

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

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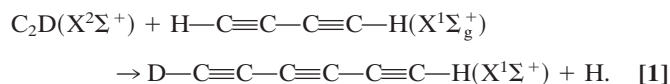
For the last four decades, the role of polyynes such as diacetylene (HCCCH) and triacetylene (HCCCCCH) in the chemical evolution of the atmosphere of Saturn's moon Titan has been a subject of vigorous research. These polyacetylenes are thought to serve as an UV radiation shield in planetary environments; 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

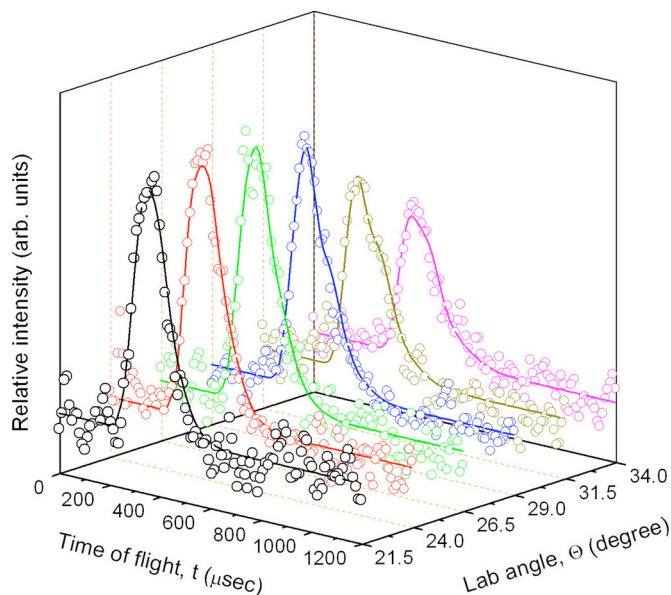
Author contributions: R.I.K. and A.M.M. designed research; X.G., Y.S.K., A.M.M., M.C.L., and Y.L.Y. performed research; and R.I.K. wrote the paper.

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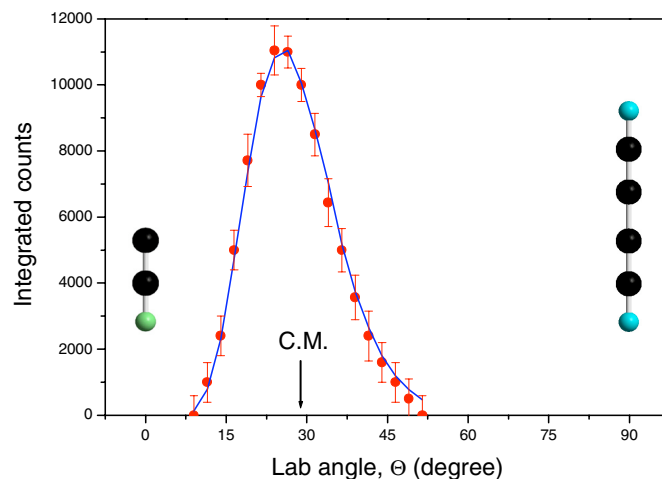
This article contains supporting information online at [www.pnas.org/cgi/content/full/0900525106/DCSupplemental](http://www.pnas.org/cgi/content/full/0900525106/DCSupplemental).



**Fig. 1.** Selected TOF spectra at mass to charge ratio  $m/z = 75$  ( $C_6HD^+$ ). Circles denote experimental data, the solid lines the calculated distributions using the best fit CM translational and angular distributions (Fig. 3).

inelastically scattered diacetylene dimers are presented in *SI Text, Fig. S1, and Fig. S2* (18); this finding suggests that, within the experimental uncertainties, the molecular hydrogen channel leading to a  $C_6D$  and/or  $C_6H_2$  molecule via molecular hydrogen and/or a deuterium atom ejection is closed. Summarized, the analysis of the TOF spectra indicates the formation of a molecule of the formula  $C_6HD$  plus a light hydrogen atom in the crossed beams reaction of the D1-ethynyl radical with diacetylene.

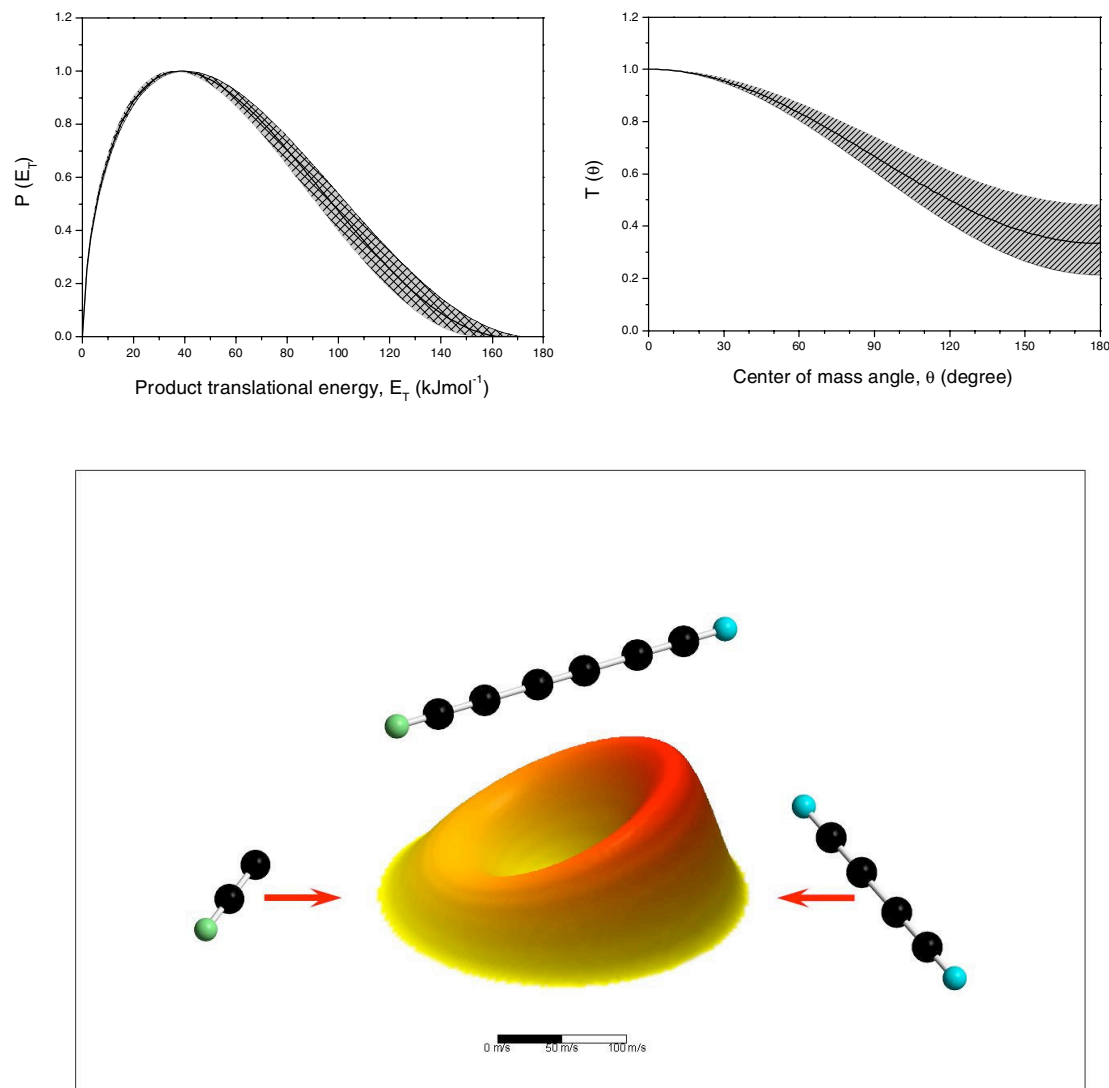
We also investigated the chemical dynamics of the reaction, because this procedure assists unraveling the nature of the  $C_6HD$  product isomer and the intermediates formed. The information on the chemical dynamics are extracted by transforming the laboratory data (TOF spectra and laboratory angular distribution; Figs. 1 and 2, respectively) into the CM coordinate system to yield a CM product flux contour map (Fig. 3) (19). The plot reports the differential cross section,  $I(\theta, u)$ , as a function of product CM scattering angle  $\theta$  and velocity  $u$ ; the flux contour plot is proportional to the product of the CM angular distribution,  $T(\theta)$ , and the CM velocity distribution,  $P(u)$ , which in turn is computed from the CM translational energy distribution,  $P(E_T)$ . The flux contour map,  $I(\theta, u)$ , can be seen as an image of the reaction, and holds all of the information of the reactive scattering process. First, an inspection of the CM translational energy distribution allows computing the reaction energy and, thus, helps to elucidate the nature of the  $C_6HD$  isomer formed. The maximum translational energy,  $E_{max}$ , released into the products represents the sum of the collision energy,  $E_c$ , and the absolute of the reaction energy,  $\Delta_r G$ . Therefore, by subtracting the collision energy ( $E_c = 40.2 \pm 2.0 \text{ kJ}\cdot\text{mol}^{-1}$ ) from the maximum amount of translational energy ( $E_{max} = 160 \pm 14 \text{ kJ}\cdot\text{mol}^{-1}$ ), we can compute the reaction exoergicity to be  $120 \pm 16 \text{ kJ}\cdot\text{mol}^{-1}$ . These data agree very well with our ab initio data of  $125 \pm 5 \text{ kJ}\cdot\text{mol}^{-1}$  to form the D1-triacetylene isomer (HC-CCCCD) plus atomic hydrogen (H). Second, the translational energy distribution peaks away from zero translational energy at  $\approx 35 \pm 5 \text{ kJ}\cdot\text{mol}^{-1}$ . This finding indicates that the exit transition state is likely to be tight and involves a significant electron rearrangement from the decomposing intermediate to the final D1-triacetylene plus hydrogen atom products; in other words, the reversed reaction of a hydrogen atom addition to D1-



**Fig. 2.** Laboratory angular distribution of the reactive scattering signal observed at  $m/z = 75$  ( $C_6HD^+$ ). The filled circles present the experimental data together with the error limits, the solid lines the calculated distribution using the best fit CM translational and angular distributions (Fig. 3). Black balls indicate carbon, green balls deuterium, and blue balls hydrogen atoms. The laboratory angular distribution (LAB) is obtained by integrating the TOF spectra at each laboratory angle and correcting for distinct data accumulation times.

triacetylene involves an entrance barrier. Third, the CM angular distribution,  $T(\theta)$ , shows intensity over the complete angular range from  $0^\circ$  to  $180^\circ$ . This pattern is characteristic of an indirect reaction mechanism, i.e., the formation of a  $C_6H_2D$  reaction intermediate, which decomposes via atomic hydrogen loss to form D1-triacetylene. Also, the CM flux contour plot is slightly forward scattered with respect to the D1-ethynyl beam, indicating that the lifetime of the reaction intermediate is less than its rotational period (20). In a molecular beams experiment, the rotational period can be used as a clock to estimate the lifetime of the decomposing complex. Based on the intensity of the poles of  $I(0^\circ)/I(180^\circ) = 2.5_{+0.8}^{-0.5}$ , the lifetime of the fragmenting  $C_6H_2D$  intermediate can be approximated to be  $0.55_{+0.17}^{-0.13}$  of its rotational period (21).

To elucidate the reaction mechanism, we are merging now our experimental findings with our electronic structure calculations of the reaction of D1-ethynyl (CCD) with diacetylene (HC-CCCH) (Fig. 4). Our computations verify the experimental results of an indirect reaction mechanism involving  $C_6H_2D$  reaction intermediate(s). Here, the reaction is initiated by a barrierless addition of the D1-ethynyl radical with its radical center to the C1 and/or C2 carbon atom of the diacetylene molecule yielding intermediates [1] and [3], respectively. The barrierless addition was verified by a careful examination of the potential energy surface in the entrance channel, which indicates that the potential energy of the system steadily and monotonically decreases as the ethynyl radical approaches diacetylene (22). Intermediates [1] and [3] are bound by 294 and 226  $\text{kJ}\cdot\text{mol}^{-1}$  with respect to the separated reactants. Structure [2] connects [1] and [3] via a D1-ethynyl group shift from the diacetylenic C2 to the C1 carbon atom. The calculations identify the  $C_6H_2D$  structure [1] as the decomposing intermediate, which emits atomic hydrogen. The computationally found tight exit transition state, which ranges  $\approx 21 \text{ kJ}\cdot\text{mol}^{-1}$  above the separated D1-triacetylene and atomic hydrogen products, was predicted experimentally based on the off-zero peaking of the CM translational energy distribution (Fig. 3). A comparison of the geometries of [1] and the final triacetylene product verifies the electronic reorganization involved in this process and, thus, the

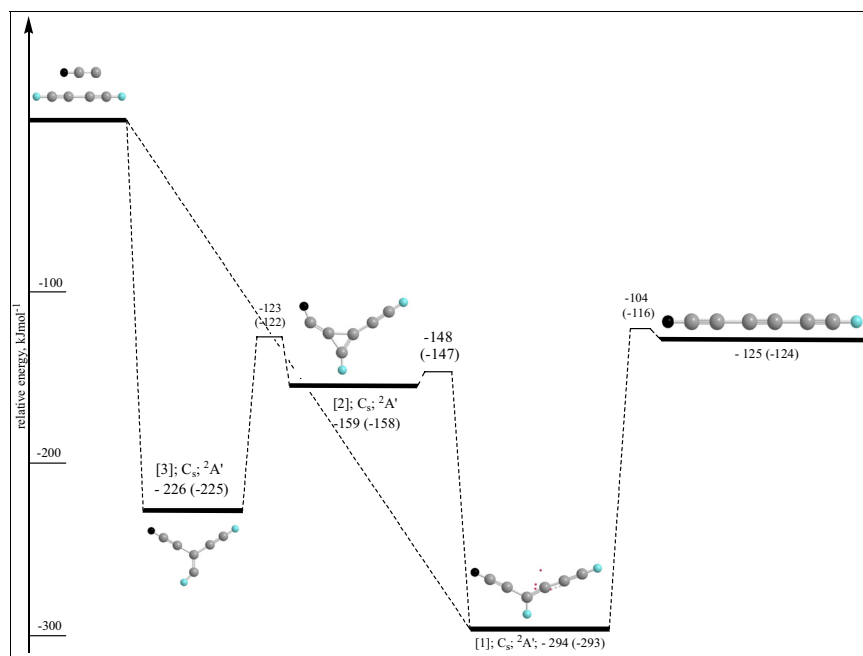


**Fig. 3.** CM translational energy distribution (*Upper Left*), CM angular distribution (*Upper Right*), and CM velocity flux contour map for the reaction of D1-ethynyl [ $C_2D(X^2\Sigma^+)$ ] with diacetylene [ $C_4H_2(X^1\Sigma_g^+)$ ] to form atomic hydrogen plus D1-triacetylene [ $DCCCCCH(X^1\Sigma^+)$ ] (*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° and of the diacetylene beam as 180°).

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 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

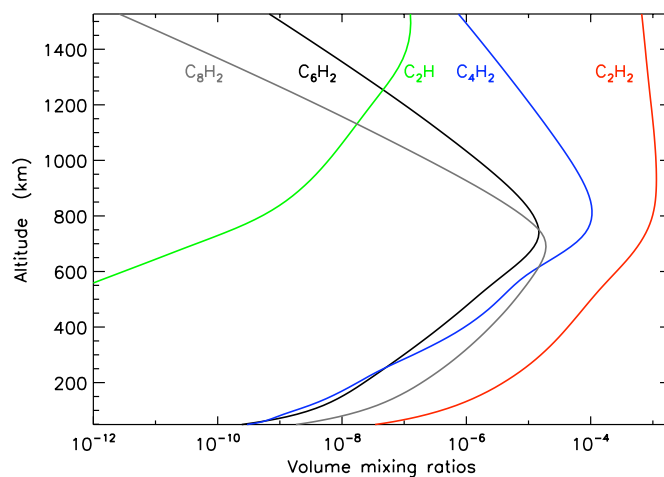


**Fig. 4.** Calculated potential energy surface of the D1-ethynyl [ $C_2D(X^2\Sigma^+)$ ] plus diacetylene [ $C_4H_2(X^1\Sigma_g^+)$ ] reaction to form D1-triacetylene [ $DCCCCCCH(X^1\Sigma^+)$ ] plus atomic hydrogen. The energies in parenthesis are the energies for the corresponding ethynyl [ $C_2H(X^2\Sigma^+)$ ] 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.

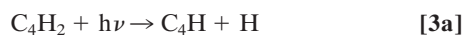
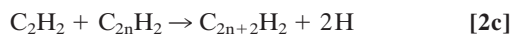
The implementation of the reaction of ethynyl radicals with diacetylene into a photochemical model of Titan's atmosphere requires two input parameters: the reaction products, i.e., triacetylene plus atomic hydrogen, and rate constants. A literature research failed to provide any rate constants for the 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<sub>2</sub>), molecular nitrogen (N<sub>2</sub>), or methane (CH<sub>4</sub>). The photodissociation is followed by subsequent reactions of polyyne radicals like 1,3-butadiynyl (C<sub>4</sub>H) to higher-order polyynes (reaction 3). Because the photodissociation cross sections and quantum yields for the photolysis of diacetylene (C<sub>4</sub>H<sub>2</sub>) and triacetylene (C<sub>6</sub>H<sub>2</sub>) 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<sub>8</sub>H<sub>2</sub>) compared with diacetylene and triacetylene is based on the lower photodissociation cross section of tetraacetylene (17). Above the homopause (≈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<sub>6</sub>H<sub>3</sub><sup>+</sup> 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<sub>8</sub>H<sub>2</sub>) and pentaacetylene (C<sub>10</sub>H<sub>2</sub>), 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<sub>2</sub>D(X<sup>2</sup>Σ<sup>+</sup>), 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<sub>2</sub>D<sub>2</sub> followed by deuterium atom loss of the latter. This beam contains also atomic carbon [C(<sup>3</sup>P)], dicarbon [C<sub>2</sub>(X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>; a<sup>3</sup>Π)], and C<sub>3</sub>(X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>). 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(<sup>3</sup>P) + C<sub>4</sub>H<sub>2</sub> (X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) reaction leads to reactive scattering signal at  $m/z = 61$  (C<sub>5</sub>H<sup>+</sup>), whereas reactive collisions of C<sub>2</sub>(X<sup>1</sup>Σ<sub>g</sub><sup>+</sup>; a<sup>3</sup>Π) with diacetylene result in the formation of C<sub>6</sub>H (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<sub>7</sub>H (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<sub>2</sub>H;  $m/z = 25$ ). Because  $m/z = 25$  can also arise from <sup>13</sup>C<sup>12</sup>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 <sup>13</sup>C<sup>12</sup>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  $2,082 \pm 50 \text{ m}\cdot\text{s}^{-1}$  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  $40.1 \text{ kJ}\cdot\text{mol}^{-1}$  ( $v_p = 599 \pm 20 \text{ m}\cdot\text{s}^{-1}$ ,  $S = 21.0 \pm 1.0$ ). 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 ≈22 kJ·mol<sup>-1</sup>. 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 ≈5 kJ·mol<sup>-1</sup>. 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<sub>6</sub>H<sub>2</sub>D 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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