

# Chemical dynamics of triacetylene formation and implications to the synthesis of polyynes in Titan's atmosphere

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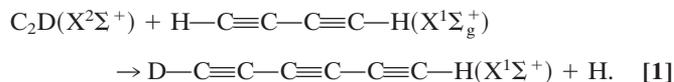
For the last four decades, the role of polyynes such as diacetylene (HCCCH) and triacetylene (HCCCCCH) in the chemical evolution of the atmosphere of Saturn's moon Titan has been a subject of vigorous research. These polyacetylenes are thought to serve as an UV radiation shield in planetary environments; thus, acting as prebiotic ozone, and are considered as important constituents of the visible haze layers on Titan. However, the underlying chemical processes that initiate the formation and control the growth of polyynes have been the least understood to date. Here, we present a combined experimental, theoretical, and modeling study on the synthesis of the polyyne triacetylene (HCCCCCH) via the bimolecular gas phase reaction of the ethynyl radical (CCH) with diacetylene (HCCCH). This elementary reaction is rapid, has no entrance barrier, and yields the triacetylene molecule via indirect scattering dynamics through complex formation in a single collision event. Photochemical models of Titan's atmosphere imply that triacetylene may serve as a building block to synthesize even more complex polyynes such as tetraacetylene (HCCCCCCH).

electronic structure calculations | planetary chemistry |  
crossed molecular beams | photochemical model

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 a new chapter in the history of Solar System exploration (1). Titan's most prominent optically visible features are the aerosol-based haze layers, which give Titan its orange-brownish color. However, the underlying chemical processes, which initiate the haze formation, have been the least understood to date (2). Based on limited laboratory studies related to the formation of soot, planetary chemists proposed that ethynyl radicals [ $C_2H(X^2\Sigma^+)$ ], which are generated in Titan by photolysis of acetylene ( $C_2H_2$ ) at wavelength  $<217$  nm, react with unsaturated hydrocarbons via organic transient species to form haze (3, 4). These considerations have led to the development of photochemical models of Titan (5–8), and to extensive laboratory studies during the last decades (9–11). It is remarkable that, based on reasonable alternative choices for the unknown reaction dynamics, photochemistry, and reaction rates, the models show completely inconsistent mechanisms for the principal routes to polyynes in Titan's atmosphere (12). The reaction products are either guessed or often analyzed off-line and ex situ (13, 14). Thus, the detailed chemical dynamics of the reactions such as the role of radicals and unstable, transient species cannot always be obtained, and reaction mechanisms can at best be inferred qualitatively. However, recent data from the Cassini-Huygens mission have revealed that the transformation of simple molecules such as acetylene (HCCH) and diacetylene (HCCCH) to complex polyacetylenes such as triacetylene (HCCCCCH) likely presents one of the most fundamental steps in the context of the evolution of planetary atmospheres (15).

Therefore, an experimental investigation of these elementary reactions under single collision conditions is desirable (16–18).

In this article, we report the results of a crossed molecular beam reaction of the isotope variant of the elementary reaction of ethynyl radicals ( $C_2H; X^2\Sigma^+$ ) with diacetylene ( $C_4H_2; X^1\Sigma_g^+$ ). These results are combined with electronic structure calculations and photochemical modeling to unravel the formation and role of the organic transient molecule triacetylene ( $C_6H_2; X^1\Sigma_g^+$ ) in the formation of more complex polyynes and their contribution to Titan's hydrocarbon chemistry (reaction 1).



This system represents the prototype reaction of photolytically generated atmospheric ethynyl radicals in Titan with the simplest polyacetylene species, diacetylene, to form triacetylene via a single collision event. A coupling of the laboratory experiments with electronic structure calculations and photochemical reaction networks not only combines experiments with theory, but also links the microscopic, single collision scale to the macroscopic setting of Saturn's moon Titan.

## Results and Discussion

Reaction 1 was studied under single collision conditions in the gas phase using the crossed molecular beams approach by crossing a supersonic beam of D1-ethynyl radicals [ $C_2D(X^2\Sigma^+)$ ] with diacetylene [ $H-C\equiv C-C\equiv C-H(X^1\Sigma_g^+)$ ]. The neutral reaction products were ionized via electron impact and mass- and velocity-analyzed in a triply differentially pumped quadrupole mass spectrometer to record TOF spectra of the ionized neutral molecules at distinct laboratory angles. Details of the experimental setup are described in *Materials and Methods*. In our experiments, we monitored signal at mass-to-charge ratios of  $m/z = 75$  and  $74$ . TOF data at  $m/z = 75$  could be fit with a single reaction channel of the mass combination of 75 atomic mass units ( $C_6HD$ ) and 1 atomic mass unit (H) (Fig. 1). The signal at  $m/z = 74$  had to be fit with two contributions: dissociative ionization of the  $C_6HD$  parent yielding  $C_6D^+$  and a second channel originating from inelastic scattering. The reactive scattering signal at  $m/z = 75$  and  $m/z = 74$  could be fit with identical center-of-mass (CM) functions as depicted below [the CM functions obtained for the  $m/z = 74$  ( $C_6H_2^+$ ) fragment of the

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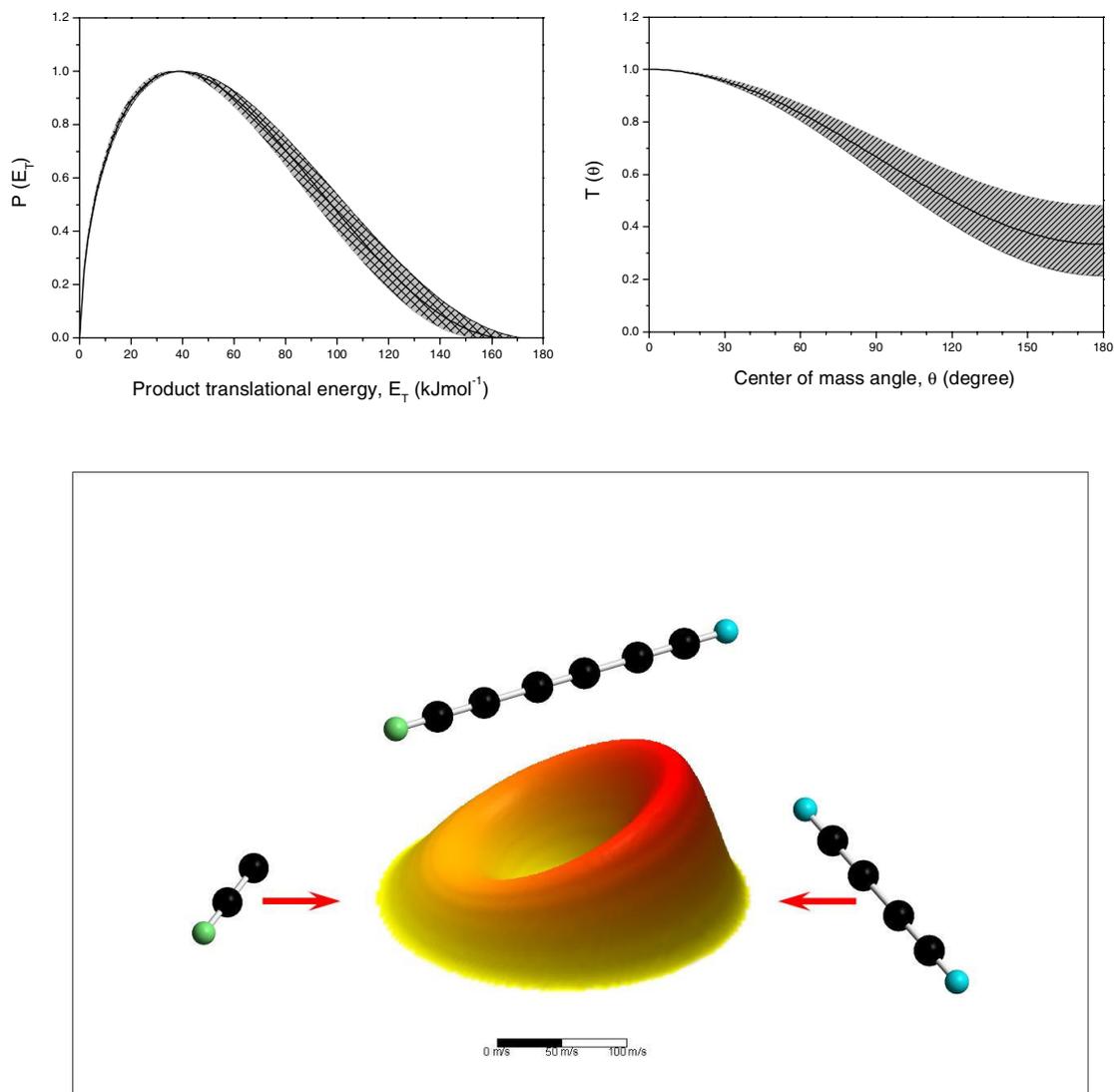
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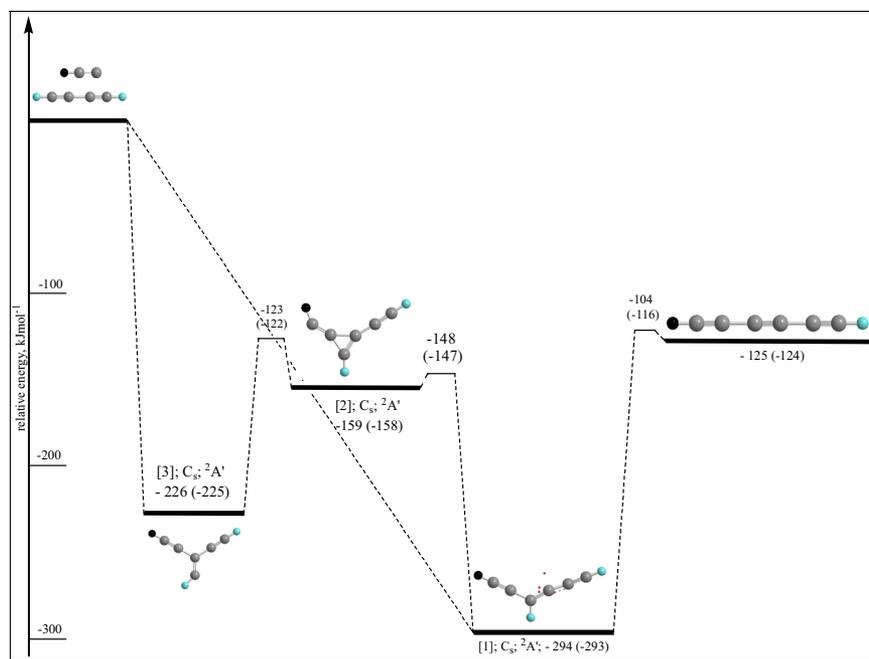


**Fig. 3.** CM translational energy distribution (*Upper Left*), CM angular distribution (*Upper Right*), and CM velocity flux contour map for the reaction of D1-ethynyl [ $C_2D(X^2\Sigma^+)$ ] with diacetylene [ $C_4H_2(X^1\Sigma_g^+)$ ] to form atomic hydrogen plus D1-triacetylene [ $DCCCCCH(X^1\Sigma^+)$ ] (*Lower*). The shaded areas of the CM translational energy and angular distributions delimit the range of acceptable fits within the error limits, whereas the solid lines define the “best fit” functions. The contour lines connect points of constant fluxes (yellow, minimum intensity; red, maximum intensity; the direction of the D1-ethynyl beam is defined as  $0^\circ$  and of the diacetylene beam as  $180^\circ$ ).

expected tight exit transition state. Last, the overall reaction was computed to be exoergic by  $125 \pm 5 \text{ kJ}\cdot\text{mol}^{-1}$ . These data agrees with the experimentally derived value of  $120 \pm 16 \text{ kJ}\cdot\text{mol}^{-1}$  to form D1-triacetylene plus atomic hydrogen. It should be stressed that the second lowest energy isomer of  $C_6H_2$ , i.e., the carbene structure  $CCCCCCH_2$ , is at least  $210 \text{ kJ}\cdot\text{mol}^{-1}$  less stable than triacetylene (23), and thus, can neither be formed in our experiments nor under conditions prevailing in Titan’s atmosphere. Are there other feasible exit channels? The competing direct hydrogen abstraction pathway to form acetylene ( $C_2H_2$ ) plus the 1,3-butadiynyl radical ( $C_4H$ ) involves a barrier of  $\approx 38 \text{ kJ}\cdot\text{mol}^{-1}$ . Likewise, the molecular hydrogen elimination channel to form the 1,3,5-hexatriynyl radical ( $C_6H$ ) is endoergic by  $8 \text{ kJ}\cdot\text{mol}^{-1}$ . Considering the low temperatures in Titan’s atmosphere of  $94$  to  $\approx 200 \text{ K}$ , both the hydrogen abstraction and the molecular hydrogen loss pathways are closed.

We transfer now our findings from the laboratory to the atmosphere of Saturn’s moon Titan. The crossed beam reactions

revealed that under single collision conditions, the exoergic reaction of ethynyl radicals with diacetylene can form triacetylene. As suggested computationally, this process has no entrance barrier. The absence of an entrance barrier presents a crucial prerequisite for a chemical reaction to be feasible under the extreme low temperature conditions in Titan’s atmosphere ( $94$  to  $200 \text{ K}$ ). These low temperatures typically block reactions that either have a significant entrance barrier or that are endoergic; therefore, chemically relevant reactions must be exoergic, proceed without entrance barrier, and must only involve transition states that are lower than the energy of the separated reactants. All these criteria are fulfilled in the bimolecular reaction of ethynyl radicals with diacetylene. We would like to outline that our experimental collision energies are higher than the equivalent temperature conditions in Titan’s atmosphere. Does this difference have any effect on the implications of the formation of triacetylene on Titan? We have combined our experiments with electronic structure calculations. The basic conclusions are

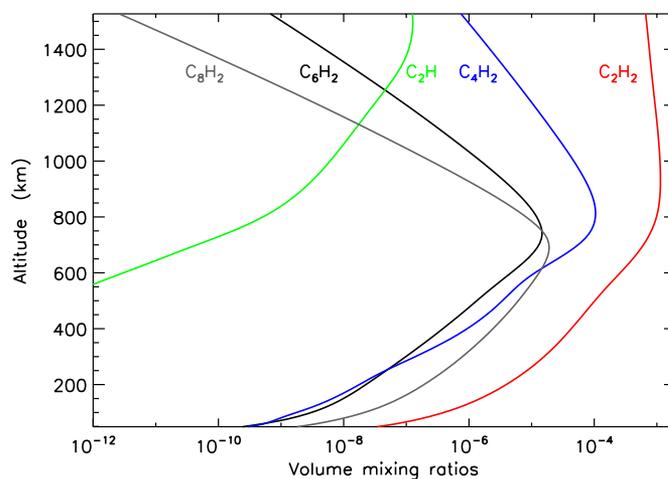


**Fig. 4.** Calculated potential energy surface of the D1-ethynyl [ $C_2D(X^2\Sigma^+)$ ] plus diacetylene [ $C_4H_2(X^1\Sigma_g^+)$ ] reaction to form D1-triacetylene [ $DCCCCCCH(X^1\Sigma^+)$ ] plus atomic hydrogen. The energies in parenthesis are the energies for the corresponding ethynyl [ $C_2H(X^2\Sigma^+)$ ] plus diacetylene [ $C_4H_2(X^1\Sigma_g^+)$ ] reaction taken from ref. 22; point groups and electronic wave functions of the intermediates are also indicated. Black balls indicate carbon, dark green balls deuterium, and blue balls hydrogen atoms.

that triacetylene can be formed in Titan's atmosphere in the prevailing temperature range and also under our experimental conditions. As a matter of fact, in the low temperature atmosphere of Titan, triacetylene is the only reaction product, because our computations suggested that the hydrogen abstraction and molecular hydrogen elimination pathways are closed. However, at higher temperatures and/or collision energies, additional pathways can open up, if the barrier to hydrogen abstraction (forming 1,3-butadiynyl plus ethynyl) or if the endoergicity of the molecular hydrogen loss (yielding 1,3,5-hexatriynyl) can be overcome. Nevertheless, the reaction mechanism to form triacetylene does not change with temperature and/or collision energy, and involves indirect scattering dynamics via addition of the ethynyl radical to the diacetylene molecule followed by hydrogen atom emission through a tight exit transition state.

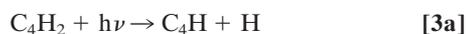
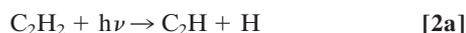
The implementation of the reaction of ethynyl radicals with diacetylene into a photochemical model of Titan's atmosphere requires two input parameters: the reaction products, i.e., triacetylene plus atomic hydrogen, and rate constants. A literature research failed to provide any rate constants for the ethynyl-diacetylene system. Due to the absence of any experimental data, we incorporated computed rate constants of  $1.5 \pm 0.5 \times 10^{-10} \text{ cm}^3 \cdot \text{s}^{-1}$  to form triacetylene plus atomic hydrogen into the model (22). Over the temperature range of 94 to 200 K, the rate constants are (within the error limits) temperature independent. This finding is characteristic of an exoergic reaction, which has no entrance barrier and which is dictated by attractive, long range forces (20). It should be noted that the computed rate constants hold a similar value as those experimentally determined for the related reaction of ethynyl radicals with acetylene yielding diacetylene plus atomic hydrogen (24, 25). Our models suggest that polyynes of the generic formula  $C_{2n}H_2$  ( $n \geq 2$ ) can be readily formed in the atmosphere of Titan via reactions of ethynyl ( $C_2H$ ) and 1,3-butadiynyl radicals ( $C_4H$ ) with (poly)acetylene molecules ( $C_{2n}H_2$ ) such as acetylene, diacetylene, and triacetylene (reactions 2 and 3). The mechanisms consist of two

steps: the photolysis of the precursor like acetylene and diacetylene (reactions 2a and 3a) and a propagation of the long-chain polyne (reactions 2b and 3b) leading effectively to a polyne extension plus two hydrogen atoms (reactions 2c and 3c) with  $n = 1, 2, 3 \dots$ . The propagation of the chain is facilitated by two factors: the lack of reaction barriers such as discussed in this article for the reaction of ethynyl with diacetylene, and the escape of hydrogen atoms from the atmosphere of Titan as a consequence of its low gravity. Quantitatively spoken, the photochemical models predict abundances relative to acetylene of  $[C_4H_2]/[C_2H_2]$ ,  $[C_6H_2]/[C_2H_2]$ , and  $[C_8H_2]/[C_2H_2]$  to be  $\approx 10^{-2}$  (Fig. 5). This model nicely simulates the abundances of diacetylene and acetylene in the neutral region of the atmosphere as



**Fig. 5.** Model profiles of the ethynyl radical ( $C_2H$ ), acetylene ( $C_2H_2$ ), diacetylene ( $C_4H_2$ ), triacetylene ( $C_6H_2$ ), and tetraacetylene ( $C_8H_2$ ). The hydrocarbon chemistry is taken from ref. 17, with updates on the rate constants and reaction products from this work.

observed by Cassini–Huygens probe (17, 26). The production of the polyynes via reactions 2 and 3 is significant throughout the entire atmosphere because of the photolysis of higher order polyynes such as diacetylene mainly by UV photons with wavelengths between 120 and 250 nm, where there is no or little shielding by the major constituents of Titan's atmosphere, i.e., molecular hydrogen ( $H_2$ ), molecular nitrogen ( $N_2$ ), or methane ( $CH_4$ ). The photodissociation is followed by subsequent reactions of polyyne radicals like 1,3-butadiynyl ( $C_4H$ ) to higher-order polyynes (reaction 3). Because the photodissociation cross sections and quantum yields for the photolysis of diacetylene ( $C_4H_2$ ) and triacetylene ( $C_6H_2$ ) and the rate constants for the reaction of the polyyne radicals are similar, the vertical profiles of diacetylene and triacetylene depict alike pattern. The larger abundance of tetraacetylene ( $C_8H_2$ ) compared with diacetylene and triacetylene is based on the lower photodissociation cross section of tetraacetylene (17). Above the homopause ( $\approx 800$  km), molecular separation becomes important, and their mixing ratios drop off exponentially with altitude.



To summarize, we have identified D1-triacetylene as the reaction product under single collision conditions in the reaction of D1-ethynyl radicals with diacetylene. The reaction exhibits no entrance barrier, is exothermic, and all transition states that are involved are below the energy of the reactant molecules. Due to these characteristics, the elementary reaction of the ethynyl radical with diacetylene represents an efficient pathway to produce triacetylene in Titan's atmosphere in those regions where density profiles of photolytically generated ethynyl radicals and diacetylene overlap. Note that the ion and neutral mass spectrometer (INMS) on board the Cassini spacecraft conducted the first composition measurements of Titan's ionosphere (27). These measurements are crucial to constrain the composition and density of minor neutral molecules formed via proton transfer processes. Here, signal in the INMS at, for example,  $m/z = 75$  suggests the existence of a  $C_6H_3^+$  cation, formed via proton transfer to a hitherto unobserved triacetylene molecule (27). Therefore, our laboratory results suggest that the neutral triacetylene molecule is expected to be present in Titan's atmosphere as well. Our models of Titan's atmosphere indicate that successive reactions of the triacetylene molecule can yield even more complex polyynes. Here, ethynyl radicals ( $CCH$ ) or 1,4-butadiynyl radicals ( $HCCCC$ ), formed via photodissociation of acetylene and diacetylene, respectively (28), may react with triacetylene to tetraacetylene ( $C_8H_2$ ) and pentaacetylene ( $C_{10}H_2$ ), respectively. This result offers important sinks for triacetylene and produces potential polyyne precursors for the organic aerosol layers. We hope that our combined experimental, theoretical, and modeling study will act as a template and trigger much needed, successive investigation of the chemistry of triacetylene and tetraacetylene and more complex systems under single collision conditions so that a more complete picture of the processes involved in the chemical processing of Titan's atmosphere will emerge.

## Materials and Methods

**Experimental.** The crossed beam experiments are carried out under single collision conditions using a crossed molecular beams machine described in ref. 29. We generated a pulsed supersonic D1-ethynyl radical beam,  $C_2D(X^2\Sigma^+)$ , in situ via laser ablation of graphite at 266 nm and seeding the ablated species in neat deuterium, which acts as a carrier as well as a reactant gas; the D1-ethynyl radical is formed in situ either via abstraction of a deuterium atom from molecular deuterium by a dicarbon molecule and/or by reaction of dicarbon with molecular deuterium forming intermediate(s) of the molecular formula  $C_2D_2$  followed by deuterium atom loss of the latter. This beam contains also atomic carbon [ $C(^3P)$ ], dicarbon [ $C_2(X^1\Sigma_g^+, a^3\Pi)$ ], and  $C_3(X^1\Sigma_g^+)$ . However, these species do not hamper with the reactive scattering signal of the reaction of D1-ethynyl with diacetylene at mass-to-charge ratios of  $m/z = 75$  and 74. Here, the  $C(^3P) + C_4H_2$  ( $X^1\Sigma_g^+$ ) reaction leads to reactive scattering signal at  $m/z = 61$  ( $C_5H^+$ ), whereas reactive collisions of  $C_2(X^1\Sigma_g^+; a^3\Pi)$  with diacetylene result in the formation of  $C_6H$  (73 atomic mass units) plus atomic hydrogen. The reactions of tricarbon with closed shell molecules like triacetylene have significant entrance barriers much higher than the collision energy used in the present experiments (30, 31); also, signal from this reaction is expected to arise at  $C_7H$  (85 atomic mass units), but was not observed experimentally. Consequently, none of the coreagents interferes with the reaction of D1-ethynyl radicals plus diacetylene. Note that molecular deuterium was preferred over molecular hydrogen, because molecular hydrogen would result in the formation of ethynyl ( $C_2H$ ;  $m/z = 25$ ). Because  $m/z = 25$  can also arise from  $^{13}C^{12}C$  in the beam, the use of D1-ethynyl ( $m/z = 26$ ) made it easier to optimize the production conditions of the D1-ethynyl radical without interferences from  $^{13}C^{12}C$  in the beam. The generated D1-ethynyl beam passes a skimmer; a four-slot chopper wheel located after the ablation zone and before the interaction region selected a segment of the pulse with a peak velocity  $v_p$  of  $2,082 \pm 50$  m s $^{-1}$  and speed ratio  $S$  of  $2.3 \pm 0.3$ . This beam crosses an argon-seeded diacetylene beam (at seeding fractions of 5%) in the main chamber at a collision energy of  $40.1$  kJ mol $^{-1}$  ( $v_p = 599 \pm 20$  m s $^{-1}$ ,  $S = 21.0 \pm 1.0$ ). Diacetylene (>99.5% purity) was synthesized according to literature (32), and purified by trap-to-trap distillation. The reactively scattered species were monitored using a triply differentially pumped detector consisting of a Brink-type electron-impact-ionizer, quadrupole mass-filter, and a Daly ion detector by recording TOF spectra at different laboratory angles at mass to charge ratios. Last, we would like to emphasize that currently, the ethynyl production route via laser ablation combined with reactive formation presents the only viable pathway to cross an intense beam of D1-ethynyl radicals with seeded hydrocarbon reactants like diacetylene in any crossed beams machine. A possible addition of a heavy carrier gas such as argon, krypton, or xenon to deuterium would certainly reduce the collision energy, but also decreases the number density of the already weak D1-ethynyl radical beam, because the concentration of deuterium in the seeding gas would be reduced as well. An alternative production rate via photodissociation of a helium-seeded bromoacetylene precursor would yield lower collision energies of  $\approx 22$  kJ mol $^{-1}$ . However, the ethynyl beam generated in the photodissociation source has a lower number density than the D1-ethynyl beam used here. This pathway in turn would substantially increase the data accumulation time considering that the diacetylene precursor is seeded at a fraction of only 5%.

**Computational.** Our electronic structure calculations were conducted at a level of theory high enough to predict relative energies of all local minima, transition states, and products of the D1-ethynyl reaction with diacetylene to a precision of  $\approx 5$  kJ mol $^{-1}$ . Stationary points were optimized at the hybrid density functional B3LYP level (33, 34) with the 6-311G\*\* basis set. Vibrational frequencies were calculated using the same B3LYP/6-311G\*\* method and were used to compute zero-point vibrational energy (ZPE) corrections and reaction rate constants without scaling. In the calculations of vibrational frequencies, we used the deuterium isotope for the relevant hydrogen atom. Relative energies of various species were refined employing the coupled cluster CCSD(T) method (35–38) with extrapolation to the complete basis set (CBS) limit and including ZPEs obtained by B3LYP calculations for all  $C_6H_2D$  intermediates. The results of ab initio calculations, such as relative energies and molecular parameters, were used in Rice–Ramsperger–Kassel–Marcus (RRKM) calculations of energy-dependent rate constants for individual unimolecular steps. The detailed procedure for such calculations has been described in detail in our previous works (22, 39). We computed rate constants as functions of available internal energy of each intermediate or transition state, where the internal energy was taken as a sum of the chemical activation energy and the collision energy, assuming that a dominant fraction of the latter is converted to internal vibrational energy. Rate constants for decomposition of reaction intermediates were used to evaluate their lifetimes. Here, under single collision conditions, the intermediates are formed with high

internal excitation, and their lifetimes are less than a few picoseconds. However, in denser atmospheres of Titan, ternary collisions might impact the chemistry. These processes can divert the internal energy, and thus, will stabilize those intermediates if the lifetime of the intermediate is longer than the time to allow a ternary collision to take place. Based on the potential energy surface (Fig. 4), we investigated the unimolecular decomposition of intermediate [1] using RRKM calculations. This treatment suggests lifetimes of intermediate [1] of 3 to 24 ns; these times cover the temperature window of 94 to 200 K relevant to Titan's atmosphere. Taking the atmospherically relevant pressure window of 1 to  $1 \times 10^{-6}$  mbar (17), and the collision cross section between intermediate [1] and a nitrogen bath molecule in Titan's atmosphere from our computations ( $1.97 \times 10^{-18}$  m<sup>2</sup>), we estimate time scales between the collisions of  $\approx 17$ –22 ns at 1 mbar and 17–22 ms at  $1 \times 10^{-6}$  mbar. A close look at these time scales indicates that the time between the collisions of intermediate [1] and a nitrogen bath molecule compared with the computed lifetime of intermediate [1] of typically a few ns is clearly too long to allow a third-body collision to be relevant in Titan's atmosphere in those regions where the ethynyl and diacetylene reactants are present. Consequently, the intermediates formed in the reaction of ethynyl radicals with diacetylene cannot be stabilized by third body collisions in the temperature range of 94–200 K and pressure window of 1 to  $1 \times 10^{-6}$  mbar; therefore, in Titan's atmosphere, all intermediates [1] decompose solely to triacetylene plus atomic hydrogen.

**Modeling.** We perform a 1D diurnally-averaged simulation of the chemical processes in the atmosphere of Titan using a complex set of hydrocarbon chemistry involving up to 450 reactions (17). The detailed reactions can be

found in the original reference. The reactions relevant to the polyynic growth 2 and 3 were highlighted here. The concentrations of chemical species are calculated to steady state by solving the mass continuity equation:

$$\frac{\partial n_i}{\partial t} + \frac{\partial \varphi_i}{\partial z} = P_i - L_i,$$

where  $n_i$  is the number density for species  $i$ ,  $\varphi_i$  the vertical flux,  $P_i$  the chemical production rate, and  $L_i$  the chemical loss rate, all evaluated at time  $t$  and altitude  $z$ .  $P_i$  and  $L_i$  are calculated based on the chemical schemes published in the literature (4, 25–27). The vertical flux is given by

$$\varphi_i = -\frac{\partial n_i}{\partial z} (D_i + K_{zz}) - n_i \left( \frac{D_i}{H_i} + \frac{K_{zz}}{H_{atm}} \right) - n_i \frac{\partial T}{\partial z} \left[ \frac{(1 + \alpha_i) D_i + K_{zz}}{T} \right] + w n_i,$$

where  $D_i$  is the molecular diffusion of the species,  $H_i$  the scale height of the species,  $H_{atm}$  the atmospheric scale height,  $\alpha_i$  the thermal diffusion parameter,  $T$  the temperature, and  $w$  the advective velocity.

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- Lorenz RD (2006) The Exploration of Titan. *J Hopkins APL Tech D* 27:133–142.
- Lavvas PP, Coustenis A, Vardavas IM (2008) Coupling photochemistry with haze formation in Titan's atmosphere. Part I: Model description. *Planet Space Sci* 56:27–66.
- Lara LM, Lellouch E, Lopez-Moreno JJ, Rodrigo R (1996) Vertical distribution of Titan's atmospheric neutral constituents. *J Geophys Res* 101:23261–23283.
- Gazeau MC, Cottin H, Vuitton V, Smith N, Raulin F (2000) Experimental and theoretical photochemistry: Application to the cometary environment and Titan's atmosphere. *Planet Space Sci* 48:437–445.
- Banaszkiewicz M, Lara LM, Rodrigo R, Lopez-Moreno JJ, Molina-Cuberos GJ (2000) A coupled model of Titan's atmosphere and ionosphere. *Icarus* 147:386–404.
- Wilson EH, Atreya SK (2004) Current state of modeling the photochemistry of Titan's mutually dependent atmosphere and ionosphere. *J Geophys Res* 109:E06002/1–39.
- Lorenz RD, McKay CP, Lunine JI (1997) Photochemically driven collapse of Titan's atmosphere. *Science* 275:642–643.
- Wilson EH, Atreya SK, Coustenis A (2003) Mechanisms for the formation of benzene in the atmosphere of Titan. *J Geophys Res* 108:1–10.
- Roush TL, Dalton JB (2004) Reflectance spectra of hydrated Titan tholins at cryogenic temperatures and implications for compositional interpretation of red objects in the outer Solar System. *Icarus* 168:158–162.
- Lebonnois S, Bakes ELO, McKay CP (2008) Transition from gaseous compounds to aerosols in Titan's atmosphere. *Icarus* 159:505–517.
- Gladstone GR, Allen M, Yung YL (1996) Hydrocarbon photochemistry in the upper atmosphere of Jupiter. *Icarus* 119:1–52.
- Vuitton V, Doussin JF, Benilan Y, Raulin F, Gazeau MC (2006) Experimental and theoretical study of hydrocarbon photochemistry applied to Titan stratosphere. *Icarus* 185:287–300.
- Aflalaye A, Sternberg R, Raulin F, Vidal-Madjar C (1995) Gas chromatography of Titan's atmosphere VI. Analysis of low-molecular-mass hydrocarbons and nitriles with BPX5 capillary columns. *J Chromatogr A* 708:283–291.
- Sternberg R, et al. (1999) Gas chromatography in space exploration capillary and micropacked columns for in situ analysis of Titan's atmosphere. *J Chromatogr A* 846:307–315.
- Rannou P, Hourdin F, McKay CP, Luz D (2004) A coupled dynamics-microphysics model of Titan's atmosphere. *Icarus* 170:443–462.
- Waite JH, Jr, et al. (2007) The process of tholin formation in Titan's upper atmosphere. *Science* 316:870–875.
- Liang MC, Yung YL, Shemansky DE (2007) Photolytically generated aerosols in the mesosphere and thermosphere of Titan. *Astrophys J Lett* 661:L199–L202.
- Schroden JJ, Davis HF (2004) Reactions of neutral transition metal atoms with small molecules in the gas phase. *Modern Trends in Chemical Reaction Dynamics*, eds Yang X, Liu K (World Scientific, Singapore), pp 215–280.
- Weis MS (1986) PhD thesis (University of California, Berkeley).
- Levine RD, Bernstein RB (1987) *Molecular Reaction Dynamics and Chemical Reactivity* (Oxford Univ Press, Oxford).
- Miller WB, Safron SA, Herschbach DR (1967) Exchange reactions of alkali atoms with alkali halides. Collision complex mechanism. *Discuss Faraday Soc* 44:108–122.
- Landra A, Krishtal S P, Kislov VV, Mebel A M, Kaiser RI (2008) Theoretical study of the C<sub>6</sub>H<sub>3</sub> potential energy surface and rate constants and product branching ratios of the C<sub>2</sub>H(<sup>2</sup>Σ<sup>+</sup>) + C<sub>4</sub>H<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) and C<sub>4</sub>H(<sup>2</sup>Σ<sup>+</sup>) + C<sub>2</sub>H<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) reactions. *J Chem Phys* 128:214301.
- Sattelmeyer KW, Stanton JF (2000) Computational Studies of C<sub>6</sub>H<sub>2</sub> Isomers. *J Am Chem Soc* 122:8220.
- Smith IWM, Herbst E, Chang Q (2004) Rapid neutral-neutral reactions at low temperatures: A new network and first results for TMC-1. *Mon Not R Astron Soc* 350:323–330.
- Chastaing D, James PL, Sims IR, Smith IWM (1996) Neutral-neutral reactions at the temperatures of interstellar clouds Rate coefficients for reactions of C<sub>2</sub>H radicals with O<sub>2</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and C<sub>3</sub>H<sub>6</sub> down to 15 K. *Faraday Discuss* 109:165–181.
- Porco CC, et al. (2005) Imaging of Titan from the Cassini spacecraft. *Nature* 434:159–168.
- Vuitton V, Yelle RV, McEwan MJ (2007) Ion chemistry and N-containing molecules in Titan's upper atmosphere. *Icarus* 191:722–742.
- Silva R, et al. (2008) H elimination and metastable lifetimes in the UV photoexcitation of diacetylene. *Proc Natl Acad Sci USA* 105:12713–12718.
- Gu X, Guo Y, Zhang F, Mebel AM, Kaiser RI (2006) Reaction dynamics of carbon-bearing radicals in circumstellar envelopes of carbon stars. *Faraday Discuss* 133:245–275.
- Guo Y, Gu X, Zhang F, Mebel AM, Kaiser RI (2007) A crossed molecular beam study on the formation of hexenediynyl radicals (H<sub>2</sub>CCCCCH; C<sub>6</sub>H<sub>3</sub> (X<sup>2</sup>A<sup>1</sup>)) via reactions of tricarbon molecules, C<sub>3</sub>(X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>), with allene (H<sub>2</sub>C=C=C<sub>2</sub>; X<sup>1</sup>A<sub>1</sub>) and methylacetylene (CH<sub>3</sub>CCH; X<sup>1</sup>A<sub>1</sub>). *Phys Chem Chem Phys* 9:1972–1979.
- Gu X, Guo Y, Mebel AM, Kaiser RI (2007) A crossed beams investigation of the reactions of tricarbon molecules, C<sub>3</sub>, with acetylene, C<sub>2</sub>H<sub>2</sub>, ethylene, C<sub>2</sub>H<sub>4</sub>, and benzene C<sub>6</sub>H<sub>6</sub>. *Chem Phys Lett* 449:44–52.
- Jones AV (1952) Infrared and Raman spectra of biacetylene. *Proc R Soc London Ser A* 211:285–295.
- Becke AD (1993) Density-functional thermochemistry. III. The role of exact exchange. *J Chem Phys* 98:5648–5652.
- Lee C, Yang W, Parr RG (1988) Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys Rev B* 37:785–789.
- Purvis GD, Bartlett RJ (1982) A full coupled-cluster singles and doubles model: The inclusion of disconnected triples. *J Chem Phys* 76:1910–1918.
- Scuseria GE, Janssen CL, Schaefer HF, III (1988) An efficient reformulation of the closed-shell coupled cluster single and double excitation (CCSD) equations. *J Chem Phys* 89:7382–7387.
- Scuseria GE, Schaefer HF, III (1989) Is coupled cluster singles and doubles (CCSD) more computationally intensive than quadratic configuration interaction (QCISD)? *J Chem Phys* 90:3700–3703.
- Pople JA, Head-Gordon M, Raghavachari K (1987) Quadratic configuration interaction: A general technique for determining electron correlation energies. *J Chem Phys* 87:5968–5975.
- Kislov VV, Nguyen TL, Mebel AM, Lin SH, Smith SC (2004) Photodissociation of benzene under collision-free conditions: An *ab initio*/Rice–Ramsperger–Kassel–Marcus study. *J Chem Phys* 120:7008–7017.
- Liang MC, et al. (2005) Meridional transport in the stratosphere of Jupiter. *Astrophys J* 635:L177–L180.