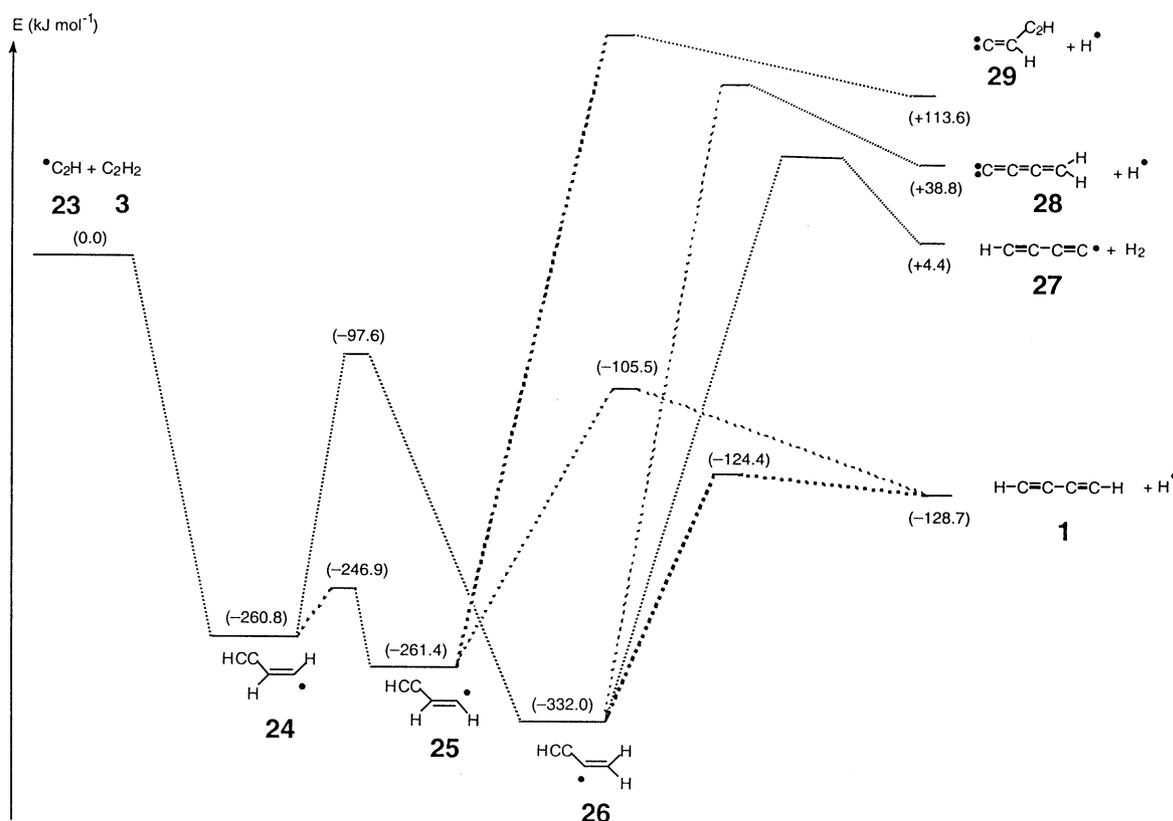


Fig. 3. Potential energy surface (UB3LYP/6-311+G\*\* + ZPVE) for the reaction of C<sub>2</sub>H + C<sub>2</sub>H<sub>2</sub>.

the unpaired electron is bound in a virtually isoenergetic  $\pi$ -orbital. In **26**, however, the unpaired electron is mainly located in a  $\sigma$ -orbital. Expelling molecular hydrogen involves two different potential energy surfaces which conically intersect or exhibit an avoided crossing. Additionally, one might conceive the formation of the carbenes **28** and **29**. Both species, however, are significantly endothermic with respect to the reactants **23** and **3** and cannot be formed in our experiments with a well-defined collision energy of only  $26.1 \text{ kJ mol}^{-1}$ .

Our experiments reveal for the first time an alternate product of the reaction of  $\text{C}_2\text{H}$  with acetylene (**3**) which has never been contemplated before: the butadiynyl radical (**27**). Once included into photochemical models this might reduce the mixing ratio of diacetylene (**1**) and therefore provide better agreement with observational data. Furthermore, **27** is highly reactive and is likely to undergo consecutive reactions, forming higher polyynes species. A reaction of **27** with methane to ‘recycle’ diacetylene is rather unlikely as this direct pathway is expected to involve a significant activation energy which cannot be overcome by the average kinetic energy of both reactants in these low temperature environments.

## 6. The reaction of $\text{C}_2\text{H}$ (**23**) with methylacetylene (**6**)

Like the  $\text{C}_2\text{H}/\text{C}_2\text{H}_2$  system, the reaction of the ethynyl radical with methylacetylene is dominated by the exchange of  $\text{C}_2\text{H}$  for an H atom. The chemical reaction dynamics involve three different channels. The barrier-less addition of the ethynyl radical to the acetylenic  $\pi$  bond leads to two different intermediates: **30** as the result of  $\text{C}_2\text{H}$  binding to the terminal acetylenic carbon atom of **6** or, less favorably, **35** from attack on the central carbon of **6**. The former process clearly dominates. *Cis/trans* stereo inversion of **30–31** involves only a small barrier and is ultrafast, near-equal distribution of both stereoisomers is anticipated. The main reaction channel (70–90%) proceeds via **31** with H atom emission to methyldiacetylene (**36**) parallel to the total angular momentum vector via a product-like exit transition state as indicated by experiment and theory. Note that the precursor **31** might also be formed from **35** via *cis/trans* isomerization to **34** and successive rearrangement including the three-membered ring intermediate **32**. However, as we already pointed out above, initial formation of **35** is negligible, hence, all subsequent paths, too. Alternate reaction paths to **36** proceed via rearrangement of **30–33** and consecutive C–H bond rupture. The corresponding emission process is not detected experimentally. Hence, this reaction path must be of minor importance.

The second product, ethynylallene (**37**) can be formed from **30** or **31** by loss of a hydrogen atom from the methyl group. Diacetylene (**1**) also might form, in principle, by ejection of a methyl group from **33** or **34**. While neither path was observed experimentally, their computation nevertheless is instructive. Methyl radicals, which are not yet

detected unambiguously on Titan, may react with diacetylene (**1**). Such attack initially forms **33** or **34**, of which **33** will dominate as it has the lower entrance barrier of only  $24.3 \text{ kJ mol}^{-1}$  compared to  $53.6 \text{ kJ mol}^{-1}$  for **34**. Note that these reactions are not barrier-less and all exit channels are endothermic with respect to diacetylene and  $\text{CH}_3$ . The energetically least demanding path proceeds through immediate C–H bond rupture in **33** to yield **36**, with a transition state located  $46.1 \text{ kJ mol}^{-1}$  above the two reactants and therefore still below the alternate entrance channel to **34**.

Analogous to the  $\text{C}_2\text{H} + \text{acetylene}$  reaction discussed above, different carbenes can be formed from  $\text{C}_2\text{H}^+$  methylacetylene, as well. All these carbenes are significantly endothermic with respect to the reactants, and their reactions are not considered further here.

## 7. The reaction of $\text{C}_2\text{H}$ (**23**) with allene (**16**)

The reaction of the  $\text{C}_2\text{H}(^2\Sigma^+)$  radical with the second  $\text{C}_3\text{H}_4$  isomer, allene, is dominated by long-range dispersion forces and proceeds barrier-less by an addition of ethynyl to a terminal carbon of allene. This process leads to the formation of the doublet radical intermediate **38** (Fig. 5) which is bound in a deep potential energy well of  $232.4 \text{ kJ mol}^{-1}$  with respect to the reactants. This complex decomposes via H atom elimination into two distinct  $\text{C}_5\text{H}_4$  isomers: ethynylallene (**37**) and 1,4-pentadiyne (**40**). Both reactions are exothermic by  $-102.4$  and  $-65.3 \text{ kJ mol}^{-1}$ , respectively. Since the reaction is dominated by large impact parameters, the attack of  $\text{C}_2\text{H}(^2\Sigma^+)$  at the central carbon atom of allene is less important (Levine and Bernstein, 1987). However, this entrance channel can lead to methyldiacetylene (**36**) after two successive rearrangement steps from the initial intermediate **39** (Fig. 5).

## 8. Summary and conclusion

Our combined crossed molecular beam experiments and electronic structure calculations reveal the chemical dynamics of elementary reactions of  $\text{C}_2\text{H}(^2\Sigma^+)$  radicals with acetylene (**3**), methylacetylene (**6**), and allene (**16**) in hydrocarbon-rich planetary and satellite atmospheres. All the potential energy surfaces involve similar characteristics. Firstly, all reactions are initiated by an addition of  $\text{C}_2\text{H}(^2\Sigma^+)$  to the C–C double or triple bond of the hydrocarbon without an entrance barrier. Secondly, all elementary processes investigated are exothermic and exclusively involve transition states located below the energy of the separated reactants. Based on these findings, the title reactions are feasible in the atmospheres of planets and moons although the average temperatures are  $< 200 \text{ K}$ . We identified further five reaction products, i.e. three  $\text{C}_5\text{H}_4$  isomers (methyldiacetylene **37**, ethynylallene **38**, and 1,3-butendiyne **41**), diacetylene **1**, and the butynyl radical **28**. Of all these characterized

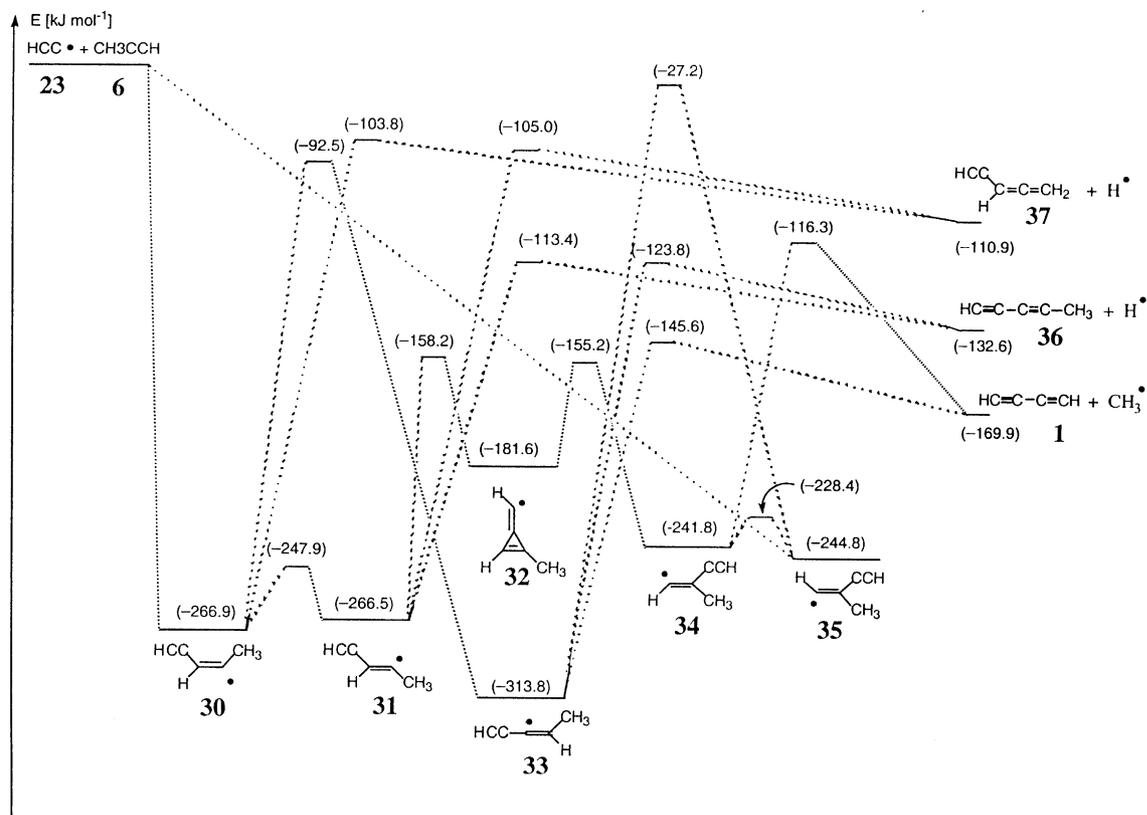


Fig. 4. Potential energy surface (UB3LYP/6-311+G\*\* + ZPVE) for the reaction of  $C_2H + CH_3CCH$ .

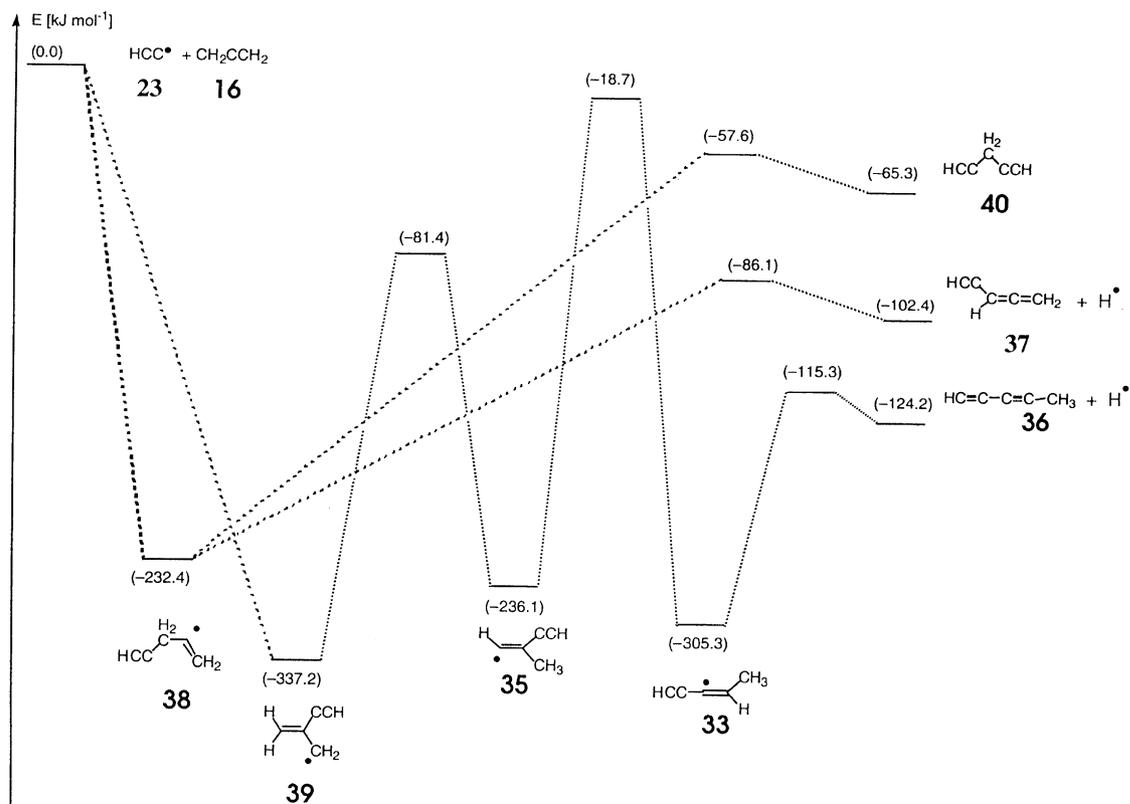


Fig. 5. Potential energy surface (UB3LYP/6-311+G\*\* + ZPVE) for the reaction of  $C_2H + H_2CCCH_2$ .

reaction products only diacetylene, HCCCCH, has been observed in Titan's atmosphere so far. The reactants, however, have all been identified unambiguously and in case of allene are postulated. Hence, all the products observed in our experiments are strongly expected to be present in Titan. Our complementary approach further allows the assignment of different intermediates such as **24**, **25**, and **26** (Fig. 3), **31** and **32** (Fig. 4), and **39** (Fig. 5) involved in the reaction channels. Under the 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 prior to detection. However, in denser atmospheres, three body collisions can divert the internal energy and stabilize these intermediates. All intermediates are free radicals and are very reactive. Therefore, these species could even undergo subsequent reactions with trace gases  $C_2H_2$  or  $C_4H_2$  to form even more complex molecules. These findings together with the unambiguous assignment of the  $C_2H$  versus H atom exchange pathway identify this reaction class as an important synthetic route to highly unsaturated hydrocarbon molecules and radicals in Titan's reducing atmosphere. Particularly, the formation of diacetylene which serves as an UV shield for Titan and is considered as 'prebiotic ozone' for Earth, has been identified for the first time experimentally as a reaction product in the  $C_2H/C_2H_2$  system. This forecast may well be verified during the NASA-ESA Cassini–Huygens mission to Titan. The Huygens spacecraft carries an IR mapping spectrometer as well as a quadrupole mass spectrometer capable of identifying elusive isomers.

## Acknowledgements

RIK is indebted to the Deutsche Forschungsgemeinschaft (DFG) for a Habilitation fellowship (IIC1-Ka1081/3-1). FS gratefully appreciates a HSP III *Doktorandenstipendium* from the DAAD (D/99/22963). This work also was supported by the University of Georgia, by the US Department of Energy and, in Germany, by the DFG.

## References

- Balucani, N., Asvany, O., Chang, A.H.H., Lin, S.H., Lee, Y.T., Kaiser, R.I., Bettinger, H.F., Schleyer, P.v.R., Schaefer III, H.F., 1999. Crossed beam reaction of cyano radicals with hydrocarbon molecules. I. Chemical dynamics of cyanobenzene ( $C_6H_5CN$ ;  $X^1A_1$ ) and perdeutero cyanobenzene ( $C_6D_5CN$ ;  $X^1A_1$ ) formation from reaction of  $CN(X^2\Sigma^+)$  with benzene  $C_6H_6$  ( $X^1A_{1g}$ ) and  $d_6$ -benzene  $C_6D_6$  ( $X^1A_{1g}$ ). *J. Chem. Phys.* 111, 7457–7471.
- Balucani, N., Asvany, O., Huang, L.C.L., Lee, Y.T., Kaiser, R.I., Osamura, Y., 2000a. Laboratory investigation of the formation of unsaturated nitriles in Titan's atmosphere. *Planet. Space Sci.* 48, 447–462.
- Balucani, N., Asvany, O., Chang, A.H.H., Lin, S.H., Lee, Y.T., Kaiser, R.I., Osamura, Y., 2000b. Crossed beam reaction of cyano radicals with hydrocarbon molecules III: chemical dynamics of vinylicyanide ( $C_2H_3CN$ ;  $X^1A$ ) formation from reaction of  $CN(X^2\Sigma^+)$  with ethylene,  $C_2H_4(X^1A_g)$ . *J. Chem. Phys.* 113, 8643–8655.
- Balucani, N., Asvany, O., Huang, L.C.L., Lee, Y.T., Kaiser, R.I., Osamura, Y., Bettinger, H.F., 2000c. Formation of nitriles in the interstellar medium via reactions of cyano radicals,  $CN(X^2\Sigma^+)$ , with unsaturated hydrocarbons. *Astrophys. J.* 545, 892–906.
- Bandy, R.E., Lakshminarayan, C., Frost, R.K., Zwier, T.S., 1992. Direct detection of  $C_4H_2$  photochemical products: possible routes to complex hydrocarbons in planetary atmospheres. *Science* 258, 1630–1632.
- Becke, A.D., 1993. Density-functional thermochemistry. III. The role of exact exchange. *J. Chem. Phys.* 98, 5648–5652.
- Chastaing, D., James, P.L., Sims, I.R., Smith, I.W.M., 1998. Neutral-neutral reactions at the temperature of interstellar clouds; rate coefficients for the reactions of  $C_2H$  radicals with  $O_2$ ,  $C_2H_2$ ,  $C_2H_4$  and  $C_3H_6$  down to 15 K. *Faraday Discuss.* 109, 165–181.
- Clarke, D.W., Ferris, J.P., 1997. Chemical evolution on Titan: comparison to the prebiotic Earth. *Origins Life Evol. Biosphere* 27, 225–248.
- Davidson, E.R., 1998. How robust is present-day DFT? *Int. J. Quant. Chem.* 69, 241–245.
- Flasar, F.M., 1998. The composition of Titan's atmosphere: a meteorological perspective. *Planet. Space Sci.* 46, 1109–1124.
- Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Zakrzewski, V.G., Montgomery, J.J.A., Stratmann, R.E., Burant, J.C., Dapprich, S., Millam, J.M., Daniels, A.D., Kudin, K.N., Strain, M.C., Farkas, O., Tomasi, J., Barone, V., Cossi, M., Cammi, R., Mennucci, B., Pomelli, C., Adamo, C., Clifford, S., Ochterski, J., Petersson, G.A., Ayala, P.Y., Cui, Q., Morokuma, K., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Cioslowski, J., Ortiz, J.V., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Gomperts, R., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Gonzalez, C., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Andres, J.L., Gonzalez, C., Head-Gordon, M., Replogle, E.S., Pople, J.A., 1999. GAUSSIAN 98, Gaussian, Inc.
- Gill, P.M.W., 1998. Density functional theory (DFT), Hartree–Fock (HF), and the self-consistent field. In: Schleyer, P.v.R., Allinger, N.L., Clark, T., Gasteiger, J., Kollman, P.A.I.S.H.F., Schreiner, P.R. (Eds.), *The Encyclopedia of Computational Chemistry*. Wiley, New York, pp. 678–689.
- Hanel, R.A., Conrath, B., Flasar, F.M., Kunde, V.G., Maguire, W.C., Pearl, J., Pirraglia, J., Samuelson, R.E., Herath, L., Allison, M., Cruikshank, D., Gautier, D., Gierasch, P., Horn, L., Koppany, R., Ponnampereuma, C., 1981. Infrared observations of the saturnian system from Voyager 1. *Science* 212, 192–195.
- Hehre, W.J., Radom, L., Schleyer, P.v.R., Pople, J.A., 1986. *Ab initio Molecular Orbital Theory*. Wiley Interscience, New York.
- Hoobler, R.J., Leone, S.R., 1999. Low-temperature rate coefficients for reactions of the ethynyl radical ( $C_2H$ ) with  $C_3H_4$  isomers methylacetylene and allene. *J. Phys. Chem. A* 103, 1342–1346.
- Huang, L.C.L., Lee, Y.T., Kaiser, R.I., 1999a. Crossed beam reaction of the cyanogen radical,  $CN$ , with  $C_2H_2$ : observation of cyanoacetylene, HCCCN. *J. Chem. Phys.* 110, 7119–7122.
- Huang, L.C.L., Balucani, N., Lee, Y.T., Kaiser, R.I., Osamura, Y., 1999b. Crossed beam reaction of the cyano radical,  $CN$ , with methylacetylene,  $CH_3CCH$ : observation of cyanopropyne,  $CH_3CCCN$ , and cyanoallene,  $H_2CCCHCN$ . *J. Chem. Phys.* 111, 2857–2860.
- Huang, L.C.L., Asvany, O., Chang, A.H.H., Balucani, N., Lin, S.H., Lee, Y.T., Kaiser, R.I., Osamura, Y., 2000. Crossed beam reaction of cyano radicals with hydrocarbon molecules IV: chemical dynamics of cyanoacetylene (HCCCN;  $X^1\Sigma^+$ ) formation from reaction of  $CN(X^2\Sigma^+)$  with acetylene ( $X^1\Sigma_g^+$ ). *J. Chem. Phys.* 113, 8656–8666.
- Huygens-Science, 1997. *The Cassini-Huygens Probe to Titan: Payload and Mission*. ESA Special Publication 1177.
- Kaiser, R.I., Ting, J.W., Huang, L.C.L., Balucani, N., Asvany, O., Lee, Y.T., Chan, H., Stranges, D., Gee, D., 1999. A versatile source to produce high-intensity, pulsed supersonic radical beams for crossed-beam experiments: the cyanogen radical  $CN(X^2\Sigma^+)$  as a case study. *Rev. Sci. Instrum.* 70, 4185–4191.

- Kaiser, R.I., Chiong, C.C., Asvany, O., Chang, A.H.H., Lee, Y.T., Stahl, F., Schleyer, P.v.R., Schaefer III, H.F., 2000. Crossed beam reaction of d1-ethynyl radicals with hydrocarbon molecules I: chemical dynamics of d1-methyldiacetylene ( $\text{CH}_3\text{CCCD}$ ;  $X^1A'$ ) and d1-ethynylallene ( $\text{H}_2\text{CCCH}(\text{C}_2\text{D})$ ;  $X^1A'$ ) formation from reaction of  $\text{C}_2\text{D}$  ( $X^2\Sigma^+$ ) with methylacetylene,  $\text{CH}_3\text{CCH}$  ( $X^1A'$ ). *J. Chem. Phys.* 114, 3488–3496.
- Koch, W., Holthausen, M.C., 2000. *A Chemist's Guide to Density Functional Theory*. Wiley-VCH, New York.
- Kohn, W., Becke, A.D., Parr, R.G., 1996. Density functional theory of electronic structure. *J. Phys. Chem.* 100, 12974–12980.
- Kunde, V.G., Aikin, A.C., Hanel, R.A., Jennings, D.E., Maguire, W.C., Samuelson, R.E., 1981.  $\text{C}_4\text{H}_2$ ,  $\text{HC}_3\text{N}$  and  $\text{C}_2\text{N}_2$  in Titan's atmosphere. *Nature* 292, 686–688.
- Lara, L.M., Lellouch, E., Lopez-Monero, J.J.R.R., 1996. Vertical distribution of Titan's atmospheric neutral constituents. *J. Geophys. Res.* 101 (E10), 23, 261–23, 283.
- Lee, Y.T., 1987. Molecular-beam studies of elementary chemical processes. *Science* 236, 793–798.
- Lee, C., Yang, W., Parr, R.G., 1988. LYP. *Phys. Rev. B* 37, 785–789.
- Levine, R.D., Bernstein, R.B., 1987. *Molecular Reaction Dynamics and Chemical Reactivity*. University Press, Oxford.
- Parr, R.G., Yang, W., 1989. *Density Functional Theory of Atoms and Molecules*. Oxford University Press, Oxford.
- Pedersen, J.O.P., Opansky, B.J., Leone, S.R., 1993. Laboratory studies of low-temperature reactions of  $\text{C}_2\text{H}$  with  $\text{C}_2\text{H}_2$  and implications for atmosphere models of Titan. *J. Phys. Chem.* 97, 6822–6829.
- Raulin, F., Coll, P., Smith, N., Benilan, Y., Bruston, P., Gazeau, M.C., 1999. New insights into Titan's organic chemistry in the gas and aerosol phases. *Adv. Space. Res.* 24, 453–460.
- Stahl, F., Schleyer, P.v.R., Bettinger, H.F., Kaiser, R.I., Lee, Y.T., Schaefer III, H.F., 2000. The reaction of the ethynyl radical with methylacetylene: astrochemical implications. *J. Chem. Phys.* 114, 3476–3487.
- Toublanc, D., Parisot, J.-P., Brillet, J., Gautier, D., Raulin, F., McKay, C.P., 1995. Photochemical modeling of Titan's atmosphere. *Icarus* 113, 2–26.
- Wong, M.W., Radom, L., 1998. Radical addition to alkenes: further assessment of theoretical procedures. *J. Phys. Chem. A* 102, 2237–2245.
- Yung, Y.L., Allen, M., Pinto, J.P., 1984. Photochemistry of the atmosphere of Titan—comparison between model and observations. *Astrophys. J. Suppl. Ser.* 55, 465–506.
- Zwier, T.S., Allen, M., 1996. Metastable diacetylene reactions as routes to large hydrocarbons in Titan's atmosphere. *Icarus* 123, 578–583.